Development of a Hydrogen Generating Thermal Control for Chemical Hydrogen Storage

by

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Abstract

This thesis investigated a potential improvement to hydrogen storage for fuel cells using a thermally efficient hydrogen storage method. The efficiency of the storage system was improved using a metal hydride system to act as a thermal control unit for an exothermic chemical hydrogen storage system.

A cylindrical shaped “hybrid” reactor was created to allow hydrogen production from a sodium borohydride packed bed reactor and the metal hydride. Additionally, a custom built pressure-composition-temperature apparatus was built to record the amount of hydrogen desorption from the metal hydride while isolating the metal from potential poisons such as oxygen.

Before using the chemical hydride packed bed, heat transfer through the reactor was studied using circulating water. The water experiments showed that an increase in heat flux to the reactor led to a faster desorption rate of hydrogen from the metal hydride resulting in a larger temperature drop throughout the reactor.

After the operating characteristics of the hybrid reactor were studied, a 10 wt% solution of sodium borohydride was created and pumped through the packed bed to produce enough hydrogen for a 300 W fuel cell. The amount of heat produced from the packed bed portion of the reactor was significant, but temperatures levelled to around 80 °C. As expected, temperature control was directly proportional to the rate of hydrogen release from the metal hydride. On average, approximately 10% of the available heat energy was transferred to the metal hydride, and the hybrid reactor operated with gravimetric and volumetric energy densities of 0.27 kWh·kg⁻¹ and 1.29 kWh·L⁻¹ respectively. If the hybrid reactor is used solely to control peak temperatures, the amount
of metal hydride necessary for thermal control could be decreased. Additionally, improvements in heat transfer as well as the hydrogen storage materials themselves would increase the energy density values further.

When compared to other energy storage devices, the hybrid reactor without improvements is competitive as a backup power generator due to its silent operation and large volumetric energy density. Since the hybrid reactor can provide quiet and cool energy storage in a relatively small volume, it may become an effective and efficient means for hydrogen storage with limited improvements.
Acknowledgements

First and foremost, I would like to show my gratitude to my supervisor, Dr. Boyd Davis for his encouragement and assistance through these past few years. His willingness to take time out of his private life to direct and guide my research was much appreciated, as was his trust and confidence in my ability to allow me to take this project in the direction I desired. Whether it was on the ice or in the lab, his open minded approach to problems and his dedication to friends and family is apparent and much admired.

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Abbreviations

- **EMF**: Electromotive force
- **PCT**: Pressure-composition-temperature
- **PEMFC**: Proton exchange membrane fuel cell
- **RTD**: Resistive temperature detector
- **SOFC**: Solid oxide fuel cell
- **USDOE**: United States Department of Energy

Chemical Formulas

- **NaAlH$_4$**: Sodium alanate
- **NaBH$_4$**: Sodium borohydride
- **H$_2$O**: Water
- **NaBO$_2$**: Metaborate
- **H$_2$**: Hydrogen
- **M**: Generic metal
- **MH$_x$**: Generic metal hydride
- **CO$_2$**: Carbon dioxide

Greek Symbols

- $\varepsilon$: Porosity
- $\phi$: Relative humidity
- $\eta$: Efficiency
- $\mu$: Dynamic viscosity (units)
- $\nu$: Kinematic viscosity (units)
- $\rho$: Density (units)

Variables

- **A**: Equilibrium constant
- **B**: Equilibrium constant
- **c**: Concentration
- **$C_a$**: Absorption constant (s$^{-1}$)
- **$C_d$**: Desorption constant (s$^{-1}$)
- **$C_p$**: Specific heat capacity (J·kg$^{-1}$·K$^{-1}$)
- **D**: Diameter (m)
- **$E_a$**: Activation energy for absorption (J·mol$^{-1}$)
$E_d$  Activation energy for desorption (J·mol\(^{-1}\))
$E_{grav}$  Gravitational energy density (kWh·kg\(^{-1}\))
$E_{vol}$  Volumetric energy density (kWh·L\(^{-1}\))
$f$  Fuel utilization of the cell
$F$  Faraday’s constant (C·mol\(^{-1}\))
$g$  Acceleration due to gravity (m·s\(^{-2}\))
$\Delta H$  Enthalpy (J·kg\(^{-1}\) or J·mol\(^{-1}\))
$k$  Thermal conductivity (W·m\(^{-1}\)·K\(^{-1}\))
$k_e$  Effective thermal conductivity (W·m\(^{-1}\)·K\(^{-1}\))
$K$  Permeability (m\(^2\))
$K_s$  Concentration constant
$L$  Length (m)
$m$  Mass (kg)
$m$  Mass flow rate (kg·s\(^{-1}\))
$M$  Molar mass (g·mol\(^{-1}\))
$n$  Moles
$\dot{n}$  Molar flow rate (mol·s\(^{-1}\))
$P$  Pressure (Pa)
$P_{FC}$  Power of the fuel cell (W)
$Q$  Energy (kJ)
$\dot{Q}$  Heat flux (W)
$R$  Universal gas constant (J·mol\(^{-1}\)·K\(^{-1}\))
$\Delta S$  Entropy (J·kg\(^{-1}\)·K\(^{-1}\) or J·mol\(^{-1}\)·K\(^{-1}\))
$t$  Time (s)
$T$  Temperature (K)
$\Delta T$  Change in temperature (K)
$u$  Velocity (m·s\(^{-1}\))
$V$  Volume (m\(^3\))
$Vc$  Operating voltage of the cell (V)
$x$  Rate of hydrogen absorbed or desorbed (kg·m\(^3\))
$z$  gas compressibility factor
Chapter 1 : Introduction

1.1 An Important Realization

This thesis investigates a potential improvement to hydrogen storage for fuel cells. As such, its broad focus is one of energy sustainability and improved efficiencies. Societies’ need for alternative and renewable energy sources is becoming increasingly evident each year. World energy consumption is directly related to economic growth, and as nations such as China and India continue to develop, their energy demands continue to increase. Eventually, the world energy demand could reach a critical point at which current energy reserves will no longer be able to supply. The escalating demand for energy, and realized environmental impact of fossil fuel use is influencing many countries to seek alternative sources of energy.

The transportation sector is an area in which an alternative energy source may have a great impact. This sector’s large energy demand is primarily fuelled by petroleum based products which harm the environment. Renewable energy sources producing electricity can provide automobiles with a clean and efficient source of power; however, there are currently no practical methods of storing this electrical energy. Hydrogen may provide a clean, renewable method to store and transport electricity through the use of a hydrogen fuel cell. This thesis is focused on an attempt to create a thermally efficient hydrogen storage solution.
1.2 Why Hydrogen

Hydrogen is the simplest, and most abundant atom on this planet. One of the most important characteristics of hydrogen is the fact that it has the highest energy to weight ratio, or gravimetric energy density, of the energy sources known today. For this reason, much of the current hydrogen research is being applied to portable applications such as vehicles or electronics, where overall weight is an important design consideration. A major drawback to hydrogen is that large quantities do not exist in a readily usable form. Since hydrogen is an energy carrier, it must be synthesized from other energy sources, and then used to transfer energy to another use. Clean and efficient hydrogen production and storage methods still remain a great challenge. Currently, hydrogen is produced from a variety of sources including fossil fuels, biomass, and water electrolysis.

1.3 Fuel Cells

The first “fuel cell” was demonstrated by William Grove in 1839 when he effectively reversed the water electrolysis reaction by replacing the power supply with an ammeter and measuring the small current produced.\textsuperscript{1} There are many different types of fuel cells which utilize different electrodes, electrolytes, and fuels; however, to illustrate the operation of a fuel cell, the proton exchange membrane fuel cell (PEMFC) will be used.
In a PEMFC, a proton conducting polymer membrane serves as the electrolyte and separates the anode and the cathode. Hydrogen is then exposed to the anode and diffuses to the anode catalyst where it dissociates into protons and electrons. Since the exchange membrane is electrically insulating, the electrons are forced to travel through an external circuit while the protons are conducted through the membrane to the cathode. On the opposite side of the PEMFC, oxygen molecules from an air stream react on the cathode catalyst with the protons from the membrane and the electrons from the external circuit. This reaction produces water in vapour or liquid form. Figure 1.1 displays the PEMFC operation.

![Figure 1.1 - PEMFC operation](image)

1. Hydrogen fuel is channeled through field flow plates to the anode on one side of the fuel cell, while oxygen from the air is channeled to the cathode on the other side of the cell.

2. At the anode, a platinum catalyst causes the hydrogen to split into positive hydrogen ions (protons) and negatively charged electrons.

3. The Polymer Electrolyte Membrane (PEM) allows only the positively charged ions to pass through it to the cathode. The negatively charged electrons must travel along an external circuit to the cathode, creating an electrical current.

4. At the cathode, the electrons and positively charged hydrogen ions combine with oxygen to form water, which flows out of the cell.

Figure 1.1 - PEMFC operation
Other types of fuel cells, such as the Solid Oxide Fuel Cell (SOFC), are able to convert hydrocarbon fuels into electricity and carbon dioxide. Table 1.1 displays the various types of fuel cells along with their operating characteristics.

<table>
<thead>
<tr>
<th>Fuel Cell Type</th>
<th>Electrolyte Mobility</th>
<th>Operating Temp.</th>
<th>Applications</th>
<th>Advantages</th>
<th>Disadvantages</th>
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<tr>
<td>Alkaline</td>
<td>Aqueous alkaline solution</td>
<td>OH⁻</td>
<td>50-200°C</td>
<td>Military, Space</td>
<td>Fast cathode reaction</td>
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<td>Proton Exchange Membrane</td>
<td>Polymer membrane</td>
<td>H⁺</td>
<td>30-100°C</td>
<td>Portable applications</td>
<td>Low temperature</td>
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<tr>
<td>Direct Methanol</td>
<td>Polymer membrane</td>
<td>H⁺</td>
<td>20-90°C</td>
<td>Low power portable applications</td>
<td>Low temperature</td>
</tr>
<tr>
<td>Phosphoric Acid</td>
<td>Molten phosphoric acid</td>
<td>H⁺</td>
<td>~220°C</td>
<td>Distributed generation</td>
<td>Increased hydrogen impurity tolerance</td>
</tr>
<tr>
<td>Molten Carbonate</td>
<td>Molten alkaline carbonate</td>
<td>CO₃²⁻</td>
<td>~650°C</td>
<td>Large scale distributed generation</td>
<td>Variety of catalysts</td>
</tr>
<tr>
<td>Solid Oxide</td>
<td>Ceramic oxide</td>
<td>O²⁻</td>
<td>500-1000°C</td>
<td>Electric utility, Auxiliary power</td>
<td>Variety of fuel types</td>
</tr>
</tbody>
</table>

Data provided by: Larminie and Dicks¹ and the U.S. Department of Energy: Hydrogen, Fuel Cells and Infrastructure Technologies Program.

Fuel cells have many advantages over other energy conversion devices such as the internal combustion engine. For example, fuel cells are fairly simplistic and contain few moving parts. Fuel cells also produce fewer emissions, are modular, and are very quiet.

The operating voltage of a fuel cell may also be related to its efficiency. For a hydrogen fuel cell, the electromotive force (EMF) produced if all of the energy from the hydrogen fuel were transformed into electrical energy can also be related by:

\[ EMF = \frac{E}{n} \]

where \( E \) is the standard electrode potential and \( n \) is the number of electrons transferred in the reaction.
\[ \text{EMF} = \frac{-\Delta H_f}{2F} \]

Equation 1.1

where \( \Delta H_f \) is the enthalpy of formation and \( F \) is Faraday’s constant. However, there are two different values that can be used for the enthalpy of formation. This difference is created when considering the formation of steam or liquid water as the product at the cathode of the fuel cell.\(^1\)

The difference between the two \( \Delta H_f \) values is the molar enthalpy of vaporisation of water. The larger and smaller values are known as the higher and lower heating values respectively. It is more accurate to use the higher heating value (HHV) in all calculations since using the lower heating value (LHV) results in higher and sometimes unrealistic efficiencies. Therefore, using the HHV of \(-285.84 \text{ kJ mol}^{-1}\) in Equation 1.1 results in an open circuit voltage of 1.48V. This voltage is the result of a 100% efficient system. A fuel cell’s efficiency is therefore described by:

\[ \eta = f \frac{V_C}{1.48} \times 100\% \]

Equation 1.2

where \( f \) is the fuel utilization of the cell, and \( V_C \) is the operating voltage of the cell. Typical fuel cell voltages range from 0.6 to 0.8 V which results in efficiencies around 50%. To create a more useful voltage as well as current, cells are combined in series and parallel circuits to form a fuel cell stack.\(^1\)

Since a PEMFC operates at a lower temperature and offers a higher power density than most other fuel cells, it has been widely accepted for use with automobiles and other
portable applications. However, the PEMFC is not without problems and many challenges opposing the hydrogen economy still remain.

1.4 Obstacles to the Hydrogen Economy

Many challenges in the simple operation of a fuel cell still remain. A PEMFC performs best when operating with high purity hydrogen; however, pure hydrogen is hard to obtain because the primary source of hydrogen is steam reformation. Low level impurities, such as carbon monoxide, in the hydrogen produced from this method poison the expensive, platinum catalysts of the fuel cell. Furthermore, the typical Nafion membrane within a PEMFC must remain hydrated, and water management problems are common. If the temperature of the fuel cell drops to below freezing, water within the membrane will freeze and ultimately damage the material. For these reasons, work is needed to develop new and inexpensive materials for the fuel cell which will allow for more robust operating conditions.

Once hydrogen is produced, there must be a storage and distribution system. At present, hydrogen is transported via pipelines in industrial settings. There are over 16 000 km of hydrogen pipeline around the world; the longest of which is 400 km long, located in a densely populated area of Europe, and operating at 100 atmospheres of pressure.³ Liquid hydrogen is also used to provide hydrogen fuelling stations such as the California Fuel Cell Partnership Hydrogen Station. A cryogenic tanker truck is able to carry approximately 4000 kg of hydrogen, but experiences the boil off problem associated with liquid hydrogen. A further option is to produce the hydrogen on site at fuelling centres. As hydrogen use in the transportation sector increases, an efficient
distribution system and infrastructure will be required. Furthermore, this system will most certainly be dependent on the type of hydrogen storage used.

Hydrogen has a high gravimetric energy density, but it also has a very low volumetric energy density. It is very difficult to store a sufficient amount of hydrogen in a small and light enough volume such that the energy density of the entire storage system competes with traditional fuels. The challenge of hydrogen storage has proved to be a very significant obstacle to implementation of the hydrogen economy to date. This thesis focuses on improvements to hydrogen storage through the synergistic use of exothermic and endothermic hydrogen storage systems.
Chapter 2 : Literature Review

As mentioned, one key factor in the development of fuel cells as part of a solution to the move to non-fossil fuel based energy is the storage of hydrogen. This chapter reviews hydrogen storage methods as a precursor to the discussion of the central goal of the thesis – efficient thermal control of reactive chemical hydrides through the adsorption of heat by metal hydrides.

2.1 Hydrogen Storage Methods

While research is being conducted in areas such as hydrogen production, fuel cells, and other upstream applications, there is much room for progress in hydrogen storage. In the transportation sector, hydrogen storage is particularly important. A safe, efficient, and economical method of storing hydrogen must be available to complete the transition from a fossil fuel based society to a hydrogen economy using renewable resources.

Although molecular hydrogen has a high gravimetric energy density, its low volumetric energy density has prevented it from becoming a widely used transportation fuel. For an automotive application, hydrogen storage systems must meet strict gravimetric and volumetric energy density levels to compete with gasoline. These systems must also meet fuelling speed and other requirements such as cost to satisfy the expectations of consumers and keep fuelling stations practical. Through the
FreedomCAR and Fuel Partnership, the U.S. Department of Energy (USDOE) has set storage targets, some of which are outlined in Table 2.1.

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<td>2007</td>
<td>1.5</td>
<td>1.2</td>
<td>4.5</td>
<td>6</td>
<td>10</td>
</tr>
<tr>
<td>2010</td>
<td>2</td>
<td>1.5</td>
<td>6</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>2015</td>
<td>3</td>
<td>2.7</td>
<td>9</td>
<td>2</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Data provided by: U.S. Department of Energy: Hydrogen, Fuel Cells, and Infrastructure Technologies Program

Since the storage capacity details in Table 2.1 include the entire system in the requirements, the storage capacities of the material itself must be larger. For example, the mass of the reactor or storage unit itself will decrease the gravimetric capacity of the entire system. Therefore, the storage material must be capable of holding more hydrogen than the guidelines suggested to make up for this added weight.

Hydrogen storage techniques currently include compression, liquefaction, chemical compounds, and absorption. Currently, chemical bonding of hydrogen is the only storage technique that can produce energy densities approaching the requirements stated in Table 2.1. Liquid and high pressure hydrogen storage methods are already at the commercial prototype stage, but the other methods are still under development.

2.1.1 Liquid and Compressed Hydrogen

Liquid hydrogen can be stored in tanks at extremely low, cryogenic temperatures (around 21.2 K) and at ambient pressures. Naturally, the volumetric energy density for liquid hydrogen, 70.8 g·L⁻¹, is quite high since the hydrogen is in liquid form. The Joule-Thompson (Linde) cycle is the simplest method to liquefy hydrogen. The gas is first
compressed and then cooled using a heat exchanger. Then it passes through a throttling valve where it experiences an isenthalpic expansion producing some liquid which is separated. Some gases have high inversion temperatures, above room temperature, which allow for cooling upon expansion. Hydrogen, however, does not have a high inversion temperature. Therefore, hydrogen must be kept below its inversion temperature of 202 K. Above this temperature, the hydrogen gas would heat upon expansion through the throttling valve, and liquid hydrogen would not form. This extensive process requires 15.2 kWh·kg⁻¹ or 110.3 kJ·mol⁻¹ to produce liquid hydrogen at room temperature, which is about 40% of the HHV of hydrogen. Therefore, 40% of the energy available is already lost in the liquefaction process. This method of hydrogen storage also experiences losses due to heat leaks which cause some of the hydrogen to “boil off” at a rate of about 1% each day. Although the gravimetric and volumetric energy densities of liquid hydrogen are attractive, the large amounts of energy required to liquefy hydrogen and constant storage losses through heat leaks limit the practical applications of this technology.⁵, ⁶, ⁷

The next approach to high density hydrogen storage is to simply store hydrogen in gaseous form. Conventional hydrogen tanks can store compressed hydrogen at about 1% gravimetric hydrogen (wt%); however, new research has led to the construction of lighter composite, high strength cylinders capable of pressures up to 80 MPa. At this pressure, hydrogen approaches a volumetric energy density of 36 g·L⁻¹. Assuming perfect intercooling, the compression process to 80 MPa will theoretically consume 2.21 kWh·kg⁻¹. The true energy consumption is significantly more since the compression process is not isothermal. The advantages to using compressed hydrogen are that the process is fairly simple and filling a tank can be achieved in a relatively short amount of time. The
disadvantages are that the tanks can only achieve lower energy densities of about 1.3 kWh·kg⁻¹ (3.3 wt%), and a large amount of the energy that hydrogen can carry is lost when acquiring the high hydrogen pressures stated above.⁵,⁷,⁸

2.1.2 Complex Hydrides and Hydrogenated Fluids

Metal-hydrogen complexes formed from light metals such as lithium, magnesium, or aluminium provide a promising storage method for vehicular applications because of their light weight and the number of hydrogen atoms per metal atom stored. Complex hydrides generally perform a transition to an ionic or covalent compound upon hydrogen absorption. Hydrogen desorption occurs under elevated temperatures in the presence of a catalyst.

Recently, attention has been given to alanates such as the complex hydride sodium alanate (NaAlH₄), which can theoretically contain 7.4 wt% hydrogen; however, for adequate kinetics, the reaction requires temperatures greater than 150 °C. Furthermore, the reaction was considered irreversible until the work of Bogdanovic et al. who used transition-metal catalysts, such as titanium oxide, with NaAlH₄ which enhanced the reaction kinetics, and allowed for a reversible hydrogen storage capacity of 3.7 wt% at approximately 100 °C. At 120 °C, this reversible capacity is released in 5 hours. An additional 1.8 wt% hydrogen can be released if the temperature is raised to between 150 and 250 °C; however, hysteresis is prominent during cycling, and after 25 cycles, the average hydrogen capacity was measured at 4 wt%. Although, the catalyzed alanates have now been proven to be reversible, the reaction kinetics are still too slow to be useful
in a vehicular application. Furthermore, the USDOE has abandoned most alanate work due to safety concerns.⁹,¹⁰

Another avenue of hydrogen storage is the use of a hydrogenated fluid. A hydrogenated fluid is able to store and produce hydrogen through a dehydrogenation-hydrogenation reaction. These fluids are usually aromatic hydrocarbons such as cyclohexane, methylcyclohexane, or decalin, and have several advantages over other hydrogen storage technologies. First, the cyclic hydrocarbons are reversible and can contain high hydrogen contents of 6 to 8 wt%.¹¹ They also have high boiling points of 80 to 190 °C, and since the compounds are liquid, the present infrastructure for fuel delivery can be utilized.¹¹ These fluids are a promising hydrogen storage technology, but many operating characteristics limit the use of the presently investigated fluids onboard a vehicle.

Although the dehydrogenation reaction is endothermic and the chemical equilibrium is favourable, high temperatures are required for dehydrogenation. Several studies have shown that even with platinum catalysts, operating temperatures of around 350 °C are required for high conversion and adequate reaction kinetics.¹¹,¹² Currently, some researchers are exploring methods to lower these operating temperatures, but this work is still in very early development. Unless operating temperatures can be lowered, it is unlikely that this method will be used on board an automobile; however, these fluids could be used for transporting hydrogen to fuelling stations where hydrogen generation occurs on site.
2.1.3 Chemical Hydrides

Chemical hydrides are materials that produce hydrogen through a chemical reaction with another substance such as water. These materials have the advantage of producing hydrogen almost immediately or “on demand.” They generally exhibit greater gravimetric energy densities than most hydrogen storage methods, and most chemical hydrides are stable. Therefore, these materials do not “leak” a large, if any, amount of hydrogen during long periods of storage without usage. The main downside to such materials is that most are not fully reversible and cannot be recycled. Furthermore, the chemical reactors needed to house the reaction lower both the gravimetric and volumetric energy density of the entire storage system. Sodium borohydride (NaBH₄) is an example of a chemical hydride that is under development due to its ability to store hydrogen in a stable and safe solution.

Sodium borohydride reacts with water to produce hydrogen in the following hydrolysis reaction:

\[
NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 \tag{Equation 2.1}
\]

The standard state enthalpy change of the above reaction at 25 °C is -217 kJ and is therefore exothermic. Unfortunately, the rate of hydrogen release during the hydrolysis reaction is low. This is due to an increase in pH of the solution as the basic metaborate (NaBO₂) product is formed. The reaction rate can be increased with the addition of acid, catalysts, or an increase in temperature.\textsuperscript{13} Furthermore, the amount of heat energy produced by the NaBH₄ reaction is quite large and a suitable heat management system is required.
The hydrogen storage capacity of NaBH₄ is 10.9 wt% and can be calculated by dividing the molar mass of hydrogen produced by the total molar mass of NaBH₄ plus the molar mass of the stoichiometric amount of water needed for reaction. As stated previously, a PEMFC produces water as a by-product. If this water is recycled to produce hydrogen from NaBH₄, the storage capacity increases to 21 wt%. However, one important factor to consider is that the by-product of the chemical reaction, NaBO₂, is still carried on-board. Therefore, it must be included in the storage capacity calculations. If this product is included, the storage capacity drops from 21 wt% to 12 wt%. It is also important to note that if a hydrated form of NaBO₂ forms, such as NaBO₂·4H₂O, the storage capacity decreases to a level that no longer meets the USDOE requirements stated previously. The NaBH₄ solution is usually stabilized with the addition of sodium hydroxide (NaOH). The stabilized solution can then be reacted with a catalyst or small amount of acid to produce hydrogen.¹⁴,¹⁵ However, the catalyst, base, pumps, and reactor vessel all decrease the total gravimetric storage capacity of the storage system. In addition, considerable excess water is used to keep the product NaBO₂ in solution. Regardless, NaBH₄ still represents a starting point for hydrogen storage.

Sodium borohydride is a promising hydrogen storage chemical due to its large storage capacity, but there are also many other chemicals such as lithium borohydride, calcium hydride, sodium aluminium hydride, etc. which are currently being researched. Development in other storage methods that have higher operating temperatures is in early stages and is often hampered by cost.¹⁶,¹⁷,¹⁸
2.1.4 Metal Hydrides

Hydrogen reacts with many different transition metals and their alloys to form hydrides. These compounds absorb hydrogen like a sponge when exposed to elevated hydrogen pressures. The absorption process is exothermic and therefore releases heat. The following equation is used to describe the absorption process of hydrogen into a generic metal, M:

\[ M + \frac{x}{2}H_2 \leftrightarrow MH_x \]

Equation 2.2

To release hydrogen, heat must be applied to the metal hydride to activate the endothermic desorption process. Many properties of metal hydrides can also be tailored by using different intermetallic compounds. Researchers have literally produced thousands of metal hydride compounds, many of which are listed with their properties in The Hydpark Metal Hydrides Database.19

The main thermodynamic expression used to analyze a metal hydride and its properties is the isothermal, pressure-composition-temperature (PCT) hysteresis loop. Figure 2.1 displays a single isotherm from a typical PCT plot including various mathematical representations for the characteristics of the curve.
Metal hydrides can be described as moving from a pure metal solution phase ($\alpha$-phase) to that of a metal-hydrogen solution ($\beta$-phase). As the hydrogen pressure is increased, hydrogen is exothermically dissolved into the alloy’s lattice structure with hydrogen atoms occupying the interstitial sites of the lattice. The hydrogen concentration in the material follows Sievert’s law, which is Henry’s law for a dissociating solute:\(^21\)

\[ c \approx K_s^{-1} P^{1/2} \]

Equation 2.3

where $K_s$ is a constant for a given temperature. The temperature dependence of $K_s$ can be expressed as:

---

*Figure 2.1 – Metal hydride isotherm\(^{20}\)*
\[
\ln K_s = \frac{1}{RT} \left[ \Delta H_s - T \Delta S_s \right]
\]

Equation 2.4

where \( \Delta H_s \) and \( \Delta S_s \) are the solution enthalpy and solution entropy of reaction respectively. Figure 2.2 displays the PCT plot which consists of several isotherms. The figure also includes labels for the regions associated with the phases of the metal hydride. The hydrogen absorption is represented pictorially to the left and right of the graph.

![Figure 2.2 – PCT plot showing phase regions for a typical metal hydride](image)

When both phases co-exist, there is a plateau in the isotherm. The length of this plateau represents the reversible amount of hydrogen stored in the material. Few experimentally measured isotherms exhibit flat plateaus due to compositional inhomogeneities.

The upper and lower plateaus in Figure 2.1 represent the pressures required for absorption and desorption of hydrogen respectively and the difference between these plateaus represents hysteresis. Although quantitative results of hysteresis are few, most researchers believe that it is an effect brought on by the resistance to the abrupt increase of molar volume when transitioning from a saturated solution of hydrogen in metal to hydride phase. The plateau pressure will increase with temperature, and the behaviour
is usually close enough to the van’t Hoff equation for engineering design purposes. This is described mathematically by:  

\[ \ln P = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \]  

Equation 2.5

where \( \Delta H \) represents the enthalpy of the hydriding reaction and characterizes the stability of the metal hydrogen bond. The \( \Delta S \) term represents the entropy of the hydriding reaction and corresponds to the entropy change from molecular hydrogen gas to dissolved solid hydrogen.  

Metal hydrides also have several other interesting properties. The material usually requires “activation” where the material is hydrogenated for the first time. Activation requires extra energy to surpass barriers such as oxide films. This process often depends on surface structures, and involves the internal cracking or decrepitation of the metal particles which increases the surface area. Decrepitation is simply the self-pulverization of the larger metal particles into a finer powder. This is due to the brittle nature of the alloys and the fact that the metal expands when hydrogenated. This aspect of the metal hydride affects packing density, hydrogen storage capacity, and thermal conductivity.

Most metal hydrides exhibit poor thermal conductivity and so other materials, such as aluminium foam or copper fins, may be needed to increase heat transfer throughout the material. Unfortunately, many metal hydrides are sensitive to hydrogen impurities such as carbon dioxide (CO\(_2\)), and oxygen. Therefore, the hydride vessel must isolate the hydride material from other gases that might lead to degradation of the material. Cycling metal hydrides through absorption and desorption also results in the stabilizing to a lower amount of hydrogen storage capacity than when first saturated.
This effect can be attributed to changes in the metal lattice structure and the introduction of impurities.\textsuperscript{22,23,24}

Since numerous combinations of elements result in metal hydrides, most have been classified into several categories: AB\textsubscript{5}, AB\textsubscript{2}, AB, A\textsubscript{2}B, and others. AB\textsubscript{5} intermetallic compounds, such as LaNi\textsubscript{5}, exhibit low hysteresis, easy activation, and good tolerance to small amounts of O\textsubscript{2} and H\textsubscript{2}O impurities present in the hydrogen gas. An example of an AB\textsubscript{2} alloy is TiMn\textsubscript{1.5}. These alloys are less costly than the AB\textsubscript{5} alloys, but are more difficult to activate. They do, however, tend to show higher hydrogen storage capacity than the AB\textsubscript{5} alloys. TiFe, an AB alloy, displays two distinct plateaus. These alloys are usually slow and difficult to activate. They are also highly sensitive to impurities. An example of an A\textsubscript{2}B alloy is Mg\textsubscript{2}Ni. These alloys generally require high desorption temperature. Many researchers have attempted to lower the desorption temperature with the addition of other metal elements, but have been unsuccessful.

Table 2.2 displays select characteristics of different metal hydrides.

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Type</th>
<th>Enthalpy of Reaction ([\text{kJ} \cdot \text{mol}^{-1}])</th>
<th>Entropy ([\text{kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}])</th>
<th>Desorption Pressure ([\text{atm} @ 25^\circ\text{C}])</th>
<th>Density ([\text{g} \cdot \text{cm}^{-3}])</th>
<th>Reversible Storage Capacity ([\text{wt}%])</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaNi\textsubscript{5}</td>
<td>AB\textsubscript{5}</td>
<td>30.8</td>
<td>0.108</td>
<td>1.8</td>
<td>8.4</td>
<td>1.28</td>
</tr>
<tr>
<td>TiMn\textsubscript{1.5}</td>
<td>AB\textsubscript{2}</td>
<td>28.7</td>
<td>0.114</td>
<td>8.4</td>
<td>6.4</td>
<td>1.15</td>
</tr>
<tr>
<td>TiFe</td>
<td>AB</td>
<td>28.1</td>
<td>0.106</td>
<td>4.1</td>
<td>6.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Mg\textsubscript{2}NiH\textsubscript{4}</td>
<td>A\textsubscript{2}B</td>
<td>-64.5</td>
<td>-0.122</td>
<td>(10^5)</td>
<td>N/A</td>
<td>3.3</td>
</tr>
</tbody>
</table>

Note: The enthalpy of reaction values stated in the above table are taken as per mole of hydrogen. The values stated for TiFe represent the lower plateau for this material.

Although there are many different types of metal hydrides, they all share similar hydrogen storage characteristics.
The main advantage to using metal hydrides is the ability to reversibly store hydrogen at ambient temperatures and pressures. Metal hydrides are able to absorb large amounts of hydrogen, but are relatively heavy. Therefore, the volumetric capacity of these materials is quite high, but the storage system is affected by the large mass of the material, and the gravimetric storage capacity is quite low.

### 2.2 Thermally Efficient Hydrogen Storage

There is potential for the endothermic desorption reaction of metal hydrides to regulate temperatures in a chemical reactor that liberates hydrogen exothermically. The purpose of this work is to study the interaction between a reactor generating heat and a desorbing metal hydride acting as a temperature management system.

#### 2.2.1 The Hybrid Method

The hybrid method is an attempt to manage the thermal efficiency of a chemical hydride system using a metal hydride. For example, the excess energy produced during hydrolysis of a chemical hydride, such as NaBH₄, could be used in the energy requirement of an endothermic hydrogen desorption of a metal hydride such as LaNi₅. Coupling an exothermic hydrogen storage method with an endothermic storage method leads to effective heat management by utilizing energy that would otherwise be lost to the environment. Therefore, the entire hydrogen storage system is more thermally efficient and compact. Figure 2.3 displays an example of a hybrid hydrogen storage system.
In the schematic, water is injected into the inner cylinder of a reactor containing a chemical hydride. Through a hydrolysis reaction, hydrogen and heat are produced. The heat then travels outwards toward the external environment where it is absorbed by an endothermic metal hydride, which produces additional hydrogen gas. Figure 2.3 is meant only to display the hybrid storage concept, and the actual design of the reactor will depend on the nature of the hydrogen storage materials used.

The concept of a hybrid hydrogen storage system is certainly intriguing because of the increase in thermal efficiency; however, it may not be beneficial from an energy density perspective. The addition of an endothermic hydrogen storage material will lower the gravimetric energy density of the entire system. Approximate calculations were made in an attempt to predict these operating characteristics and are displayed in Table 2.3. The calculations used a 10 wt% NaBH₄ solution for the chemical hydride and
LaNi₅, which is a typical metal hydride. The details for the calculations are outlined in Appendix A. The ratio of chemical solution to metal hydride was chosen such that the heat of reaction from the NaBH₄ solution was balanced with the heat of reaction of the metal. The values represented in Table 2.3 assume a fuel cell operating at 100% efficiency.

<table>
<thead>
<tr>
<th></th>
<th>NaBH₄ Solution</th>
<th>LaNi₅</th>
<th>Hybrid System</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gravimetric Energy Density (kWh·kg⁻¹)</strong></td>
<td>0.83</td>
<td>0.52</td>
<td>0.55</td>
</tr>
<tr>
<td><strong>Volumetric Energy Density (kWh·L⁻¹)</strong></td>
<td>0.89</td>
<td>4.35</td>
<td>2.61</td>
</tr>
<tr>
<td><strong>Energy Efficiency (%)</strong></td>
<td>84</td>
<td>97</td>
<td>99</td>
</tr>
</tbody>
</table>

It is also possible that this concept of exothermic and endothermic hydrogen storage systems could be applied in reverse, i.e. a chemical hydride providing heat for a metal hydride storage system to liberate hydrogen from the metal hydride at higher temperatures. This would avoid the parasitic losses involved with metal hydride storage because hydrogen would not be required as a fuel to heat the metal hydride and release hydrogen. However, this thesis focuses on the use of a metal hydride system to balance the heat from a chemical hydride system.

Assuming the geometry of the reactor as shown in Figure 2.3, temperature control of the inner portion of the hybrid reactor could be important for a number of reasons. For example, if volatile compounds are used to produce hydrogen and heat, it may be necessary to control temperatures throughout the reactor to maintain reaction rates. Additionally, the operation of a PEM fuel cell requires that heat be removed since the reversible cell potential decreases with an increase in operating temperature. Therefore,
hot hydrogen gas fed to a PEM fuel cell may have an adverse affect, and temperature control of the hydrogen producing materials may be necessary.

If heat management is a priority, this hybrid solution is a more compact method to remove heat from a system when compared to other methods such as a traditional heat exchanger, because it is also able to generate additional hydrogen.
Chapter 3 : Experimental

3.1 Overview

The goal of this thesis was to investigate the possibility of operating a chemical hydride storage device in a thermally controlled manner using an endothermic metal hydride for temperature control. The testing program was designed in such a way as to show the effectiveness of a metal hydride heat absorption unit. This unit would replace a conventional cooling system that is driven by power from the fuel cell with one that would generate hydrogen and require no parasitic energy from the fuel cell.

In order to achieve the stated goal, it was first necessary to construct an experimental apparatus to measure hydrogen absorption and desorption from the metal hydride to be used in conjunction with the chemical hydride reactor that liberates hydrogen and produces heat. A complex reactor was required to generate the heat and hydrogen from the chemical hydride, transfer this heat to the metal hydride, and measure the hydrogen desorption from the metal hydride.

It was required that the “hybrid” reactor must be able to transfer heat easily from the chemical hydride reaction zone to the metal hydride. The reactor must also need to be leak tight. After fabrication, the hybrid reactor was tested with chemical hydride reactions. A number of different methods producing heat were utilised to examine the hybrid reactor’s ability to transfer heat. The hybrid experiments included calibration with temperature controlled water, the use of a packed bed NaBH₄ reactor, as well as using NaBH₄ in powder form.
The following sections describe the apparatuses built as well as the experimental techniques performed.

3.2 Metal Hydride Experimental Techniques

A large variety of experimental methods and equipment exists to adequately measure the hydrogen storage capacity of a metal hydride. These methods can be grouped into two basic categories: gravimetric or volumetric. The selection for a particular type of apparatus is greatly influenced by operating criteria such as material type, pressure and temperature range, mass of material, and type of measurement.

As the name implies, gravimetric methods monitor the change in weight of a sample as absorption or desorption of hydrogen occurs. In a gravimetric system, a microbalance head is mounted in a vacuum-pressure vessel. The major sources of error within this system are attributed to buoyancy, thermal, and mechanical disturbances.

Some of these error sources can be corrected by taring the opposite arm on the balance with a mass of non-absorbing material. The gravimetric method has been used for determining hydrogen storage in both carbon materials and metal hydrides.

Volumetric devices are widely used to measure hydrogen storage capacity. The volumetric technique closely monitors changes in the pressure of the system, and hydrogen storage capacity is calculated from the calibrated volume of the apparatus. The popularity of this device originates from its simple concept and ability to conduct measurements over a wide range of pressures and temperatures. These properties allow for volumetric instruments to be built “in-house” allowing the researcher to have an comprehensive knowledge of operation and also reduce costs. Volumetric apparatuses
are sometimes also referred to as Sievert or PCT instruments, and many variations of the volumetric apparatus have also been made. For example, some have attempted to perform hydrogen absorption and desorption at constant pressure.\textsuperscript{29} Another type of volumetric apparatus utilizes a differential pressure gauge with a reference and sample volume.\textsuperscript{30} These two modifications of the volumetric device were designed and constructed for the experiments performed in this thesis. The first device, herein called the “Sievert Apparatus” was constructed and used for several experiments. It was a direct method for measuring hydrogen evolution; however, it was disassembled in favour of a differential setup. A full description of the Sievert Apparatus and associated experiments performed is located in Appendix B.

### 3.3 PCT Apparatus

Following the Sievert Apparatus, it was decided that a differential setup was required to eliminate many of the sources of error that were found. Therefore, the Sievert Apparatus was rebuilt into a new differential setup, termed the “PCT” apparatus. This new apparatus is shown in Figure 3.1, and a photo is shown in Figure C.1.
The differential setup contained two volumetrically balanced sections of equal volume. The smaller volumes, marked “reference” and “sample” in Figure 3.1, were both placed in a temperature controlled atmosphere such as a furnace or water bath. The remainder of the apparatus was held in a temperature controlled enclosure.

The metal hydride sample was placed in one of the smaller volumes of the apparatus. During hydrogen absorption or desorption, the pressure in the section containing the sample will either increase or decrease. Since the pressure in the section without a sample will not vary, and the two sections are identical in volume, the hydrogen capacity can be calculated from the difference in pressures.

*Figure 3.1 - PCT apparatus schematic*
This technique has several advantages over the traditional, single volume setup (Sievert Apparatus). The apparatus is less sensitive to temperature fluctuations because both sections of the apparatus are equal in volume and experience the same fluctuations. This could occur when expanding hydrogen into the different sections of the apparatus, or from the external environment. The inherent accuracy of the differential pressure measurements is also much greater than that of an absolute pressure sensor. This is due to the fact that the accuracy of a pressure sensor is related to the span of the sensor. Since differential pressure sensors measure a much smaller span or range of pressures, the absolute error in these measurements is much smaller. Thus, the differential setup eliminated many sources of error while still maintaining a large range of operating pressures and temperatures.30

The PCT apparatus had several features that still need to be explained. The apparatus contained the Swagelok pressure transducers from the former Sievert system in order to measure the absolute pressure in both sections of the apparatus. A Honeywell Sensotec differential pressure transducer with accuracy of 0.2% of the span joined each section of the PCT device. Larger, one litre, volumes were also added to each section of the apparatus in order to provide a much larger reservoir for desorption. This extra volume was necessary for some desorption kinetic experiments to avoid hitting the desorption pressure plateau. The metering valves (ME-0) and (ME-1) were used to restrict flow of hydrogen into and out of the apparatus so that target pressures were easier to acquire. The temperatures of the apparatus and of the sample were measured in the same manner as the Sievert apparatus described in Appendix B with one minor difference. Instead of a single thermocouple, two are used in the PCT apparatus and are
placed on the surface of the sample and reference reservoir volumes. The average of the readings from these thermocouples is used for temperature control. A single, 60W resistive heating plate is used to maintain the apparatus at a constant temperature of 35 °C. A Numatics solenoid manifold was purchased to account for the added bellows valves (BV in Figure 3.1), and a Fieldpoint data acquisition system was used for automation and to record data. To view more details about the apparatus, please see Appendix C.

Using the PCT apparatus, several material characteristics of a metal hydride can be monitored. Kinetic experiments can be performed to monitor the rate of absorption or desorption from a metal hydride. A PCT curve can also be created to determine pressure plateaus for the material. These experiments can be performed on different metal hydrides to determine which hydride is suitable for a particular application. For this thesis, only one type of metal hydride material was used, LaNi₅.

### 3.3.1 Absorption Kinetics

The purpose of the absorption experiment was simply to track the amount of hydrogen absorbed with time. This kinetic experiment with the PCT apparatus began with the sample holder placed in a water/oil bath or furnace at an elevated temperature and under vacuum for one hour to ensure full desorption. The sample was then allowed to reach a target, constant temperature for absorption. The reference and sample reservoirs were then pressurized to a large enough pressure such that upon desorption, the total pressure in the apparatus would not decrease below the absorption plateau pressure. If the pressure were to decrease below this plateau, further absorption would not occur.
Once the starting pressure has been reached, valves BV1 and BV2 (see Figure 3.1) were opened simultaneously to expose the sample and reference volumes to hydrogen. The pressure in the reference chamber would remain constant, and upon absorption, the pressure in the sample chamber would decrease. This decrease in pressure was measured by the differential pressure gauge, and the number of moles absorbed was calculated as:

\[ n = \frac{\Delta P V_{\text{RES}}}{zRT} \]

Equation 3.1

where \( \Delta P \) is the pressure difference measured by the differential sensor, \( V_{\text{RES}} \) is the sample reservoir volume, \( R \) is the universal gas constant, \( T \) is the temperature of the reservoir and \( z \) is the gas compressibility factor calculated according to Kouremenos et al.\(^{31}\)

The experimental run ended when no significant pressure decrease had been noticed within a specified time frame. Typically, if a large sample size was used, the large reservoir volumes separated by BV0 and BV3 were used and pressurized with hydrogen. Additionally, a large sample could absorb much more than the differential pressure gauge span of 207 kPa (30 psi). In this situation, the PCT apparatus would equalize the pressure between both sides of the apparatus by opening BV4 and BV5 for one half of a second. The experiment would then continue; however, now the previous total number of moles absorbed were added to the future number of moles that would continue to be absorbed. This equalizing process could repeat indefinitely throughout the experiment. One further feature of the absorption kinetics experiment is the ability to input a plateau pressure threshold. If no pressure change was noticed within a specified time frame, the experiment ended unless the absolute pressure was within 15\% of the
plateau pressure. If this was the case, the experiment repeated from the beginning by re-pressurizing the reservoirs. In this situation, the total sum of hydrogen moles absorbed was also used for calculations.

### 3.3.2 Desorption Kinetics

The purpose of the desorption experiment was to track the amount of hydrogen desorbed from the sample with time, and the operation was basically the absorption process in reverse. Valves BV1 and BV2 were both kept closed, and the apparatus was vacuumed completely or to the desired desorption pressure. The sample was then allowed to reach a desired, constant temperature, and BV1 and BV2 were opened to the rest of the apparatus simultaneously. Again, the pressure in the reference chamber would remain constant while, upon desorption, the pressure in the sample chamber would increase. The increase in pressure was measured by the differential gauge, and the number of moles desorbed was calculated using the same formula as Equation 3.1. If a large sample size was used, the large reservoir volumes would be used during desorption to ensure that the pressure did not increase above the desorption plateau pressure. Similar to the absorption kinetics experiment, an equalizing pressure routine and a plateau pressure threshold was used throughout the experiment. If the absolute pressure was within 15% of the plateau pressure, the experiment would repeat from the beginning by evacuating the reservoirs.
3.3.3 PCT Measurement

The PCT measurement process was used to create the metal hydride isotherms explained in Section 2.1.4. To create the isotherm, a series of absorption and desorption experiments was performed.

The sample was first exposed to a starting pressure of hydrogen below the material’s absorption plateau pressure. If the pressure had not changed significantly in a set time period, the number of moles absorbed was recorded, and the pressure was increased by a set amount. This process was repeated until a target end pressure was reached. To keep track of the total amount of hydrogen absorbed, the number of moles absorbed in each individual cycle was added to the number of moles absorbed in previous cycles. Hydrogen will only be absorbed once the pressure surpasses the material’s absorption pressure plateau. Since each pressure increment was relatively small, the absorption plateau appeared because the material stopped absorbing hydrogen when the pressure was equal to this plateau.

To attain the desorption plateau, the cyclic process was repeated, but the pressure was decreased in each iteration. To keep track of the total amount of hydrogen desorbed, the number of moles desorbed per cycle was subtracted from the total number of moles in previous cycles. The desorption plateau was realized when the pressure increments drop below the sample’s desorption plateau. Figure 3.2 shows the PCT process with operating pressure trends (shown as a dotted line with arrowheads) to demonstrate how the plateaus are realized.
The number of moles absorbed or desorbed per cycle was calculated using Equation 3.1. To calculate the total number of moles absorbed or desorbed throughout the entire PCT process, the following calculation was performed:

\[ n_{\text{tot}} = n_{\text{previous}} \pm \frac{\Delta PV_{\text{RES}}}{zRT} \]

Equation 3.2

where \( n_{\text{tot}} \) represents the total number of moles of hydrogen that the sample contains, and \( n_{\text{previous}} \) represents the total number of moles of hydrogen that the sample contained after the previous cycle. The uncertainty for all PCT calculations is explained in Appendix D.

### 3.3.4 PCT Volume Calibrations

As mentioned, the measurement technique used for the PCT apparatus volume calibrations was simply based on a difference of pressures. Two “difference of pressures” methods were used to try to accurately calculate the rest of the volumes in the process.
system. Each method relied on a carefully calibrated volume which was attached to the apparatus.

The first method, herein called the “forward method,” charged this calibrated volume attached to the PCT apparatus with hydrogen. This volume was then isolated from the apparatus while the apparatus was evacuated. Once a vacuum pressure had been obtained, the calibrated volume containing hydrogen was opened to either reservoir, and the pressures were monitored. In a second method, named the “reverse method,” the calibration volume was evacuated and then either reservoir was pressurized with hydrogen gas. The calibration volume was then opened to the unknown reservoir volume, and the pressures were monitored.

An automated program was written to perform both the forward and reverse volume calibration methods. Average values of starting and ending pressures as well as temperature were used to calculate the different apparatus volume sections.

Since both of these volumes relied on a single, smaller volume, this calibration volume was carefully determined using water. The empty volume was weighed and then filled with water. The filled volume was then weighed again, and the volume was determined using the density of water and the difference of the two weights. The temperature of the water was monitored using a resistive temperature detector (RTD) probe to accurately determine the density of the water used. The density of the water was calculated according to the following formula:\textsuperscript{32}
\[
\rho = a_s \left[ 1 - \frac{(T - a_1)(T - a_2)}{a_3(T - a_4)} \right]
\]

Equation 3.3

where \( a_1/°C = -3.983035 \pm 0.00067 \)
\( a_2/°C = 301.797 \)
\( a_3/°C^2 = 522528.9 \)
\( a_4/°C = 69.34881 \)
\( a_5/(kg \cdot m^{-3}) = 999.972 \)

This volume calibration method was also used on the sample holders, exterior valve, and tubes exiting the apparatus. Between each volume calibration, the volumes under examination were placed in an oven at 100 °C overnight to eliminate any leftover water. A summary of the volume calibrations using water is displayed in Table E.1.

The water volume calibrations resulted in the following averages:

- Calibration Volume = 25.90 ± 0.01 cm³
- Tube 1 = 8.42 ± 0.07 cm³
- Tube 2 = 8.37 ± 0.07 cm³
- Tube 3 = 4.11 ± 0.07 cm³
- Tube 4 = 4.91 ± 0.07 cm³
- Sample Volume = 0.51 ± 0.007 cm³
- Reference Volume = 0.52 ± 0.007 cm³
- Large Sample Reservoir = 996.5 ± 1.65 cm³
- Large Reference Reservoir = 985.9 ± 1.65 cm³

The uncertainty calculations are shown in Appendix E. The large volumes were measured using water calibrations, and the theoretical volume of the tubing leading to them.

The rest of the volume portions of the PCT apparatus were estimated using two methods. The first method adopted the theoretical volumes from component schematics as well as measured tube lengths and diameters. This method produced the following volumes:
- Reservoir Volume = 94 ± 4 cm³
- Large Reservoir Volume = 1006 ± 50 cm³
- Reservoir and Large Reservoir Volume = 1100 ± 50 cm³

Theoretically, the sample side and reference side should be identical in volume and hence no difference between the two apparatus sides is noted above. The error calculations for these volumes are also explained in Appendix E.

The second method used for the interior volumes used the “calibration” volume pressure technique explained previously. Using this method, the following PCT apparatus volumes were calculated:

- Sample Side Reservoir Volume = 90 ± 18 cm³
- Reference Side Reservoir Volume = 92 ± 13 cm³

The smaller reservoir volumes were accurately predicted, but the error associated with the large volumes using this pressure calibration method was too large to accurately determine the true volumes using this method. Gas expansion into the large reservoir volumes led to a temperature change which resulted in erroneous pressure readings. For this reason, the larger volumes were calibrated using water. The attempted calibrations using the pressure method for these volumes were not reported.

Although the error associated with the pressure calibration method was found to be much larger than that of the theoretical calculations, the actual results were quite similar. For this reason, the following reservoir volumes were chosen:

- Sample Side Reservoir Volume = 92 ± 4 cm³
- Reference Side Reservoir Volume = 93 ± 4 cm³
These reservoir volumes represent an average value between the theoretical and pressure volume calibration techniques. The error chosen was based on the variance between the two calibration methods.

3.3.5 PCT Performance

To evaluate the PCT apparatus, several portions of the apparatus had to be calibrated, and all volumes had to be checked for leaks. Following these checks, a sample of metal hydride was used to check the accuracy and performance of the PCT apparatus by comparing the apparatus results to a standard set of results given by a metal hydride material company called Treibacher Industrie AG.

The PCT apparatus was checked for gas leaks by observing the pressure change over a period of several days. The PCT apparatus was contained in a temperature controlled, and insulated environment, to avoid errors in pressure readings from fluctuations in ambient temperatures.
It can be seen from Figure 3.3 that the temperature control of the apparatus was adequately maintained at approximately 308 K or 35 °C. Additionally, the differential pressure gauge did not fluctuate significantly. Therefore, external temperature fluctuations affected the apparatus equally on the reference and sample volumes. The fact that the differential gauge does not fluctuate with external temperature effects is the PCT apparatus’ greatest advantage over other experimental techniques.

During an absorption experiment, the temperatures of the volumes were affected by gas expansion while pressurizing the reservoirs. This effect can be seen in Figure 3.4 when the reservoirs were filled with hydrogen to relatively high pressures above 1000 kPa.
Figure 3.4 shows that the temperatures of the reservoir volumes increased by as much as one degree due to gas expansion\(^a\). These temperature fluctuations were deemed acceptable because they were usually less than one degree and the error associated with the temperature readings was taken as one degree.

Although the main portions of the apparatus were held at a constant temperature, the small sample and reference volumes were placed in a water bath, oil bath, or furnace which may have been at a much different temperature. Therefore, as the gas traveled from the reservoir volumes to the sample or reference volume, it would have changed in temperature and pressure. This factor was not accounted for directly, and could represent another source of error for the apparatus. Since the volumes of the sample and reference areas are much smaller than that of the reservoirs, it was assumed that this effect was negligible. Furthermore, it was also assumed that the uncertainty taken for each volume was large enough to include this potential effect.

\(^a\) Hydrogen has a low inversion temperature of 202 K. Above this temperature, hydrogen gas will heat upon expansion.\(^5\)
3.3.6 Benchmarking Using the PCT Process

In order to ascertain how well the PCT apparatus performs, a number of tests were undertaken with a small sample size (0.2527 g) of LaNi\textsubscript{5} provided by Treibacher. This individual sample was taken from a large batch of material that was previously activated using the hybrid reactor later described in Section 3.4. The experiments illustrated some operating characteristics of LaNi\textsubscript{5} and some of the tests were compared to a benchmark plot which was also provided by Treibacher.

The activation process of the large batch of LaNi\textsubscript{5} was performed at room temperature and at an elevated hydrogen pressure of approximately 6500 kPa. Figure 3.5 displays a sample before and after activation. The self pulverisation or decrepitation of the metal was easily noticed.

The first test performed was a benchmarking PCT test at 25°C. The sample of LaNi\textsubscript{5} and reference were kept at this temperature using an oil bath. Initial results from...
the PCT process were quite promising. Figure 3.6 shows the first PCT run and cycle for the material immediately after the first activation.

![Diagram](image.png)

*Figure 3.6 – First benchmarking PCT run*

It was noticed that a sharp or abrupt drop appeared towards the end of the desorption portion of the PCT routine at approximately 0.3 wt%. A second PCT test was performed immediately afterwards to check for repeatability. Figure 3.7 shows the second PCT test.
The abrupt drop was noticed again in the second run; however, the pressure plateaus and weight percent values seemed to have an acceptable amount of variation. Figure 3.8 and Figure 3.9 show a comparison between the two runs for absorption and desorption respectively.
The comparisons show that the apparatus was very precise in determining the pressure plateaus of the metal hydride. The difference between the runs in the pressure plateaus for both comparisons was approximately 5 kPa. Both curves revealed a decrease in storage capacity between runs. This degradation in storage capacity was attributed to the effects of cycling the material.

A comparison between the results measured and those recorded as standard by Treibacher is shown below.
It was assumed that during the large batch activation process the sample was not fully activated because of the difference in storage capacity as shown in Figure 3.10; however, the desorption plateau pressures were deemed acceptable since the variations from the standard data were within the error limits of the pressure transducers. Therefore, the desorption pressure plateau for the LaNi$_5$ was confirmed to be approximately 210 kPa. Additionally, the standard data provided by Treibacher did not include any associated experimental error.

**Effect of Temperature**

After the first two benchmarking PCT runs were carefully examined, a number of kinetics tests were performed as explained in the following section. After several kinetics tests, the PCT test was performed again, but at an elevated temperature of 80°C to display the effect of temperature on the plateau pressures. The result is shown in Figure 3.11.
As expected, an increase in temperature resulted in higher pressure plateaus. Since desorption of hydrogen from the metal alloy is endothermic, it was expected that an increase in temperature would promote desorption. This effect is further demonstrated by the kinetic experiments in Section 3.3.7. Therefore, a higher pressure was required to keep this reaction from occurring. Additionally, hysteresis was more prominent and the reversible capacity of the material is decreased slightly.
Design Stage Uncertainty

The design stage uncertainty during the PCT process is shown in Figure 3.12.

![Figure 3.12 - PCT run shown with uncertainty](image)

It was evident that the error associated with the storage capacity values in the PCT graph was additive and started relatively small, but increased steadily until the experiment was finished. The error associated with the pressures recorded was constant and solely dependent on the pressure transducers.

The additive error was a direct result of the way the PCT test was performed. Since the PCT experiment was a series of repeated absorptions or desorptions, the total number of moles at each step was recorded and added to the previous step. This was the cause of the accumulating error. A method to avoid this error would be to fully desorb the sample after each absorption before incrementing the pressure. In this way, the number of moles absorbed can be recorded without adding it to the previous step. The
same method could be used for desorption. In this case, the sample would have to be fully absorbed before attempting each desorption step.

The reason why this approach was not utilized was due to the large amount of time (perhaps longer than 48 hours) it would require to perform the full experiment. Since the goal of the thesis was to determine the feasibility of metal hydrides to act as a thermal control, the PCT experiment was more useful for obtaining the operating plateau pressures for a sample.

The first tests performed using the PCT apparatus were two PCT experiments. Both initial runs displayed a sharp drop at the end of the desorption portion of the experiment. A comparison with the standard data provided by Treibacher in Figure 3.10 confirmed that this was a sign of either incomplete activation or oxygen poisoning. Since the activation process was performed at room temperature, there was not enough energy available to fully strip the oxide layer from the metal’s surface. A subsequent activation process was performed at 200 °C, and a new PCT curve was created as shown in Figure 3.13.

![Figure 3.13 - PCT curve after new activation process](image-url)
The total amount of sample used to create the PCT curve above was doubled to approximately 0.4 g. Since there was more sample available for absorption and desorption, a larger span of the differential pressure transducer was used. This could be a possible explanation for the improved desorption plateau shown in Figure 3.13, since the steep drop in the desorption curve normally experienced at 0.3 wt% did not occur. Unfortunately, the total storage capacity after the new activation process did not increase when compared to the first run of the original activation process. Therefore, either oxygen poisoning from the sample was not eliminated, or the error associated with the method to produce the PCT curve was simply too large.

### 3.3.7 Kinetics

After the first benchmarking PCT tests were performed, two kinetics tests were run at 25°C to test the rate of hydrogen release as well as the repeatability of the PCT apparatus during the “kinetics” routine. A comparison between the first kinetics test and the second is shown in Figure 3.14 and Figure 3.15 for absorption and desorption respectively.
From the absorption and desorption comparison, good precision and repeatability of the maximum weight percent recorded was demonstrated. In both experimental runs, the amount of hydrogen recovered from the alloy was less than that measured during the absorption process. Furthermore, it seemed that the rate of hydrogen uptake as well as release was improved from cycling the sample. One possible reason for this rate increase
was due to the fact that the sample was not fully activated. Therefore, upon each cycle, the sample became more activated and more responsive to changes in pressure.

**Effect of Pressure**

A third kinetic test was performed immediately after the previous work to test the effect of high pressure on the rate of absorption. The following figure shows a comparison between the second absorption kinetics test performed at 600 kPa and a test performed at approximately 1900 kPa. Both tests were performed at 25 °C.

![Figure 3.16 - Pressure comparison on absorption kinetics](image)

From Figure 3.16, it can be seen that an increase in pressure will result in a more rapid hydrogen absorption. The increase in hydrogen pressure increased the concentration of the hydrogen since the operating volumes were not changing. This increase of concentration led to a more rapid rate of reaction during hydrogen absorption.
**Effect of Temperature**

To compare the effect of temperature during absorption, the temperature was increased from 25 °C to 80 °C and the pressure was increased such that the operating pressure was larger than the absorption pressure plateau at this temperature. Figure 3.17 and Figure 3.18 show the effect of temperature on the absorption and desorption process respectively.

![Figure 3.17 - Effect of temperature on absorption](image)

*Figure 3.17 - Effect of temperature on absorption*
From the preceding figures, it can be seen that increasing the temperature of the sample resulted in improved kinetics for the desorption process, but not for the absorption process. As expected, an increase in temperature promoted the desorption reaction since this process is endothermic. Conversely, an increase in temperature had an adverse effect on the exothermic absorption process.

**Design Stage Uncertainty**

The design stage uncertainty in the quantity of hydrogen absorbed or desorbed is demonstrated in Figure 3.19.
Since the absorption or desorption experiment is measured continually instead of in intervals as with the PCT experiment, kinetics experiments are inherently more accurate than the PCT type experiment.

Throughout the kinetic and PCT experiments it was immediately noticed that a bounce in the pressure readings occurs as valves BV1 and BV2 are opened to allow gas flow between the reservoirs and the sample or reference volume (see Figure 3.1). This was due to a rapid expansion of gas flow into an empty volume. For this reason, the actual data calculations and recordings were started one half of a second after the valves were opened.

Furthermore, since the sample side and reference side were not exactly identical in volume, a differential pressure was noticed immediately after the two valves were opened. To account for this effect, an average starting differential pressure was recorded over the length of another half of a second. The starting differential pressure was then included in all subsequent measurements and calculations.
In total, the two effects described above create an interval of one second where data is not recorded, but the sample could be absorbing or desorbing hydrogen. The amount of hydrogen released or absorbed during this time was assumed negligible in all calculations since this amount should lie within the calculated uncertainties.

3.4 Hybrid Reactor

The hybrid reactor was designed so that the heat produced from the chemical hydride reaction would be transferred to another material to achieve thermal control of the chemical hydride reaction. The objective of the hybrid reactor was to lower the operating temperature of the chemical hydride reaction using an endothermic hydrogen producing material. A catalytic packed bed reactor was used to produce hydrogen from NaBH$_4$, and the metal hydride LaNi$_5$ was chosen to act as a thermal control material while releasing additional hydrogen.

To optimize heat transfer between the two hydrogen storage regions, the hybrid reactor was designed with the heat producing chemical reactor located in the middle of the reactor and a ring or shell of metal hydride surrounding. The hybrid reactor was also designed to isolate the metal hydride from the external environment to prevent contamination from external poisons such as oxygen. A schematic of the chosen design is shown in Figure 3.20 and Figure 3.21.
The vessel displayed above was also used for batch metal hydride sample activation and was constructed from standard sized materials. The hybrid reactor was made from stainless steel and consisted of a 20.32 cm (8”) tall, 5.08 cm (2”) diameter, schedule 80 outer pipe. The bottom of the reactor was capped. A 1.91 cm (¾”), schedule 80 inner pipe ran through the entire length of the reactor. This allowed for a 1.91 cm (¾”) copper tube (not shown) to run through this inner pipe to provide an area for a heating or cooling fluid. The vessel was sealed using class 300 flanges and a 20% glass filled Teflon gasket. A single hole was tapped in the top lid to allow hydrogen to enter or leave the interior portion of the reactor. The first vessel was created as described and used for high pressure operation during metal hydride activation. The vessel used for
experimental procedures was the same design as shown above; however, class 150 flanges and schedule 40 pipe were used since the operating pressures are much less than those used for activation. This allowed for a vessel with thinner walls, which results in improved heat transfer. Pictures of the hybrid reactor used throughout the experiments are shown in Appendix F.

Tygon tubes were connected to the copper tube running through the middle of the reactor outlined above. This allowed either water or NaBH₄ solution to be pumped through the inner portion of the reactor. A rotary pump was used to move the working fluid that allowed accurate flow rates of 4 to 250 mL per minute. A detailed schematic of the packed bed reactor setup is shown below.

![Figure 3.22 - Hybrid experimental setup](image)

As seen in Figure 3.22 the experimental setup also made use of a separator flask when using a chemical hydride. The tube leading to the separator flask was coiled in a reservoir containing water at ambient temperatures to partially cool the gas stream before entering the separator. This was performed to condense any water vapour present in the
gas stream. The water reservoir also held a water-filled inverted 2 L graduated cylinder. As the hydrogen left the separator flask, it passed through a mass flow meter, and entered the graduated cylinder. The water contained in the cylinder was displaced by the incoming hydrogen gas, and the rate of displacement was recorded. In this way, the graduated cylinder was used to confirm that the readings from the mass flow meter were correct. Since the amount of hydrogen produced during each experimental run was far greater than the volume of the graduated cylinder, the cylinder was only used periodically throughout the experimental runs.

In the water tests, only water was pumped through the copper tubing, and no packed bed was present. The separator flask, hydrogen mass flow meter, and inverted graduated cylinder were not needed when water was used as a circulating fluid. Finally, a number of thermocouples were fixed to the surfaces of the hybrid reactor. Figure 3.23 displays how three thermocouples were placed 120 degrees apart on the outer surface of the reactor as well as on the surface of the copper tube. An RTD probe was used to monitor the temperature of the inner portion of the copper tube as well as the exit temperature of the fluid. A thin film of heat transfer paste with a heat transfer coefficient of 8.3 kW·m⁻¹K⁻¹ was also used on the surface of the copper tube to optimize heat transfer between the two hydrogen storage regions.
For operation of the hybrid reactor, 466 g of LaNi$_5$ was packed into the outer shell. The approximate height of the LaNi$_5$ from the bottom of the reactor was measured to be 13 cm.

To create the NaBH$_4$ solution, 10 wt% NaBH$_4$ was base stabilized by 5 wt% NaOH. Water was used as the solvent such that hydrolysis could occur in the presence of a catalyst. When NaBH$_4$ solution was used, the copper tube was packed with a catalyst (0.5% ruthenium on alumina support) to create a packed bed reactor. Unfortunately, a large amount of water is needed to keep the product of the hydrolysis reaction, metaborate, dissolved in solution. Therefore, the amount of NaBH$_4$ is restricted to approximately 10 wt%. Larger values risk metaborate precipitation within the solution.
which leads to clogging of the packed bed reactor.\textsuperscript{15,33} The NaBH$_4$ solution was specified hydrogen at a rate sufficient to run a 300 W fuel cell for a specified duration. For the case of a one hour run time, approximately 36 g of NaBH$_4$ was needed.

Neglecting the physical weight of the reactor itself, the ideal energy densities of the hybrid method using the stated amounts of metal and chemical hydride were calculated to be 0.5 kWh·kg$^{-1}$ and 1 kWh·L$^{-1}$. The calculations are similar to those shown in Appendix A.
Chapter 4 : Results and Discussion

The PCT apparatus was used to measure the amount of hydrogen released by the metal hydride while isolating the material from poisons such as oxygen throughout operation. With the PCT apparatus constructed and tested for functionality and accuracy, it was then possible to test the hybrid reactor that was the main focus for this thesis.

4.1 Hybrid Reactor

To study the heat transfer characteristics of the hybrid reactor described in Section 3.4, a number of approaches were taken. First, the metal hydride was studied while absorbing and desorbing hydrogen with no heat transfer from the chemical hydride. This was necessary to observe the kinetics of absorption and desorption from the large sample of metal hydride material used. The tests also served to develop consistent desorption methods from this large amount of metal hydride, and to study the heat transfer between the hydride and the surrounding hybrid reactor.

The second experimental approach was to study the metal hydride absorption and desorption kinetics using heat from temperature controlled circulating water. These tests were useful to determine what operating characteristics improve desorption from the metal hydride. The water experiments also served as a measure of what to expect when the hybrid reactor was operating with a chemical hydride as the heat source.

A packed bed NaBH₄ reactor was used as the heat source in the final series of tests with the hybrid reactor. These experiments were performed to analyze the main goal of
this thesis: thermal control of an exothermic chemical hydride reaction using an endothermic metal hydride.

4.1.1 Large Sample Kinetics

The hybrid reactor experiments made use of a larger amount of metal hydride material than what was used in previous experimentation. Since the metal hydride had poor thermal conductivity, the absorption and desorption kinetics as well as the heat transfer throughout the reactor were unknown. Therefore, the first hybrid reactor experiments were performed without fluid occupying the interior in order to observe the heat transfer throughout the large amount of metal hydride present in the hybrid reactor. Figure 4.1 displays the temperature trends for an absorption process.

![Figure 4.1 - Absorption temperature trends for the hybrid reactor](image_url)
The labels for each thermocouple in Figure 4.1 correspond to the schematic of the reactor explained previously in Figure 3.23. The upper regions of the hybrid reactor did not experience a large temperature variation because metal hydride material was not present in this region.

The heat producing absorption reaction was immediately evident; however, an interesting feature was also present. Although the top layer of the metal alloy (which physically corresponds to the thermocouples positioned at the “middle”) was the first exposed to the hydrogen gas, the bottom layer of the metal alloy exhibited absorption first since this area of the reactor was the first to experience a temperature increase. A simple solution could be that the bottom of the reactor experienced an improved heat transfer rate by means of conduction with the laboratory bench top.

Another possible explanation for this phenomenon is slightly more complicated and can be explained as follows. Prior to hydrogen absorption, no hydrogen molecules were present in the metal lattice. Upon first absorption, the hydrogen molecules were absorbed in the top layer of the metal hydride; however, the molecules quickly diffused through the metal alloy to the bottom of the reactor. This diffusion occurred by means of small amounts of desorption and absorption throughout the length of the metal hydride. The small amounts of absorption and desorption increased and decreased the local temperatures of the reactor respectively, but the net effect resulted in no significant temperature increase. Once the hydrogen at the bottom of the reactor became saturated, only absorption was possible. Therefore, the absorption area at the bottom of the reactor started to increase in temperature before the upper portions of the metal alloy.
Figure 4.2 - Desorption temperature trends of the hybrid reactor

Figure 4.2 indicates that the lower segment of the reactor was first to release hydrogen because that area was the first to experience a temperature decrease. It was evident that the desorption process was directly opposite to the absorption process.

Hydrogen molecules were leaving the metal on the surface of the upper portion of the metal alloy. This process would lead to a temperature drop, but this is not what was recorded. As the hydrogen molecules were leaving the metal alloy, different hydrogen molecules could have been diffusing from the lower areas of the alloy to fill the now empty lattice points. This movement could have resulted in small amounts of absorption during this process in the upper portion of the metal. This absorption might have been enough to balance out the temperature as small amounts of desorption occur. Meanwhile, the hydrogen molecules in the bottom of the alloy were also desorbing and diffusing towards the top of the metal lattice. However, in this portion of the metal, there was no re-absorption of hydrogen. There would have been no more hydrogen left to fill this
portion of the metal. Therefore, the temperature in this portion of the metal could only decrease. Since re-absorption may have been occurring on a small scale in the upper portion of the metal, the lower portion of the metal experienced a temperature drop first.

To test this hypothesis, a new reactor would have to be fabricated such that a long column of metal hydride is used. The reactor should be insulated from the external environment, and thermocouples could be placed along the column’s length to record the temperature trends. If more accuracy is desired, one would have to physically record the movement of the hydrogen molecules through the metal alloy. To the author’s knowledge, neutron diffraction is the only tool that allows researchers to see hydrogen entering and leaving hydrogen storage materials in real time.\(^{34}\)

If the above explanation was correct, it would have an effect on efficient heat transfer. It is known that “counter-flow” operation in a heat exchanger leads to higher efficiencies. Furthermore, a counter-flow heat exchanger minimizes thermal stresses due to more uniform temperature distributions.\(^{35}\) Since the lower portion of the hybrid reactor was the first to reach a lower temperature, more efficient heat transfer would result if the hot operating fluid should enter the hybrid reactor in the opposite region. The same holds true during the absorption process. Since the bottom of the reactor was the first to increase in temperature, the cooler operating fluid should enter the hybrid reactor at the top for efficient heat exchange.

### 4.1.2 Baseline Heat Transfer Studies

After some insight of absorption and desorption from a large bed of metal hydride was established, it was decided to test the rate of heat transfer throughout the hybrid
reactor using a simple means. Water was used as a circulating fluid to gain an understanding of the heat transfer from the interior of the hybrid reactor to the metal hydride. The variables that were controlled included: water flow rate, water temperature, and metal hydride desorption method.

To test the operating characteristics of the metal hydride in the hybrid reactor, circulating water from a heated reservoir was used. Operating temperatures of 25 °C and 80 °C were used for comparison. During experiments at 80 °C, too much heat was lost before entering the reactor during slow flow rates despite the insulated tubing. For this reason, all tests at elevated temperatures required a minimum flow rate of 250 mL·min⁻¹.

**Large Sample Kinetics**

At operating temperatures of 25 °C and 80 °C, the desorption plateau of the metal hydride was reached far too quickly upon hydrogen release since a large amount of metal hydride was used. This effect can be seen in Figure 4.3 and Figure 4.4.

![Figure 4.3 - Desorption kinetics of hybrid reactor with circulating water at 25 °C](image)
From the above figures it can be seen that performing a kinetics experiment on the hybrid reactor was not practical. Since a large amount of metal hydride was used, the desorption plateau was reached too quickly in both temperature ranges. Under these conditions, it took too long for the metal hydride to release all of the stored hydrogen.

Furthermore, in Figure 4.4, the poor accuracy of measuring hydrogen desorption from a large sample was well illustrated. The amount of hydrogen released from the metal was well over the 1.1 wt% maximum shown in previous experiments which used material from the same batch of activated metal alloy. This was a direct result of using the larger reservoir volumes to avoid reaching the desorption pressure plateau. Using these volumes compounded the uncertainty in the total reservoir volume used for calculations. Additionally, since large amounts of hydrogen were released from the metal hydride, the changes in temperature of the hydrogen and of the metal hydride itself led to erroneous pressure readings. In total, the added error represented a total of approximately 0.3 wt%.
Throughout the desorption kinetics at 80 °C, the sample was able to release hydrogen at a faster rate due to the elevated operating temperature. As the metal hydride material increased in temperature from heat carried by the circulating water, the desorption plateau continually increased. Since the plateau was always increasing, the desorption of hydrogen from the metal hydride was also constantly occurring. This effect can also be seen in Figure 4.5 where the operating pressure far exceeded the desorption plateau pressure of approximately 220 kPa at 25 °C. The pressure trend repeats after equilibrating because the volumes were vacuumed (as indicated by the large pressure drops) and desorption was allowed to resume until completion.

![Figure 4.5 - As the metal hydride temperature increases, the desorption plateau increases](image)

The desorption method illustrated in Figure 4.5 could act as a passive temperature control method since desorption is constantly occurring with increased operating temperatures; however, this method was too time consuming to utilize in the water baseline tests where the objective was to study larger amounts of desorption and heat
transfer with the metal hydride. Nevertheless, the discovery of this passive desorption
method was put to use in the chemical hydride experiments described in Section 4.1.3.

Due to the operating characteristics outlined above, a different method was required for the desorption of hydrogen from the metal hydride for the hybrid experiments. The metal was desorbed using two methods. The first method simply placed a continuous vacuum on the metal hydride. Without metal hydride desorption, the vacuum was capable of reaching an absolute pressure of approximately 10 kPa. The second method pulsed a vacuum on the reservoirs connected to the metal hydride to maintain the operating pressure at 150 kPa. During testing with these two methods, an actual accurate recording of hydrogen released from the metal hydride during desorption was not possible.

In order to compare the heat transfer throughout the desorption experiments, three observations were evaluated. The first observation was the temperature difference between the entering water temperature and the temperature in the reactor. This value is denoted as $\Delta T_{\text{rec}}$ in the tables following.

The average approximate heat flux was also calculated using the equation: $^{35}$

$$\dot{Q} = \dot{m}C_p \Delta T$$

$$\dot{Q} = \dot{m}C_p (T_{\text{IN}} - T_{\text{OUT}})$$

Equation 4.1

where $\dot{m}$ is the mass flow converted from litres per minute to kilograms per second using the density of water at the specified temperature. $C_p$ represents the specific heat capacity of the water. $T_{\text{IN}}$ and $T_{\text{OUT}}$ are the temperatures of the water at the inlet and exit of the reactor respectively.
It should be noted that the average heat flux is simply a rough approximation of the heat flux through the metal hydride since heat was also transferred through other portions of the hybrid reactor before the exit temperature was physically measured. It was also observed that during the elevated temperature experiments, the reservoir was not able to maintain a temperature of 80 °C. The temperature gradually decreased to about 70 °C in all elevated temperature runs. Therefore, in all calculations for these runs, an average inlet temperature of 75 °C was used. Even though these values are simply approximations, they serve as an adequate means of comparison for qualitative observations.

The final means of observation was simply the time it took for the metal hydride to finish desorption. Since it was not possible to measure the amount of hydrogen desorbed from the metal hydride using the new methods explained above, the time to completion was taken as the midpoint at which the temperature profile started to increase in slope. The data recorded during a full vacuum desorption with a flow rate of 50 mL·min⁻¹ and a temperature of 25 °C is displayed in Figure 4.6 and Figure 4.7.
Figure 4.6 - Temperature profile of hybrid reactor under vacuum

Figure 4.7 - Sample pressure and outer low temperature profile of reactor during full vacuum

Figure 4.7 displays the point at which desorption was assumed to be finished. This point corresponded to the midpoint of the first increase in slope of the temperature trend for the outer, lower thermocouple on the hybrid reactor. The temperatures in this
region of the reactor would only increase when desorption from the metal hydride was finished. When comparing this point to the pressure drop in the experiment, the two values occurred at roughly the same time. This point seemed to be consistent and reasonable throughout all experiments since the rate of hydrogen desorption was decreasing and the temperature profiles had started to increase.

**Effect of Flow Rate**

A larger flow rate of water will increase the amount of heat entering the hybrid reactor. Therefore, the hybrid reactor was operated under various water flow rates, and the effect of flow rate on hydrogen desorption from the metal hydride was observed.

The first observation made from the series of water tests was that an increase in flow rate resulted in a faster desorption of hydrogen from the metal hydride. This effect can be seen in Table 4.1.

<table>
<thead>
<tr>
<th>Flow Rate [mL·min⁻¹]</th>
<th>Water Temperature [K]</th>
<th>Metal Desorption Method</th>
<th>Exit Fluid Temperature [K]</th>
<th>( \Delta T_{\text{ret}} ) [K]</th>
<th>Average Heat Flux (W)</th>
<th>Desorption Time (s)</th>
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<tr>
<td>10</td>
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<td>Vacuum</td>
<td>296.04</td>
<td>4.09</td>
<td>7.33</td>
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<td>295.70</td>
<td>0.90</td>
<td>42.64</td>
<td>6890</td>
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<tr>
<td>250</td>
<td>298</td>
<td>150 kPa</td>
<td>295.03</td>
<td>1.75</td>
<td>10.85</td>
<td>13969</td>
</tr>
<tr>
<td>50</td>
<td>298</td>
<td>150 kPa</td>
<td>296.30</td>
<td>0.47</td>
<td>32.22</td>
<td>12794</td>
</tr>
</tbody>
</table>

The differences in desorption time shown in Table 4.1 are represented graphically using the reactor temperature in Figure 4.8.
At low flow rates, the temperature in the water dropped significantly. This resulted in a smaller temperature gradient between the reactor and the external environment. Since a smaller temperature gradient existed, the heat flux through the metal hydride also decreased. Less heat was available for desorption of the metal hydride. Since desorption of hydrogen from the metal hydride is endothermic, the low flow rate experiments took longer to desorb hydrogen from the metal. Although the desorption of hydrogen from the metal hydride took a longer period of time at smaller flow rates and the interior of the reactor remained cooler. This effect is also displayed in Figure 4.8 as well as Figure 4.9.

Figure 4.8 - An increase in flow rate results in a faster desorption time
Small temperature deviations or “lumps” were noticed in the reactor temperature trends of Figure 4.9. These anomalies were investigated and it was determined that the temperature of the water reservoir was not constant.

Figure 4.10 shows that although the reservoir temperature was roughly maintained at 25 °C, the slight variations of 0.5 degrees did have a noticeable impact on the reactor temperature. Since the temperature variations were relatively small, it was assumed that the average inlet temperature was constant, and that the overall temperature trend was not significantly affected.


![Graph showing change in reactor temperature with reservoir temperature](image)

**Figure 4.10 - Change in reactor temperature with reservoir temperature**


**Effect of Desorption Method**

The desorption methods explained previously were tested under various flow rates and operating temperatures to confirm that a larger pressure gradient will result in a larger amount of hydrogen desorption from the metal hydride. As expected, the water testing revealed that a full vacuum applied to the metal hydride resulted in a faster desorption time than when a constant pressure was maintained throughout desorption. As a result, the temperature drop in the reactor was increased during a large pressure gradient. Table 4.2 displays these results.
Table 4.2  Effect of Metal Hydride Desorption Method

<table>
<thead>
<tr>
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<tr>
<td>50</td>
<td>298</td>
<td>Vacuum</td>
<td>296.04</td>
<td>4.09</td>
<td>7.33</td>
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<tr>
<td>50</td>
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<td>32.22</td>
<td>12794</td>
</tr>
<tr>
<td>250</td>
<td>348</td>
<td>Vacuum</td>
<td>340.77</td>
<td>7.35</td>
<td>124.91</td>
<td>2855</td>
</tr>
<tr>
<td>250</td>
<td>348</td>
<td>150 kPa</td>
<td>343.26</td>
<td>4.36</td>
<td>82.83</td>
<td>3090</td>
</tr>
</tbody>
</table>

In all cases, a continuous vacuum applied to the metal hydride resulted in a faster desorption time. A larger pressure gradient applied to the metal hydride resulted in increased kinetics of desorption. The temperature drop in the reactor was larger due to the faster desorption kinetics of the endothermic metal hydride.

Effect of Water Temperature

To confirm another operating characteristic, the effect of water temperature on the desorption time of the metal hydride reactor was tested. To avoid losing a large amount of heat between the water reservoir and the hybrid reactor, the flow rate was increased to 250 mL·min⁻¹ for the elevated temperature experiments. Again, as expected a higher water temperature also resulted in a faster desorption rate, and a larger temperature drop in the reactor (Table 4.3).

Table 4.3  Effect of Water Temperature on Desorption

<table>
<thead>
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<tr>
<td>250</td>
<td>298</td>
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<td>250</td>
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<td>250</td>
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</tr>
<tr>
<td>250</td>
<td>348</td>
<td>150 kPa</td>
<td>343.26</td>
<td>4.36</td>
<td>82.83</td>
<td>3090</td>
</tr>
</tbody>
</table>
The higher fluid temperatures promoted the endothermic desorption reaction of the metal hydride by providing larger amounts of heat energy. This led to a more rapid desorption of hydrogen from the metal, and a larger water temperature decrease.

**Summary of Water Experiments**

In summary, faster desorption of hydrogen from the metal hydride resulted in a larger relative temperature decrease for the inner portion of the hybrid reactor. An increase in the flow rate of the water increased the heat flux to the metal hydride; however, the reactor temperature did not drop by more than 1 °C since the fluid flow rate was too large. Conversely, a slow flow rate resulted in too little heat flux to the metal hydride, but reactor temperatures were cooler. It was also determined that the lower segment of the metal hydride bed was the first to experience a change in temperature during absorption and desorption. Therefore, for optimum heat transfer efficiency, the heat producing fluid should run from the top of the reactor towards the bottom. To promote desorption, the following operating characteristics should be maximized: heat flux to the metal hydride, operating temperature of the fluid, and the pressure gradient applied to the metal alloy.

4.1.3 Packed Bed Reactor

After the basic operating characteristics of the hybrid reactor were established, heat production from the chemical hydride packed bed reactor was investigated. The combination of the inner NaBH₄ reactor and the surrounding metal hydride shell truly represented a hybrid hydrogen generating reactor. During operation of the hybrid reactor,
hydrogen and excess heat were produced from the NaBH₄ chemical hydride reaction. The heat was transferred to a bed of surrounding metal hydride, which released additional hydrogen upon desorption.

A NaBH₄ solution was prepared and pumped through a packed bed of catalyst at a flow rate of 6 mL·min⁻¹ (see Section 3.4). This flow rate corresponded to the hydrogen production needed for a 300 W fuel cell operating at 100% efficiency, or approximately 1.5 L·min⁻¹ of hydrogen. The calculations are similar to those described in Appendix A.

The NaBH₄ solution was pumped from the bottom of the reactor to the top. In this group of experiments, the operating temperature profile as well as the amount of hydrogen production from both hydrogen storage methods were monitored in order to determine the operating characteristics of the hybrid reactor.

**Baseline Tests**

Two baseline tests were performed while the metal hydride was fully desorbed to gain an understanding of the heat transfer in the packed bed reactor without any temperature control methods. Figure 4.11 shows the temperature trends of the hybrid reactor while the packed bed reactor was operating without metal hydride desorption.
As expected, the inner portions of the reactor were heated well before the outer portions of the reactor. This was directly due to the poor heat transfer characteristics of the metal hydride. Without desorption of the metal hydride the interior of the reactor was operating at a temperature of around 352 K or about 79 °C. At approximately 3000 seconds, the solution flow was stopped because the inner portions of the reactor had reached a steady state. The hydrogen flow rate is shown in Figure 4.12. The averaged flow rate and reactor temperature are shown in Figure 4.13.
The smoothed flow rate recorded from the flow meter seemed to be almost exactly the same as the theoretical calculation of $1.54 \text{ L} \cdot \text{min}^{-1}$ of dry hydrogen gas. At approximately 1700 seconds, the flow was recorded using the inverted cylinder (shown in Figure 3.22) and a gas production rate of $1.7 \text{ L} \cdot \text{min}^{-1}$ was calculated.
Since the operating temperature of the reactor was close to 80 °C, it was assumed that some of the water was vapourized. This vapourization could lead to an increase in gas production leading to a larger flow rate than the theoretical value. It was assumed that the flow meter was either calibrated incorrectly. In either case, it was safe to assume that the amount of catalyst present in the reactor was adequate, and that the NaBH₄ was reacting to completion. Further into the experimental process, the flow meter was recalibrated.

In an attempt to increase the interior temperature of the reactor, the flow rate of the NaBH₄ solution was doubled to 12 mL·min⁻¹. Since there was excess catalyst present in the reactor, doubling the flow rate should have doubled the rate of hydrogen production as well as the amount of heat produced. Figure 4.14 displays the flow rate and reactor temperature when the solution flow rate was doubled to 12 mL·min⁻¹.

![Figure 4.14 - Hybrid reactor operating at a solution flow rate of 12 mL·min⁻¹](image-url)
As expected, the flow rate of hydrogen production was doubled to approximately 3 L·min⁻¹ or greater. This flow rate sometimes exceeded the maximum recording capability of the flow meter which was also 3 L·min⁻¹, and so anything above that value was recorded as 3 L·min⁻¹. The increase in reactor temperature, however, was not substantial. The temperature increase was only about 8 degrees to 360 K or 87 °C.

Since the heat of vapourization of water is quite significant, it can be assumed that the operating temperature of the reactor will rarely reach 100 °C. Furthermore, as temperatures in the reactor increase, larger amounts of water will be vapourized, and it can be expected that the product of reaction, metaborate, might precipitate, and clog the reactor. All subsequent hybrid reactor tests were performed at the original flow rate of 6 mL·min⁻¹.

**Temperature Control Methods**

After the control tests, two methods of metal hydride desorption for temperature control were studied with the packed bed reactor in operation. Similar to the water experiments, the first method simply controlled the reservoir volumes to a pressure threshold by intermittent vacuum. During this method, all reservoir volumes were connected to the metal hydride sample, and so an accurate measurement of hydrogen release using the differential pressure transducer was not possible.

In the second method, the metal hydride released hydrogen without any removal from the reservoirs. This method was basically a means of the passive control described earlier in Section 4.1.2 since both pressure plateaus of the metal hydride increased as the
total temperature of the reactor increased. In this way, the desorption pressure plateau would always increase allowing desorption to continually occur.

**Constant Pressure Desorption**

Measuring the hydrogen production from the hybrid reactor was necessary throughout the packed bed experiments. For this reason, the constant vacuum desorption method used in the water experiments was not performed. Instead, the effect of a constant pressure atmosphere on desorption of hydrogen from the metal hydride was studied.

Figure 4.15 displays the reactor temperature and hydrogen production rate of the hybrid reactor under constant pressure conditions.

![Figure 4.15 - Hybrid reactor temperature under constant pressure desorption conditions](image)

Figure 4.15 - Hybrid reactor temperature under constant pressure desorption conditions
From Figure 4.15, it can be seen that an abnormal reading occurred from the hydrogen flow meter. This experimental run was performed directly after the run which doubled the hydrogen production to 3 L·min$^{-1}$ as shown in Figure 4.14. It was assumed that maxing out the flow meter for a long period of time resulted in an incorrect calibration for the flow meter which led to these erroneous readings. The mass flow meter was subsequently recalibrated; however, it can be assumed that a similar amount of hydrogen and heat production was produced throughout the run since the packed bed reactor operating characteristics were very repeatable. Since the hybrid reactor temperatures were maintained below the baseline of 79 °C, it was determined that the constant pressure operation of the metal hydride desorption led to a decrease in reactor temperature throughout the one hour run. The operating temperatures of the entire apparatus as well as the hydrogen pressure of the metal hydride can be seen in Figure 4.16.
From the above figure, it can be seen that the interior reactor temperatures were much larger than those of the exterior portion of the apparatus. This was due to the poor heat transfer of the metal hydride, but also to the endothermic desorption of hydrogen from the metal hydride. The highest exterior temperature recorded was approximately 320 K or 47 °C.

**Passive Desorption Method**

The second desorption method studied utilized passive temperature control by simply allowing the metal hydride to release hydrogen continually as the temperature of the metal increased. This situation could arise if the hydrogen desorbed from the metal hydride was stored in a reservoir for future fuel cell use. Figure 4.17 displays the
temperature trends recorded during the passive control method of the metal hydride desorption.

![Figure 4.17 - Hybrid reactor temperature under passive desorption conditions](image)

It can be seen from Figure 4.17 that the passive control method also reduced the operating reactor temperature for approximately 3000 seconds. Figure 4.18 displays the operating temperatures and pressures for the hybrid reactor under the passive control method.
Figure 4.18 - Operating temperatures of the hybrid reactor under passive control conditions

Under passive control conditions, the highest external temperature was roughly 330 K or 57 ºC; however, not all hydrogen was desorbed from the metal hydride. At the time the experiment was stopped, only approximately 0.3 wt% hydrogen had been released from the metal hydride. Figure 4.18 also displays that the operating pressure was increasing with temperature. This was occurring because the metal hydride desorption pressure was also increasing with temperature. The repetitive pattern in the hydrogen pressure is due to the apparatus equilibrating itself while using the differential pressure transducer. Since it was possible to measure the hydrogen evolution using the differential transducer, the apparatus was programmed to equalize the pressure when the differential pressure was too close to the transducer’s maximum.
**Desorption Method Comparison**

To gain a true understanding of which desorption method performs the best, a direct comparison was needed as shown in Figure 4.19.

![Figure 4.19 - Temperature of interior reactor during hybrid reactor experiments](image)

Figure 4.19 displays the interior reactor temperatures during the NaBH₄ control test, which did not include any hydrogen desorption from the metal hydride, as well as the interior reactor temperatures for the other two desorption methods.

Upon comparison between the two hydrogen desorption methods used, it was determined that the pressure controlled method was more effective for maintaining lower temperatures. Since the pressure gradient applied to the metal hydride was relatively large and consistent, desorption occurred more quickly. The faster desorption kinetics resulted in a lower operating temperature for the interior of the reactor.
Although the constant pressure operation maintained a cooler reactor temperature, the passive control method was able to cool the reactor almost as much as the constant pressure method. This desorption method also did not release as much hydrogen throughout the experiment.

The amount of hydrogen desorbed during the passive temperature controlled method could be monitored directly; however, this was not possible for the pressure controlled desorption method. Therefore, a rough approximate for hydrogen desorption was created using the pressure trends throughout the experiment. Figure 4.20 and Figure 4.21 show the pressure trend for the constant pressure experiment.

![Figure 4.20 - Constant pressure control during hybrid hydrogen desorption](image)
From the magnified portion of the pressure trend shown in Figure 4.21, the hydrogen desorption rate was calculated using the slopes of the trend when the pressure was increasing. This calculation was performed in the beginning, middle, and towards the end of the experimental run. A rough, average estimate of $0.000787 \text{ mol} \cdot \text{s}^{-1}$ of hydrogen desorption was calculated. Using this calculation method, a total of 0.92 wt% was found to have been desorbed from the metal sample. This value was very close to the 1.1 wt% value that was determined to be the maximum hydrogen storage capacity for this batch of metal alloy. Therefore, it was assumed that this hydrogen desorption rate was valid for comparison to the passive hydrogen desorption method which could be measured directly.

Figure 4.22 displays that much more hydrogen was desorbed using the constant pressure method.
Again, since more desorption was occurring during this method, temperatures throughout the entire hybrid reactor were lower. The driving pressure gradient in the passive control method was not as large, and increased only with temperature. As the temperature increased during the passive control method, the amount of hydrogen desorbed also increased; however, the total amount of hydrogen desorbed throughout the entire experiment was much less than that of the pressure controlled desorption method.

On its own, the packed bed reactor produced enough hydrogen for a 300 W fuel cell operating at 100% efficiency to run for almost one hour. With the added hydrogen from the metal hydride using the constant pressure method, the fuel cell power could have increased to 500 W, or the run time could have been extended by about 40 minutes. The passive control method increased the available hydrogen enough to power a 320 W fuel cell, or extend the run time of a 300 W fuel cell by approximately 5 minutes.
Although the maximum cooling effect of the metal hydride was only a difference of about 10 ºC between the two desorption methods, clearly the constant pressure desorption method produced more available energy in the form of hydrogen.

**Extended Run Times**

In both of the above hydrogen desorption methods, the reactor was not able to reach a steady state, and so the experiment was repeated for a longer duration. Figure 4.23 and Figure 4.24 display the data recorded for the extended run using passive control desorption.

![Graph: Extended run for the hybrid reactor under passive desorption conditions](image.png)
A larger hydrogen flow rate of about 1.7 L·min$^{-1}$ is shown in Figure 4.23. This is simply due to the fact that the flow meter was recalibrated. The new calibration agreed with the flow rate measured using the inverted graduated cylinder.

A large drop in operating pressure can be seen in Figure 4.24 at approximately 5200 seconds. At this point in time, automated software controlling the apparatus had determined that the pressure had reached a steady state. The apparatus was programmed to vacuum the reservoirs and repeat the desorption process if the steady state pressure was above a certain value (in this case the value was programmed to be 200 kPa). After the apparatus vacuumed the reservoirs, the sample was allowed to perform desorption again. For this reason, the pressure started to rise again, and the temperatures in the reactor began to drop. This effect was short-lived, however, because soon thereafter, the packed bed reactor ran out of NaBH$_4$ solution and the experiment was stopped. To
compare the temperatures of a short and extended run, as well as the repeatability, Figure 4.25 was created.

![Figure 4.25 - Inner reactor temperature for multiple runs of the hybrid reactor under passive control](image)

From the above figure, it was determined that heat transfer throughout the hybrid reactor was consistent which led to repeatable operating characteristics. In the extended runs, steady state conditions were reached at approximately 5000 seconds when the inner reactor temperatures stabilized at 348 K or 75 ºC. From Figure 4.24 it can be seen that at approximately 5000 seconds desorption had come to completion before the reservoirs were vacuumed. Since the heat transfer characteristics were repeatable, it was assumed that in both extended runs, desorption had slowed to almost nothing at approximately 5000 seconds, and the inner reactor temperature had reached a steady state of 75 ºC. If the run was extended further, and the apparatus was not permitted to vacuum the reservoirs to repeat desorption, it would be expected that temperatures might reach a maximum of 79 ºC. This temperature corresponds to the maximum that was reached during the control test when no desorption was present.
The same process was also applied to the pressure controlled desorption method to study extended run conditions. The results are displayed in Figure 4.26, Figure 4.27, and Figure 4.28.

*Figure 4.26 - Extended run for the hybrid reactor under pressure controlled desorption conditions*
For the pressure controlled conditions, a steady state of approximately 350 K was also reached; however, the desorption process ended much sooner. The temperature increases in the exterior portions of the reactor, seen at approximately 3800 seconds in
Figure 4.27, indicated that desorption had slowed to almost nothing. Shortly thereafter, the reactor temperatures approached steady state. As with the passively controlled desorption method, the heat transfer characteristics of the pressure controlled desorption method were also very repeatable. Figure 4.29 illustrates a comparison between the desorption methods for the extended run times.

![Figure 4.29 - Direct comparison of hybrid reactor desorption methods for extended run times](image.png)

The steady state of 352 K that the control test reached is marked as a dashed line in the above figure. It was observed that although the pressure controlled reactor maintained a cooler temperature in the inner portion of the reactor, this control method was the first to approach steady state conditions. This was due to the fact that the metal was fully desorbed at approximately 3800 seconds. After this time, the reactor temperature quickly increased to steady state.
With the passive control method, the inner reactor temperature was slightly larger, but not as much desorption from the metal occurred. After the reservoirs were vacuumed at approximately 5800 seconds, and desorption was allowed to continue, more hydrogen was released from the metal causing the interior reactor to drop in temperature. This effect showed that, even at roughly steady state conditions, desorption from the metal hydride was able to create a significant temperature drop of about 5 degrees. Further attempts at pulsing desorption after reaching steady state operating temperatures were not performed.

**Summary**

A summary of the average inner reactor temperatures and run times of the hybrid reactor operating under various conditions is displayed in Table 4.4. An approximate energy balance was used to try to estimate the efficiency of heat transfer to the metal hydride throughout desorption. These calculations are outlined in Appendix G.

<table>
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Since a greater amount of desorption was occurring throughout the pressure controlled desorption method, the amount of heat transferred to the metal hydride was much larger. The end result was an increased heat transfer efficiency and lower temperatures throughout the hybrid reactor.
As expected, temperature control of the hybrid reactor is directly proportional to the rate of hydrogen release from the metal hydride. If low temperatures are required in the inner reactor, then large amounts of desorption must occur. Therefore, a larger amount of metal hydride will be needed to extend the operating time of the reactor under temperature control. Conversely, slow desorption of hydrogen from the metal hydride will extend the run time of the hybrid reactor, but the temperature drop throughout the reactor will not be as significant.

Using the same calculations as stated earlier in Section 2.2.1, it was determined that about 3 kg of LaNi₅ metal hydride would be needed to balance the amount of heat produced from the chemical hydride at a solution flow rate of about 6 mL·min⁻¹ for a run time of one hour; however, this calculation assumes that all heat produced is transferred directly to the metal hydride. Nevertheless, if a 466.36 g sample of metal hydride was able to absorb an average of 10% of the available heat energy, then a 3 kg mass of metal hydride could potentially absorb 64% of the heat energy. Neglecting the weight of the reactor itself, the gravimetric and volumetric energy density of a reactor using 3 kg of LaNi₅ metal hydride and the same amount of chemical hydride (36 g) would be 0.27 kWh·kg⁻¹ and 1.29 kWh·L⁻¹ respectively.

4.1.4 Higher Temperature Operation

Had it been possible, it would have been useful to test the system at temperatures above 100 ºC. This would be possible if the hydrogen were to be produced under high pressure, if steam were used, and if the reactant material was solid. Additionally, other chemical hydrogen storage methods may be developed that have higher operating
temperatures. Currently, there are limited practical methods of reacting solid chemical hydrides with water vapour above 100 °C. An attempt was made, as part of this work, to react NaBH₄ with strongly acidified water and temperature spikes close to 100 °C were observed, but given the configuration of the reactor attached to the PCT apparatus, it was not possible to maintain these reaction conditions for long periods of time. Furthermore, mass transfer limitations, caused by the reaction product metaborate, between the acidified water and the NaBH₄ powder prevented the full reaction from occurring.

4.2 Hybrid Reactor Applications

To compare the effectiveness of the hybrid reactor to other energy storage methods, the hybrid reactor’s operating conditions were calculated for several applications including automobiles and several portable devices. The values calculated in this section can be determined from equations listed in Appendix A as well as Equation 4.1.

Automotive

The design requirements for an automotive application using the hybrid reactor are fairly intensive. Assuming a small vehicle operates at 108 hp or about 81 kW and a generous running time of five hours, the power produced by the automotive fuel cell should be 405 kWh. The total amount of hydrogen needed for such a fuel cell (operating at 70% efficiency) is about 14 kg. To obtain this amount of hydrogen from the hybrid reactor, a 225 kg solution of 10 wt% NaBH₄ and 755 kg of AB₂ metal alloy would be required. Furthermore, these figures only include the weight of the hydrogen storage...
materials themselves and not of the hybrid reactor or other operating equipment that would be required. If only part of the operating heat produced is captured by the metal hydride, then operating temperatures would be larger, but less heavy metal hydride material would be required. Regardless, the weight of NaBH₄ solution alone is too large when compared to the weight of 45 litres of gasoline (33 kg).

If only a NaBH₄ solution was used to satisfy the requirements of a small automobile, the energy densities of the system with no heat control methods would be 0.58 kWh·kg⁻¹ and 0.62 kWh·L⁻¹, and 396 MJ of energy would be lost to the environment. The energy densities of the materials for an automobile using the hybrid reactor solution would be 0.41 kWh·kg⁻¹ and 1.18 kWh·L⁻¹. Since the addition of the metal hydride only improves the thermal efficiency and volumetric energy density of the system, the overall hybrid reactor using these hydrogen storage materials would not meet the USDOE targets of 1.5 kWh·kg⁻¹ and 1.2 kWh·L⁻¹ as outlined in Section 2.1. Clearly, such a solution on board a vehicle is not possible due to the large additions in weight.

Nevertheless, as advances in hydrogen storage materials are made, the hybrid reactor may become practical for automotive applications and certainly more useful in portable devices. The main restriction to the current hybrid reactor is the weight of the materials involved. If lightweight, endothermic hydrogen storage materials are improved or discovered, the gravimetric energy density of the system would increase while still maintaining thermal control, replacing bulky and heavy heat dissipation systems (which would be impractical with some portable systems) and utilizing heat that would otherwise be lost to the environment.
Additionally, the advantages of the hybrid reactor in terms of volumetric capacity cannot be overlooked. For example, assume that all of the heat produced from the NaBH₄ packed bed reactor in the single hour hybrid reactor experiments (205 kJ) is transferred perfectly to the metal hydride. It was stated earlier that approximately 3 kg of LaNi₅ material would be needed. This amount of metal hydride can fit into approximately 357 mL of space. If the same amount of heat were to be absorbed by a heat exchanger operating at 100% efficiency using an ethylene glycol solution (density of 1057 kg·m⁻³ and specific heat capacity of 3.7 kJ·kg⁻¹·K), approximately 6 kg of circulating solution would be needed. This figure assumes that the glycol solution is increased by ten degrees throughout the heat exchanger and does not dissipate heat through a radiator. Therefore, without including all of the necessary pumping equipment, it would take approximately 5.7 L of ethylene glycol to absorb the same amount of energy that 357 mL of metal hydride could. If these calculations are extended to just half of the amount of energy removed from an automobile operating on a packed bed reactor (198 MJ), the volume becomes 1690 L compared to 65 L of the AB₂ type metal hydride described above. For the automobile example, it was assumed that the ethylene glycol temperature is increased by 30 degrees through the heat exchanger. Clearly, in either case, the hybrid reactor is a much more compact design for temperature control.

**Portable Power**

The portable power sector is a market that shows potential for fuel cell applications. The amount of hydrogen needed for various portable devices is much less than that of an automobile, and therefore, not as much material is needed for storage;
however, thermal control is a critical aspect of their function. The hybrid reactor calculations were applied for the power requirements of two portable devices: a laptop and a cell phone. Table 4.5 displays a summary of the hybrid reactor sized for these devices compared to a standard lithium ion battery.

Table 4.5 Hybrid Reactor Comparison for Portable Devices

<table>
<thead>
<tr>
<th></th>
<th>Li-Ion Battery</th>
<th>Hybrid Reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Laptop</td>
<td>Laptop</td>
</tr>
<tr>
<td>Gravimetric Energy Density (kWh·kg⁻¹)</td>
<td>0.6</td>
<td>0.4</td>
</tr>
<tr>
<td>Volumetric Energy Density (kWh·L⁻¹)</td>
<td>1.8</td>
<td>1.3</td>
</tr>
<tr>
<td>Mass (g)</td>
<td>79</td>
<td>105</td>
</tr>
<tr>
<td>Volume (mL)</td>
<td>26</td>
<td>36</td>
</tr>
</tbody>
</table>

The calculations assumed that the laptop and cell phone were operating at 20 W and 0.5 W respectively using a 75% efficient fuel cell. The lithium ion battery used by the laptop was assumed to be operating at 10.8 V and 4400 mAh. Similarly, the battery used in the calculations for the cell phone was assumed to be operating at 3.6 V and 900 mAh. As in the automotive example, a 10 wt% NaBH₄ solution was used and all of the heat produced was coupled to the metal hydride in the hybrid reactor. All energy density values were calculated for the energy storage materials only. The calculations also do not account for the fuel cell required for the hybrid system, or if applicable, the cooling mechanisms used in the portable devices.

Upon comparison, the material energy densities for these two small devices were still slightly higher than those of the hybrid reactor. Therefore, the hybrid reactor would weigh more and take up more space than a conventional lithium ion battery in both devices; however, it should be noted that once the material necessary to house the lithium ion material is included, the battery’s energy densities are lowered to 0.16 kWh·kg⁻¹ and 0.27 kWh·L⁻¹. These two values are a dramatic decrease in storage density, and if a
light enough, and small enough housing were created for the hybrid reactor, the hybrid method might be a competitive solution to the lithium ion battery.

The hybrid reactor was also compared to a standard sized gasoline generator as a final means of comparison in portable power. For this assessment, a “Champion” 3.5 kW generator was used. The generator weighs 45 kg (empty), is approximately 115 L in volume, and can hold 15 L of gasoline. Its operational time with this amount of fuel is six hours when running at 100% capacity. For a valid comparison, the hybrid reactor was assumed to be coupled with two “Ballard” Mark1020 ACS fuel cells. These fuel cells are designed for back-up power generation and each can produce 1.62 kW of power. In total, these two fuel cells would take up 25 L of space and weigh 21 kg. A fuel cell efficiency of 50% was assumed. Since improvements to the hybrid reactor could be made to reduce the weight of the reactor, the fuel cell system calculations included only the weight of the fuel cells and the storage materials. The results of the comparison are displayed in Table 4.6.

<table>
<thead>
<tr>
<th>Table 4.6 Hybrid Reactor Comparison with Diesel Generator</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Storage Material System</strong></td>
</tr>
<tr>
<td><strong>Gravimetric Energy Density (kWh·kg⁻¹)</strong></td>
</tr>
<tr>
<td>Generator</td>
</tr>
<tr>
<td>1.4</td>
</tr>
<tr>
<td><strong>Volumetric Energy Density (kWh·L⁻¹)</strong></td>
</tr>
<tr>
<td>Generator</td>
</tr>
<tr>
<td>1.9</td>
</tr>
<tr>
<td><strong>Mass (kg)</strong></td>
</tr>
<tr>
<td>Generator</td>
</tr>
<tr>
<td>11</td>
</tr>
<tr>
<td><strong>Volume (L)</strong></td>
</tr>
<tr>
<td>Generator</td>
</tr>
<tr>
<td>15</td>
</tr>
</tbody>
</table>

It can be seen from the comparison above, that the hybrid reactor is a competitive option for back up portable power. The gravimetric energy density is slightly less than that of the gasoline generator, but there is a significant advantage in volumetric energy density. It is expected that the energy densities of the hybrid system will lower when
including the weight and volume of the material storage system, but improvements in heat transfer, reactor design, and materials could limit this decrease.

Not only is a gasoline generator loud, but it also generates a lot of heat. The hybrid reactor is almost silent, and has significant temperature control. Both of these features make the hybrid reactor a competitor in the portable back up power market. For example, the military may have a significant interest in a cool and quiet power unit for silent watch applications. Rural homeowners in particular may also be interested in a quiet power generator.

A disadvantage to the hybrid reactor and a significant operating obstacle is how the reactor must be recharged. The liquid NaBH₄ solution can be easily refilled just as gasoline; however, the metal hydride portion of the reactor must be pressurized with hydrogen gas. This leaves three options. The first option is to refill both hydrogen storage materials separately requiring a sophisticated refuelling device. The second option is to replace the storage unit in the form of cartridges; however, this option could be quite cumbersome considering the mass of each cartridge would be approximately 66 kg. The final, and most practical option, is to allow the metal hydride to be recharged by continual operation of the chemical hydride after the fuel cells have been powered off.

Overall, the generator comparison revealed that the hybrid reactor already has potential in the portable power market. With advances in hydrogen storage materials as well as in the design of the reactor itself, this type of hydrogen storage may become a more efficient means of portable power in the near future.
4.3  *Peak Temperature Control*

In most of the previous discussion, it was assumed much of the heat generated by the chemical hydride was captured by the metal hydride for thermal control. A more efficient means of temperature control might be to simply limit the operating temperature of the chemical hydride, which may be necessary to control reaction rates, or for practical functioning of a chemical reactor. If a certain operating temperature is exceeded, desorption from the metal hydride could occur to prevent the temperature from increasing significantly further. This concept is displayed in Figure 4.30.

![Figure 4.30 - Peak temperature control](image)

The standard hydrogen production with operating temperature of a chemical hydride is displayed in Figure 4.30 as a solid line. At a certain temperature threshold, the metal hydride would begin to release hydrogen by absorbing heat. This trend is shown as a dotted line in the figure above. In the case of a packed bed reactor, the flow rate could
be reduced to decrease temperatures further since any reduction in hydrogen created would be made up for by hydrogen released from the metal hydride.

As was seen in Section 3.3.6, the desorption pressure plateau increases as a metal hydride is heated. For this reason, two methods could be used to operate peak temperature control. The first method would maintain the metal hydride at a hydrogen pressure above the desorption pressure plateau corresponding to the peak target temperature. Therefore, no desorption could occur prior to reaching this temperature. After this temperature is reached, desorption could occur by active or passive means as shown in Section 4.1.3.

The second method involves tailoring the metal hydride material used to the target peak pressure. Some metal hydride materials require high temperatures to release hydrogen at large enough pressures to be useful for a fuel cell. For example, TiFe$_{0.8}$Ni$_{0.2}$ requires temperatures of 98 °C for hydrogen desorption pressures greater than 245 kPa.$^{19}$ If the materials chosen are specific to the target peak temperature, it would not be necessary to maintain the metal hydride at increased hydrogen pressures. Instead, desorption would occur as soon as the peak temperatures are reached.

Since it would only be necessary to limit the operating temperature using this method, only a small amount of the heat produced would need to be captured. Therefore, a much smaller amount of metal hydride material would be needed for operation resulting in an increase in gravimetric storage density while maintaining compact temperature control.
Chapter 5 : Modelling

The purpose of the computer model was to study the transient heat transfer within the hybrid hydrogen storage reactor. If an accurate computer model can be created, it would be possible to study different reactor shapes and configurations under various operating conditions. To simplify the model, a NaBH$_4$ packed bed reactor was not modelled. Instead, a simple pipe filled with moving water was used similar to the water standard experiments (Section 4.1.2). A software package named Comsol Multiphysics (v3.3) was used.

5.1 Computer Model

5.1.1 Domain

The hybrid hydrogen storage system, as shown in Figure 5.1, was modeled as a two-dimensional, axi-symmetric system. The governing equations were solved using cylindrical co-ordinates due to the symmetry of the storage tank. A cross-section of the hybrid reactor containing metal hydride was modelled to simplify the domain.
The dimensions of the cross-section were those of the real hybrid model described earlier in Section 3.4. Therefore, the height and outer radius of the model were 0.130 m and 0.021 m (5.125 x 0.8345 in.) respectively. The interior and exterior walls of the reactor were modelled as a conductive film with the appropriate thickness. For this reason, the reactor radius seemed too small at first glance, but the method of heat transfer should have been similar to the real hybrid reactor. The inner portion of the tank contained the moving water which entered at the bottom of the reactor, and the outer portion held LaNi$_5$. The governing equations used within the model are described in the following sections.

5.1.2 Metal Hydride

The hydrogen absorption and desorption process within a metal hydride is complex due to simultaneous heat and mass transfer during a chemical formation
reaction. Additionally, the gas activity, heat transfer, and changing physical properties of this porous medium create further complexity.

An energy equation was created for both the solid and gas phase in the metal hydride. However, Jemni and Ben Nasrallah\textsuperscript{37} support the assumption of thermal equilibrium between the metal alloy and hydrogen gas. They also proved that the convective transport terms can be neglected for the conditions being modelled.\textsuperscript{38} Therefore, a single energy equation was created as follows:

\[
\left(\rho C_p\right)_e \frac{\partial T}{\partial t} = \nabla \cdot \left(k_e \nabla T - x \left(\Delta H + T \left(C_{pg} - C_{ps}\right)\right)\right)
\]

Equation 5.1

where \(k_e, C_{pg}, C_{ps}\), and \(x\) are the effective thermal conductivity of the hydride bed, specific heat capacity of the gas and solid phases respectively, and the rate of hydrogen absorbed or desorbed per unit volume. Additionally, an effective heat capacity term was created, \(C_{pe}\), which is volume averaged from the gas and solid, and is defined as:

\[
\left(\rho C_p\right)_e = \left(\varepsilon \rho_g C_{pg} + (1 - \varepsilon) \rho_s C_{ps}\right)
\]

Equation 5.2

where \(\varepsilon, \rho_g, \rho_s\) represent the porosity of the metal hydride bed, the density of the gas, and the density of the solid respectively.

The ideal gas law was used to calculate the gas density as follows:

\[
\rho_g = \frac{M_g P_g}{RT}
\]

Equation 5.3

where \(M_g, P_g, R,\) and \(T\) represent the molar mass of the gas, pressure of the gas, universal gas constant, and temperature respectively.
The gas velocity within the reactor was calculated using Darcy’s law.

\[ u_g = -\frac{K}{\mu_g} \nabla P_g \]

Equation 5.4

where \( u_g, K, \mu_g \), represent the gas velocity, permeability of the hydride bed, and dynamic viscosity of hydrogen gas respectively.

The dynamic viscosity term is calculated using:

\[ \mu_g = 9.05 \times 10^{-6} \left( \frac{T}{293} \right)^{0.68} \]

Equation 5.5

The mass balance for the hydrogen gas is:

\[ \varepsilon \frac{\partial P_g}{\partial t} + \nabla \cdot (\rho_g u_g) = -x \]

Equation 5.6

For the software package, Equation 5.3, Equation 5.4, and Equation 5.6 were combined to produce a single equation for the mass balance of hydrogen gas:

\[ \frac{\varepsilon M_g}{RT} \frac{\partial P_g}{\partial t} + \nabla \cdot \left( -\frac{K}{\nu_g} \nabla P_g \right) + \left( \frac{M_g}{R} \frac{\partial (1/T)}{\partial t} \right) P_g = -x \]

Equation 5.7

where \( \nu_g \) represents the kinematic viscosity of the hydrogen gas.

Under the assumption that the solid is fixed, the mass balance for this region is simply:

\[ (1 - \varepsilon) \frac{\partial P_s}{\partial t} = x \]

Equation 5.8
The expression for the quantity of hydrogen desorbed from the solid per unit volume and unit time is\(^{40}\):

\[
x_d = C_d \exp \left( -\frac{E_d}{RT} \right) \frac{P_g - P_{eqd}}{P_{eqd}} (\rho_s - \rho_{se})
\]

Equation 5.9

where \(C_d\) is the desorption constant, \(E_d\) is the activation energy for desorption, \(P_{eqd}\) is the equilibrium pressure for desorption, and \(\rho_{se}\), is the density of the metal hydride when it has desorbed all of the hydrogen gas that can be reversibly stored.

Similarly, the expression for the quantity of hydrogen absorbed into the solid per unit volume and unit time is\(^{40}\):

\[
x_a = C_a \exp \left( -\frac{E_a}{RT} \right) \ln \left( \frac{P_g}{P_{eqa}} \right) (\rho_{sa} - \rho_s)
\]

Equation 5.10

where \(C_a\) is the absorption constant, \(E_a\) is the activation energy for desorption, \(P_{eqa}\) is the equilibrium pressure for absorption, and \(\rho_{sa}\), is the density of the metal hydride when it is fully saturated with all of the hydrogen gas that can be reversibly stored.

Both absorption and desorption equilibrium pressures are calculated from the van’t Hoff expression below:

\[
\ln P_{eq} = A - \frac{B}{T}
\]

Equation 5.11

where \(A\) and \(B\) are determined from the Hydride Material Listing Database\(^{19}\) and are different values for both absorption and desorption reactions. The difference in the
values is a result of hysteresis. Including these terms in the model allows for a more accurate representation of the behaviour in the tank.

Additionally, a function was created which allows for simultaneous absorption or desorption throughout the tank based on Equation 5.9 and Equation 5.10. The two expressions for mass absorption or desorption were combined in this function to create a single output. The absorption contribution was used if the result calculated was positive. Conversely, if the mass fraction calculated was negative, this result was used for desorption. This function is essential in the model because in dynamic situations with rapid variations in pressure or temperature there may be areas of the hydride bed which are desorbing hydrogen, while other areas may be absorbing.

5.1.3 Pipe Flow

The energy equation for the interior portion of the reactor includes both conduction and convection due to the moving water and can be described as:

\[ \rho_w C_{pw} \frac{\partial T}{\partial t} = \nabla \cdot (k_w \nabla T - \rho_w C_{pw} u T) \]

Equation 5.12

where \( C_{pw}, k_w, u, \) and \( \rho_w \) are the specific heat, thermal conductivity, velocity, and density of the moving fluid (water).

The pipe flow for the interior portion of the reactor was modelled using the incompressible Navier-Stokes equation for an incompressible fluid:

\[ \rho_w \frac{\partial u}{\partial t} = -\nabla P + \mu \nabla^2 u + \rho_w g \]

Equation 5.13
where $\mu$, $P$, and $g$ are the viscosity of the fluid, the pressure acting on the fluid and the acceleration due to gravity respectively.

5.1.4 Boundary Conditions

At the bottom boundary, or inlet, of the inner portion of the reactor the temperature and velocity of the water were set as constant. Axial symmetry was chosen for the left-most boundary of the domain. The other side of the inner reactor was modelled with no-slip conditions and a conductive film for heat transfer. The conductive film is incorporated into the model by assuming a density, heat capacity, thermal conductivity, and wall thickness while maintaining continuity across the boundary. In this model, the wall thicknesses used were those of the hybrid reactor. The material properties of stainless steel were used. The top portion of the inner reactor was assumed to be at zero gauge pressure, with heat leaving the reactor by convective flux.

The top boundary for the outer, metal hydride portion of the reactor was modelled to also have a convective flux carried by the exiting hydrogen gas. The bottom and side boundaries for this portion of the model were set to have a highly conductive layer, as well as heat transfer by means of convection with the ambient air. Finally, the mass flux of hydrogen leaving the reactor at the top, outer boundary was set to be constant.

5.1.5 Initial Conditions

To start the model, the temperature in the inner portion of the reactor was set to the temperature of the water inlet. Additionally, the fluid in this region was set to zero
initial fluid velocity and pressure. The temperature of the metal hydride was set to an ambient temperature of 298 K. The metal hydride was assumed to be fully saturated, and the tank was in a state of equilibrium. The starting pressure was calculated as the desorption equilibrium pressure at the starting temperature condition (156 kPa at 298 K). The initial conditions and other material properties are listed in Table 5.1.

In order to compare the model results with the hybrid experimental results of the water standards discussed in Section 4.1.2, a constant mass flux of hydrogen leaving the reactor was assumed. The value was chosen such that it matched the rate of desorption from the actual hybrid reactor operating under a flow rate of 250 mL·min⁻¹ of water at a temperature of 298 K. The value calculated was 1.11·10⁻⁶ kg·s⁻¹. The model was also studied at water temperatures of 298 and 353 K (25 and 80 ºC) with flow rates ranging between 50 mL·min⁻¹ and 250 mL·min⁻¹.

<table>
<thead>
<tr>
<th>Table 5.1</th>
<th>Material Properties and Starting Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Property</td>
<td>LaNi₅</td>
</tr>
<tr>
<td>Specific Heat Capacity, $C_p$ [J·kg⁻¹·K⁻¹]</td>
<td>419</td>
</tr>
<tr>
<td>Effective Thermal Conductivity, $k_e$ [W·m⁻¹·K⁻¹]</td>
<td>1.32</td>
</tr>
<tr>
<td>Heat of Formation, $H$ [J·kg⁻¹·H₂⁻¹]</td>
<td>-1.539·10⁷</td>
</tr>
<tr>
<td>Permeability, $K$ [m⁻¹]</td>
<td>$10^8$</td>
</tr>
<tr>
<td>Density [kg·m⁻³]</td>
<td>N/A</td>
</tr>
<tr>
<td>Saturated Density, $\rho_{ss}$ [kg·m⁻³]</td>
<td>8527</td>
</tr>
<tr>
<td>Empty Density, $\rho_{se}$ [kg·m⁻³]</td>
<td>8400</td>
</tr>
<tr>
<td>Porosity, $\varepsilon$</td>
<td>0.5</td>
</tr>
<tr>
<td>Absorption Constant, $C_a$ [s⁻¹]</td>
<td>59.187</td>
</tr>
<tr>
<td>Desorption Constant, $C_d$ [s⁻¹]</td>
<td>9.57</td>
</tr>
<tr>
<td>Absorption Activation Energy, $E_a$ [J·mol⁻¹]</td>
<td>21179.6</td>
</tr>
<tr>
<td>Desorption Activation Energy, $E_d$ [J·mol⁻¹]</td>
<td>15473</td>
</tr>
<tr>
<td>Equilibrium Absorption Coefficient, $A_a$</td>
<td>17.608</td>
</tr>
<tr>
<td>Equilibrium Absorption Coefficient, $B_a$</td>
<td>3704.6</td>
</tr>
<tr>
<td>Equilibrium Desorption Coefficient, $A_d$</td>
<td>17.478</td>
</tr>
<tr>
<td>Equilibrium Desorption Coefficient, $B_d$</td>
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</tr>
<tr>
<td>Molecular Weight, $M$ [g·mol⁻¹]</td>
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</tr>
<tr>
<td>Universal Gas Constant, $R$ [J·mol⁻¹·K⁻¹]</td>
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</tr>
<tr>
<td>Initial Temperature, $T_0$ [K]</td>
<td>298</td>
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<tr>
<td>Initial Desorption Pressure, $P_o$ [Pa]</td>
<td>N/A</td>
</tr>
<tr>
<td>Mass Flow Rate, $m$ [kg·s⁻¹]</td>
<td>N/A</td>
</tr>
</tbody>
</table>
5.2 Results and Discussion

Effect of Water Temperature

The computer model was simulated using water temperatures of 298 and 353 K (25 and 80 °C). The temperature comparison for the top point of the outer wall is shown in Figure 5.2.

![Temperature trends of top portion of outer wall](image)

*Figure 5.2 - Temperature trends of top portion of outer wall*

The initial drop in temperature was due to hydrogen desorption from the metal hydride. The temperature increased slowly, but did not reach its initial starting point because desorption throughout the metal hydride was still occurring. The temperature rise in this portion of the hybrid reactor was mainly due to convection with the environment since the thermal conductivity of the metal hydride was so low. However, the thermal conductivity of the metal hydride was large enough to keep the entire temperature of the metal hydride larger during the higher temperature simulation.
cross section at the middle of the reactor for the density profile of simulation at 298 K and at 353 K is shown in Figure 5.3 and Figure 5.4 respectively.

![Figure 5.3 - Density profile for metal hydride bed at fluid temperatures of 298 K](image)

![Figure 5.4 - Density profile for metal hydride at fluid temperatures of 353 K](image)

Hydrogen desorption from the metal hydride was modeled as a density decrease throughout the reactor with time. It was apparent from the density profile, that desorption
was occurring more rapidly near the walls of the reactor where larger amounts of heat transfer were possible. Although desorption was more rapid in these areas, it was evident that desorption was also occurring in small amounts throughout the entire reactor. The density profile of the simulation using a water temperature of 353 K displayed a more rapid desorption on the inner radius next to the water. This effect was simply due to the larger amount of heat available for desorption in this area of the reactor. Desorption on the outer radius of the reactor was nearly identical in both simulations due to similar convective heat transfer in this area as well as the poor thermal conductivity of the metal hydride bed.

**Effect of Flow Rate**

Unfortunately, when different flow rates of the same operating temperature were simulated, almost exactly the same results were produced. As seen in the experimental results of Section 4.1.2, an increase in fluid flow rate should result in an increase of metal hydride desorption. Since this did not occur in the simulation, the heat transfer from the fluid to the rest of the apparatus was not modeled properly. The boundary between the metal hydride and the working fluid of the model was simulated as a highly conductive thin film with an appropriate thickness to save computational resources and time. This approach may not have been satisfactory. An increase in thermal conductivity between the fluid domain and the metal hydride domain might improve this aspect.
Comparison to Experimental Data

To estimate the validity of the model, the results were compared with the experimental data gathered in Section 4.1.2. Figure 5.5 displays a comparison of the model and experimental data operating at a fluid temperature of 298 K and flow rate of 250 ml min\(^{-1}\).

![Figure 5.5 - Comparison of model and experimental data with fluid temperature of 298 K](image)

The results from the above figure looked promising. The outer temperature of the simulated reactor was in close agreement with the actual temperatures recorded. The model temperature seemed to drop faster, indicating that desorption from the metal hydride was simulated too quickly; however, the predicted temperature increase in this region seemed to follow the same trend as what was recorded during the experiment. Since the temperatures in this area of the hybrid reactor were in close agreement, it was
assumed that the desorption kinetics of the metal hydride were modeled correctly. During high temperature operations, heat transfer throughout the model was not acceptable.

*Figure 5.6 - Comparison of model and experimental data with fluid temperature of 353 K*

When levels of heat transfer were significant (higher operating temperatures), the average reactor temperatures, as shown in Figure 5.6, were not in agreement. The reactor temperature did not drop significantly and the outer temperature did not increase. These features were also indications that heat transfer from the fluid portion of the reactor to the metal hydride was not modelled correctly.
Summary

The computer model provided a preliminary analysis of an advanced problem involving the chemical formation reactions of the metal hydride and simultaneous heat and mass transfer of multiple fluids. The desorption kinetics of the metal hydride were modelled correctly, but heat transfer throughout the reactor was not. It was determined that using the assumption of heat transfer through a highly conductive film was not an adequate means of modeling the walls of the reactor. Since temperatures in the inner portion of the reactor should have experienced a larger decrease, the simulation of heat transfer in this area should be improved. In order to confirm the poor heat transfer simulations in the hybrid reactor, the model could be reconstructed using the actual wall thicknesses in each section of the reactor.

If the computer model were improved and could accurately determine the heat transfer throughout the hybrid reactor, then it would be possible to predict the operating characteristics of different sized reactors. Therefore, the amount of metal hydride needed for various run times and heat producing chemicals could easily be determined. Finally, the inner portion of the reactor containing water could be replaced with a modeled packed bed reactor; however, adding this to the simulation would significantly increase the size and complexity of the problem.
Chapter 6 : Conclusions and Recommendations

6.1 Conclusions

The goal of this thesis was to investigate the potential for a metal hydride system to act as a thermal control unit for an exothermic hydrogen storage system. To address this idea, a cylindrical shaped reactor was constructed to allow hydrogen production from a NaBH₄ packed bed reactor and the metal hydride LaNi₅.

The “hybrid” reactor was first studied using the metal hydride under absorption and desorption cycles. These tests were necessary to observe the kinetics of reaction with the large amount of metal hydride present in the reactor. It was observed that the temperature of the lower segment of the metal hydride was the first to respond to the addition or removal of hydrogen. This would indicate that the hot fluid should enter from the top of the reactor for a counter flow heat exchange leading to optimum heat transfer.

The second set of experiments cycled heated water through the interior of the hybrid reactor to determine the heat transfer throughout. These water experiments showed that an increase in heat flux to the reactor led to a faster desorption rate of hydrogen from the metal hydride resulting in a larger temperature drop throughout the reactor. Both a faster flow rate and higher temperature of the water increased the heat flux.

After the operating characteristics of the hybrid reactor were established with the water experiments, the packed bed reactor was used. A 10 wt% solution of NaBH₄ was
created and pumped through the packed bed to produce enough hydrogen for a 300 W fuel cell.

The first tests using the packed bed were performed with no hydrogen release from the metal hydride to establish a baseline for heat transfer from the packed bed. The amount of heat produced from this reaction was significant, but reactor temperatures levelled to around 80 °C. Additionally, the amount of gas produced from the NaBH₄ reaction was measured to be slightly larger than theoretical due, likely due to water vapourization at this temperature.

During operation of the NaBH₄ packed bed, desorption of hydrogen from LaNi₅ was performed using two methods. The first method maintained a constant hydrogen pressure in the metal hydride portion of the hybrid reactor by intermittent vacuum. The second method utilized passive temperature control by allowing the metal hydride to release hydrogen continually as the metal hydride temperature increased. Upon comparison of the two desorption methods, it was determined that the constant pressure method maintained lower operating temperatures by promoting increased amounts of desorption from the metal hydride. As expected, temperature control was directly proportional to the rate of hydrogen release from the metal hydride. Large amounts of metal hydride material would be required to keep the reactor operating temperatures from increasing significantly. However, if the hybrid system was designed to function only to maintain temperatures during peak output, the amount of hydrogen storage material required could be reasonable in relation to the overall system.

On average, approximately 10% of the available heat energy was transferred to the mass of LaNi₅. This could be sufficient for peak thermal control, however, it was
determined that for the same packed bed operating conditions this number could be increased to 64% if the mass of metal hydride was increased to 3 kg. Throughout experimentation, the hybrid reactor operated with gravimetric and volumetric energy densities of 0.27 kWh·kg⁻¹ and 1.29 kWh·L⁻¹.

Even when assuming ideal heat transfer, the weight of the materials used in the hybrid reactor are too large for applications such as the automobile or a laptop; however, the hybrid reactor is a compact heat exchanger when compared to other traditional heat removal systems that may not even produce hydrogen. For this reason, the hybrid reactor is competitive as a backup power generator compared to a standard gasoline generator. Further specific applications of the hybrid reactor may include: military silent watch programs where noise levels and thermal signatures of energy devices are critical, portable systems requiring large amounts of thermal control, and novel high temperature hydrogen storage methods where cooling the output hydrogen would be required for use in the fuel cell.

If the hybrid reactor is operated as a means to control peak operating temperatures, less metal hydride material would be required in the storage system. Therefore, the overall gravimetric energy density would increase while maintaining the compact heat exchanger characteristics.

The hybrid reactor can provide quiet and cool operation in a relatively small volume. With improvements in the reactor design for increased heat transfer as well as in the hydrogen storage materials themselves, the hybrid reactor may become an effective and efficient means for hydrogen storage.
6.2 Recommendations and Future Work

6.2.1 Suggested PCT Improvements

To improve the PCT apparatus further, a few modifications would be required. There was concern that the sample may have been exposed to oxygen due to small leaks in the apparatus. To prevent these small leaks, the fittings in the apparatus could be changed to a Swagelok “VCR” type fitting, or switched to permanent welded tubing.

To improve the accuracy of the apparatus, a buffer volume filled with inert packing material could be added to either the reference or sample reservoir to try to match the volumes of each section of the apparatus exactly. This would eliminate the need to take a starting differential pressure during which time absorption or desorption may be occurring. Switching the current gauge pressure transducers with more accurate absolute sensors could also improve the accuracy of the pressure plateaus during PCT experiments. Finally, to improve the PCT experiment accuracy further, a new process could be developed to create the PCT curve without additive error.

6.2.2 Hybrid Reactor Improvements

After examining the results from the hybrid reactor, it was concluded that efficient heat transfer between the heat producing chemical hydride and the endothermic metal hydride is crucial for successful operation. The amount of metal hydride used in the hybrid reactor experiments was too little to absorb a large amount of heat energy produced from the chemical hydride. As mentioned, an average of about 10% of the available heat energy was transferred to the metal hydride, and as a result, temperatures
in the inner portion of the reactor dropped by approximately 10 degrees. If the reactor was sized to accommodate an addition of metal hydride material in an attempt to use more of the heat energy available, the increase in size would further restrict heat transfer throughout the hybrid reactor. At this point, active methods to improve the heat transfer through the reactor would most likely be needed.

To improve the heat transfer efficiency of the reactor, several methods could be used. The effect of alternating metal hydride desorption and pulsing the solution flow through the packed bed reactor was not tried because this would likely cause problems with hydrogen generation from the packed bed reactor and result in inconsistent hydrogen release; however, this might help to maintain a lower temperature throughout the reactor. The reactor could also be constructed using a thinner walled vessel, which would lower the resistance to heat transfer. Adding high heat conductive materials such as foamed aluminium or copper throughout the packed bed will also improve heat transfer significantly. Faster desorption of hydrogen and lower reactor temperatures will result, if heat transfer throughout the packed bed is improved using additional materials; however, the energy density of the entire system will also be adversely affected. As more metal hydride is required, the overall system storage density would be lowered. This would only be beneficial if the metal hydride system was replacing a tradition coolant system that had higher mass and volume but did not generate hydrogen as it cooled.

Another method to increase the heat transfer efficiency could be to use a different metal hydride. A metal hydride with a larger heat of reaction could act as a larger heat sink. If this were the case, more of the heat from the chemical reaction could be utilized with less metal hydride material, and the run time of the reactor could be extended.
Several different types of metal alloy could also be used with the hybrid reactor. For example, an alloy with higher plateau pressures could be tested. An example of such an alloy is Ti$_{0.98}$Zr$_{0.02}$V$_{0.43}$Fe$_{0.09}$Cr$_{0.05}$Mn$_{1.5}$, which is an AB$_2$ type metal hydride. Since the enthalpy of reaction for this material is similar to LaNi$_5$ (27.4 vs. 30.8 kJ·mol$_{\text{H}_2}$⁻¹ respectively), the heat transfer through the hybrid reactor would be similar. This AB$_2$ alloy is also lighter than LaNi$_5$, and if this AB$_2$ material were to be used in the experiments above, less material would be needed to balance the heat produced from the packed bed reactor. Such a system would have slight improvements in energy densities over the system using LaNi$_5$.

**6.2.3 Future Work**

From experiments with the large metal hydride sample, it was determined that the lower segment of the metal hydride was the first to experience a temperature change. This effect is important in order to design a counter-flow heat exchanger for optimum heat transfer. To test this observation further, a long, cylindrical, and insulated reactor packed with a metal hydride should be created and studied under absorption and desorption conditions.

Throughout the packed bed experiments, it was assumed that some water vapour was produced. A condenser could be added to the experimental setup to measure the exact amount of water vapour present in the hydrogen gas produced. It would then be possible to calculate the amount of heat energy lost to the vapourization of water.
The hybrid reactor experiments revealed that efficient heat transfer throughout the reactor was crucial to lower inner reactor temperatures. If more metal hydride material is added to the reactor, active heat transfer mechanisms, such as heat transfer material, will be needed. Therefore, the effect of added heat transfer material on heat transfer through the hybrid reactor should be tested. A new hybrid reactor could also be fabricated using thinner walls, and also more heat conductive material. Further temperature control mechanisms could include pulsing or alternating the hydrogen production between the chemical hydride and the metal hydride.

If the peak temperature control method is explored, different metal hydride materials could be tested to find the ideal candidate for limiting temperatures of the packed bed reactor. Alternatively, the effect of the pulse method described above could be put to use.

Finally, if a hybrid reactor is constructed for optimum heat transfer, regardless of the application, it should be tested while coupled to a fuel cell. If the fuel cell is added to the system, hydrogen storage bladders may be needed to provide a buffer of fuel. The addition of a fuel cell should be completed as a final means to determine the performance characteristics of the complete power system.
References


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Appendix A

A.1 Hybrid System Calculations

The following calculations are an attempt to predict some of the characteristics of a hybrid hydrogen storage system. The calculations use a NaBH₄ solution and LaNi₅, which is a typical metal hydride. The following assumptions are made:

- A 300 W, 100% efficient fuel cell. Therefore, cell voltage is equal to 1.48 V using the higher heating value for hydrogen.
- The fuel cell run time is 1 hour. Therefore, the power produced is 0.3 kWh.
- The NaBH₄ solution is comprised of 10 wt% NaBH₄, 5 wt% NaOH, and the remainder water (H₂O).
- Perfect heat transfer. Therefore, there is no solution heating, and all of the excess heat energy is transferred to the metal hydride.

The calculations also assume that the NaBH₄ hydrolysis reaction proceeds as:

\[
NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2
\]

Equation A.1

The properties of each material are described in Table A.1.

<table>
<thead>
<tr>
<th>Table A.1 Material Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>Molar Mass (g·mol⁻¹)</td>
</tr>
<tr>
<td>Density (kg·m⁻³)</td>
</tr>
<tr>
<td>Heat of Reaction (kJ·mol⁻¹)</td>
</tr>
</tbody>
</table>

A.1.1 Fuel Cell Hydrogen Usage

The hydrogen usage of a fuel cell can be written as¹:

\[
m_{H_2} = \frac{P_{FC}}{2V_{fc}F}
\]

Equation A.2
where $P_{FC}$, $V_{FC}$, and $F$ are the operating power of the fuel cell, the operating voltage of the fuel cell, and Faraday’s constant respectively. In this case, the power was 300 W and the operating voltage for a 100% efficient fuel cell is 1.48 V. Therefore, the hydrogen usage was found to be $2.12 \cdot 10^{-6}$ kg·s$^{-1}$.

### A.1.2 NaBH$_4$ Solution

If the fuel cell was entirely powered by a solution of NaBH$_4$ solution, the following calculations would have to be considered.

Since four moles of hydrogen are produced from a single mole of NaBH$_4$ (Equation A.1), the amount of hydrogen needed can simply be divided by four to attain the amount of NaBH$_4$ needed. Therefore, a molar flow rate of $2.631 \cdot 10^{-4}$ mol·s$^{-1}$ NaBH$_4$ is needed in this example.

To find the total mass of NaBH$_4$ for the entire run time, the molar flow rate is easily manipulated by:

$$m = \dot{n}M_{NaBH_4}t$$

Equation A.3

where $\dot{n}$, $M_{NaBH_4}$, and $t$, is the molar flow rate of NaBH$_4$, the molar mass of NaBH$_4$, and the duration that the fuel cell is to run. Using this formula results in:

$$m = (2.631 \cdot 10^{-4})(37.93)(3600)$$

$$m = 35.9 \text{ g}$$

As explained previously in Section 2.1.3, concentrations of NaBH$_4$ larger than 10 wt% risk the precipitation of the product metaborate which could clog a packed bed reactor. Therefore, the solution prepared used only 10 wt% NaBH$_4$. If 35.9 g of NaBH$_4$
represents only 10% of the solution, it follows that the total weight of the solution should be 0.359 kg. Furthermore, 5 wt% or 17.97g and 85% or 305.4g of the solution should be NaOH, and water respectively. An average weighted density for the solution was calculated according to:

$$\rho_{sol} = \sum wt\%_{\text{component}} \rho_{\text{component}}$$

Equation A.4

where \( \rho \) represents the density of the solution and each component. The final value calculated was 1061.8 kg·m\(^{-3}\).

To calculate the energy obtained from the hydrogen produced through the hydrolysis reaction of the chemical hydride:

$$Q_{pc} = 2 \frac{e^-}{molH_2} \cdot 4 \frac{molH_2}{molNaBH_4} \cdot F \cdot V_c$$

Equation A.5

Therefore, with a 100% efficient fuel cell, one would expect to attain 1142 kJ·mol\(^{-1}\) of NaBH\(_4\). For this system, it is then expected that about 1080 KJ of energy will be produced from the hydrogen fuel cell.

This total energy is easily manipulated into energy densities using molar mass and density terms as follows:

$$E_{grav} = \frac{P_{pc}}{m_{sol}}$$

Equation A.6

$$E_{vol} = E_{grav} \cdot \rho_{sol}$$

Equation A.7

where \( P_{pc} \), and \( m_{sol} \), represent the power produced by the fuel cell measured in kWh, and the mass of the NaBH\(_4\) solution respectively. \( E_{grav} \) and \( E_{vol} \) are the gravimetric and
volumetric energy density respectively. Using Equation A.8, and Equation A.7 values of 0.83 kWh·kg⁻¹, and 0.89 kWh·L⁻¹ were found.

The heat production from the hydrolysis reaction can simply be calculated as:

\[ Q_{\text{rxn}} = \Delta H_{\text{rxn}} n_{\text{NaBH}_4} \]

Equation A.8

where \( \Delta h_{\text{rxn}} \) and \( n \) represent the heat of reaction and number of moles of NaBH₄. Using this equation, it was found that the NaBH₄ reaction should produce about 206 kJ.

The following simple calculation was used to obtain the thermal efficiency of the NaBH₄ system. The efficiency of the system can be calculated as the amount of useful energy gained from the system compared to the amount of energy that is available.

\[ \eta = \frac{\text{Useful\ Energy}}{\text{Energy\ Available}} \]

\[ \eta = \frac{\text{EnergyFromH}_2}{\text{EnergyFromH}_2 + \text{EnergyLoss} + \text{EnergyWork}} \cdot 100\% \]

\[ \eta = \frac{1080}{1080 + 206 + 0} \cdot 100\% \]

\[ \eta = 84\% \]

Equation A.9

The energy work term is the amount of energy spent to release hydrogen. In this instance, this term could represent the amount of energy needed to pump the NaBH₄ fluid through the packed bed reactor. In the calculation above, this work term was neglected.

**A.1.3 Metal Hydride**

If the fuel cell system described earlier were using hydrogen stored in a metal hydride, the following amount of metal hydride would be needed:
where \( m_m \), \( m_{H_2} \), and wt\% represent the mass of the metal hydride, mass of hydrogen, and gravimetric storage capacity of the metal hydride respectively. From Equation A.10 it was determined that 0.580 kg of metal hydride would be required for a 300 W fuel cell running for one hour.

The energy required by the metal hydride to release this hydrogen is calculated as follows:

\[
Q_m = \frac{m_m}{M_m} \Delta H
\]

where \( \Delta H \) is the heat of reaction for the metal hydride. In this example, the amount of energy required by 0.580 kg of metal hydride was calculated to be 38.25 kJ.

The energy densities can be calculated by manipulating the mass of the metal hydride similar to Equation A.6 and Equation A.7. For a metal hydride system, the energy densities were calculated as 0.52 kWh·kg\(^{-1}\) and 4.35 kWh·L\(^{-1}\).

The following simple calculation was used to obtain the thermal efficiency of the metal hydride system. The energy work term is the amount of energy spent to release hydrogen. In this instance, this term is the amount of heat needed to release the hydrogen from the metal hydride.

\[
\eta = \frac{\text{EnergyFromH}_2}{\text{EnergyFromH}_2 + \text{EnergyLoss} + \text{EnergyWork}} \cdot 100\%
\]

\[
\eta = \frac{1080}{1080 + 0 + 38.25} \cdot 100\%
\]

\[
\eta = 97\%
\]
A.1.4 Hybrid System

The hybrid system was analyzed by balancing the enthalpies of reaction for both systems. For example, if 17% of chemical hydride is used for the storage system, 6.1 g of NaBH₄ would be required. The remainder (83%) of the system would have to be 481 g of metal hydride. The heat produced from the NaBH₄ solution would be 34.95 kJ. Similarly, the heat required by the metal hydride would be approximately 34.3 kJ. Therefore, the net heat flux results in a surplus of about 0.7 kJ. Using the same thermal efficiency equation used in Equation A.9:

\[
\eta = \frac{\text{EnergyFromH}_2}{\text{EnergyFromH}_2 + \text{EnergyLoss} + \text{EnergyWork}} \cdot 100\%
\]

\[
\eta = \frac{1080}{1080 + 0.7 + 0} \cdot 100\%
\]

\[
\eta = 100\%
\]

Equation A.9

An efficiency of 100% is not possible. In this example, it is assumed that perfect heat transfer exists between the storage materials, and that almost all of the heat produced by the NaBH₄ is consumed by the metal hydride. In reality, a large portion of this heat was lost due to the heating of the solution itself as well as the reactor walls. Nevertheless, the energy densities of such a system can also be calculated as:

\[
E_{\text{grav}} = \frac{P_{FC}}{m_{tot}}
\]

\[
E_{\text{grav}} = \frac{P_{FC}}{m_{sol} + m_{m}}
\]

Equation A.12

and
Using the above equations, the energy densities of the hybrid system were calculated as 0.55 kWh·kg⁻¹ and 2.61 kWh·L⁻¹.
Appendix B

B.1 Sievert Apparatus Description

For the purposes of this thesis, the Sievert Apparatus will refer to a constant pressure design as outlined by Checchetto et al.\textsuperscript{29} This design was the first apparatus constructed to measure hydrogen storage capacities of metal hydride samples. The apparatus is depicted in Figure B.1 and was comprised of regular Swagelok as well as Swagelok VCR stainless steel fittings, valves, and tubing.

![Sievert apparatus schematic](image)

*Figure B.1 - Sievert apparatus schematic*

This apparatus attempted to maintain constant pressure by opening and closing a pneumatically controlled bellows valve (BV-2) between a reservoir cylinder and a sample
cylinder such that the pressure in the sample cylinder did not fluctuate by more than 5% of a desired target pressure. The flow rate between the two cylinders was controlled using metering valves (MV-1 and MV-2). The other valves depicted in the figure were manually controlled diaphragm valves. Inline Swagelok Ultra High Purity pressure transducers (PT-1 and PT-2) rated from vacuum to 100 bar and accurate to 0.5% of span were used to monitor the pressure in the reservoir and the sample volumes. The reservoir and calibration cylinders were approximately 75 cm$^3$. The sample holder was made from a blank Swagelok VCR gland bored out to hold material and was approximately 1 cm$^3$. A two micron stainless steel VCR gasket was used between the sample holder and the rest of the apparatus. All connections and fittings were sized for 6.35 mm (¼”) tubing. The temperature of the reservoir was measured using a surface mounted thermocouple, and the temperature of the sample was measured by placing an RTD probe to the surface of the sample holder. To control the pneumatic bellows valves, a Numatics solenoid valve manifold was used. The entire system used National Instruments Fieldpoint data acquisition modules and Labview software for automation and data recording.

B.1.1 Absorption Kinetics

To perform an absorption kinetic experiment, the sample is first placed in a water bath or furnace at an elevated temperature and the entire apparatus is first vacuumed for one hour. This ensures that the sample will be fully desorbed and will not contain any hydrogen. The sample is then allowed to reach a target, constant temperature for absorption. The calibration chamber is pressurized with hydrogen to an equivalent absorption pressure target. BV-1 is then closed and the reservoir chamber is filled with
hydrogen at a much higher pressure. To initiate the absorption run, DV-2 is manually opened and quickly closed to expose the sample to hydrogen. Since the calibration chamber has been volume calibrated, the sample chamber will reach a pressure which is only slightly higher than the target absorption pressure ($P_{eq}$).

Upon absorption of hydrogen, the sample chamber will decrease in pressure. When the sample pressure is less than a pressure value of ($P_{eq} - \Delta P$), BV-2 is opened and the reservoir fills the sample area with more hydrogen. When a pressure greater than ($P_{eq} + \Delta P$) is reached, BV-2 is closed. Therefore, the pressure within the sample volume fluctuates between two values such that $\Delta P/P_{eq} \approx 0.05$. This establishes a quasi-constant pressure within the sample volume. The total number of hydrogen moles absorbed can be calculated by 29:

$$n = \frac{\Delta P_R V_R}{R T_R}$$

Equation B.1

where $\Delta P_R$ is equal to the difference between the reservoir pressure at time zero and the reservoir pressure at the end of the run, $V_R$ is the volume of the reservoir, $R$ is the universal gas constant, and $T_R$ is the temperature of the reservoir. The experimental run ends when no significant pressure decrease has been noticed within a specified time frame.

**B.1.2 Desorption Kinetics**

The desorption procedure is similar to the absorption procedure except that the process is reversed. With the sample volume isolated, the rest of the apparatus is
evacuated. The process is triggered by opening and closing DV-2 quickly so that the sample volume pressure decreases to slightly below the desorption pressure target. As the sample releases hydrogen, the sample chamber pressure will increase. When the sample pressure is greater than a pressure value of \((P_{eq} + \Delta P)\), BV-2 is opened and the reservoir is filled with hydrogen from the sample area. When the sample pressure has reached an edge value of \((P_{eq} - \Delta P)\), BV-2 is closed. The pressure in the reservoir is recorded, and then the reservoir is vacuumed out before the next valve opening. The number of hydrogen moles absorbed can be calculated by summing the number of moles calculated between valve openings before the reservoir is vacuumed out:

\[
\sum R = \frac{P_R V_R}{RT_R}
\]

Equation B.2

where \(P_R\) is the pressure of the reservoir when filled with hydrogen, \(V_R\) is the volume of the reservoir, \(R\) is the universal gas constant, and \(T_R\) is the temperature of the reservoir. The experimental run ends when no significant pressure increase has been noticed within a specified time frame.

**B.1.3 PCT Measurement**

Again, the sample is placed under vacuum and at an elevated temperature for one hour to ensure that full desorption has occurred. The PCT curve can be created from successive absorption cycles at progressively higher target pressures. When absorption has reached equilibrium at a certain pressure, the target pressure is increased slightly, and the process repeats itself. At each equilibrium stage, the number of moles absorbed is
calculated by subtracting the number of moles left within the sample volume in the gas phase from the number of moles which have been absorbed measured from the reservoir pressure change\textsuperscript{29}:

$$n(P_{eq}) = \frac{\Delta P_R V_R}{RT_R} - \frac{P_S V_S}{RT_S}$$

Equation B.3

where $\Delta P_R$ is equal to the change is reservoir pressure, $V_R$ and $V_S$ are the volume of the reservoir and sample are respectively, $R$ is the universal gas constant, $T_R$ and $T_S$ are the temperature of the reservoir and sample respectively, and $P_S$ is the pressure of the sample volume.

### B.2 Sievert Apparatus Results

#### B.2.1 Sievert Apparatus Performance

The Sievert apparatus was first checked for gas leaks by observing the pressure change over a period of approximately three days. Figure B.2 displays the pressure trend that was observed.
Since the pressure varied with temperature, it was immediately evident that the apparatus was not insulated well, and Fibrefax insulation was added to prevent the influence of external temperature effects on the gas pressure. After observing the small temperature change in apparatus temperature in Figure B.3, it was concluded that the insulation was adequate to prevent erroneous pressure fluctuations.
B.2.2 Kinetics

The first test performed was an absorption process at 25 °C with 0.2703 g of LaNi$_5$ which was pre-activated and provided by Université du Québec à Trois-Rivières. Figure B.4 and Figure B.5 show the pressure variations and amount of hydrogen absorbed respectively.
The automated attempt at maintaining a “constant” or threshold pressure of 550 kPaG in the sample volume can be seen in Figure B.4. Since the weight percent
calculations are based on the pressure decreases in the reservoir, the weight percent trend in Figure B.5 is stepwise. Similar trends can be noticed in the desorption trends of Figure B.6 and Figure B.7.

![Figure B.6 - Pressure trends during desorption run](image)

*Figure B.6 - Pressure trends during desorption run*
Since the Sievert apparatus used an absolute or gauge pressure reading, the inherent error associated with the readings is quite large. The absorption readings with associated design stage uncertainties are shown in Figure B.8.
After the kinetics experiments were performed, it was decided to skip the PCT measurements due to the large uncertainties, and the Sievert apparatus was dismantled. The parts were used to build the new PCT apparatus.

### B.3 Discussion

#### B.3.1 Performance

The Sievert apparatus was built to simulate a constant pressure absorption or desorption environment. This was accomplished by periodically adjusting the pressure in the sample volume. The pressure in the reservoir was monitored to determine the amount of hydrogen absorbed or desorbed. From Figure B.4 and Figure B.6, it is evident that the pressure was maintained quite well. The overall pressure was maintained to within 10% of the desired pressure. This value could be improved further by restricting the gas flow.
more between the hydrogen reservoir and the sample area. In order to do this, the existing metering valves would have to be replaced with valves that have a smaller flow coefficient.

One potential disadvantage to the Sievert apparatus is the inherent “step-wise” recordings in hydrogen absorption or desorption. Figure B.5 displays the choppy trend that is created because the amount of hydrogen absorbed is based on pressure readings within the reservoir. Since the reservoir is periodically opened and closed to the sample volume, the pressure in the reservoir is static in between valve openings. The end result is a kinetics trend with flat plateaus that show no hydrogen absorption in between valve openings. This, of course, is not representative of the continual hydrogen absorption or desorption that occurs with time in the sample volume. The true kinetics must be interpolated amongst these flat plateaus to obtain a smooth curve. One potential solution to this problem could be to keep track of the pressure change in the sample volume and use those recordings to change the amount of hydrogen absorbed or desorbed during the period which the valves to the reservoir are closed. This method, however, would compound the error associated with the recordings since a total sum of moles absorbed or desorbed would have to be tracked.

Although the Sievert apparatus attempted to maintain a constant pressure by limiting the pressure change in the sample volume, a true constant pressure could not be obtained using this method. A further alternative to maintain a constant pressure would be to install a mass flow meter between a reservoir maintained at constant pressure and the sample volume. The amount of hydrogen absorbed or desorbed could then be calculated in terms of mass flow.
B.3.2 Results

Upon investigation of the design stage uncertainty associated with the Sievert apparatus, it became clear that the error was far too large to draw any conclusions about the kinetic experiments. The source of this large error is from the use of absolute pressure transducers whose pressure range is quite large (vacuum to 100 bar). Nevertheless, the sample seemed to absorb approximately 1.0 wt% of hydrogen, which is somewhat close to its theoretical reversible capacity of 1.3 wt%. Surface oxide barriers could have reduced the hydrogen storage capacity if the sample provided by Université du Québec à Trois-Rivières was not handled properly since activation. It was also unclear if the sample was freshly activated or if it had been subjected to a number of hydriding and thermal cycles. Furthermore, the volumes used in calculating the hydrogen capacity were theoretical and could have varied from the actual values. No type of volume calibration was performed for the Sievert apparatus, and the lack of known, true volumes would contribute to the large uncertainty in the results.

When observing the small relatively effects of pressure on the kinetics of a sample, it becomes evident that a constant pressure environment is crucial to obtain the thermodynamic characteristics of a metal hydride. It is much more favourable to use a differential pressure set-up where the error associated with measurements is inherently smaller than that of an apparatus which uses absolute pressure gauges. Overall, the Sievert apparatus was a good opportunity to gain experience with the electronics, pressure transducers, thermocouples, LabView programming software, and other equipment necessary to create a hydrogen pressure monitoring apparatus. Once it
was clear that a differential set-up had to be created for accurate results, the Sievert apparatus was dismantled, and its parts were used to help create the differential set-up with the PCT apparatus.

B.4 Sievert Apparatus Parts List

Table B.1 Sievert Apparatus Parts

<table>
<thead>
<tr>
<th>Company</th>
<th>Part #</th>
<th>Description</th>
<th>Quantity</th>
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B.5 Sievert Apparatus Schematic

Figure B.9 - Sievert apparatus schematic
Appendix C

C.1 PCT Apparatus Pictures

Figure C.1 - PCT interior
Figure C.2 - PCT power supply enclosure

C.2 PCT Apparatus Parts List

Table C.1 PCT Apparatus Part List

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<td>Socket Gland</td>
<td>8</td>
<td>10.04</td>
</tr>
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<td>Male Nut</td>
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<td>5.53</td>
</tr>
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<td>SS-DLVC4R-4</td>
<td>Male VCR Diaphragm Valve</td>
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</tr>
<tr>
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<td>SS-400-1-2</td>
<td>Male NPT Connector</td>
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<td>7.58</td>
</tr>
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<td>060-K818-02ZD-01</td>
<td>KZ Differential Pressure Transducer</td>
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</tr>
<tr>
<td>Company</td>
<td>Part #</td>
<td>Description</td>
<td>Quantity</td>
<td>Unit Price</td>
</tr>
<tr>
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<td>---------</td>
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<tr>
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<td>777517-00</td>
<td>FP-1000 RS-232/RS-485 Network Module</td>
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<tr>
<td>NI</td>
<td>777518-110</td>
<td>FP-AI-110 8-Ch. 16-Bit Analog Input Module</td>
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<tr>
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<td>FP-TC-120 8-Ch. Thermocouple Input Module</td>
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<tr>
<td>NI</td>
<td>777518-122</td>
<td>FP-RTD-122 8-Ch. RTD Input Module</td>
<td>1</td>
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</tr>
<tr>
<td>NI</td>
<td>777519-03</td>
<td>FP-TB-3 Isothermal Terminal Base</td>
<td>1</td>
<td>225.00</td>
</tr>
<tr>
<td>NI</td>
<td>777519-01</td>
<td>FP-TB-1 Universal Terminal Base</td>
<td>4</td>
<td>252.00</td>
</tr>
</tbody>
</table>
C.3 PCT Apparatus Schematic

Figure C.3 - PCT apparatus schematic
C.4 Electrical Schematics

Figure C.4 - PCT enclosure electrical schematic
Figure C.5 - PCT power supply electrical schematic
Appendix D

D.1 PCT Measurement Uncertainties

Uncertainty in a function of several variables may be calculated by:\n
\[
\delta q = \sqrt{\left(\frac{\partial q}{\partial x}\delta x\right)^2 + \ldots + \left(\frac{\partial q}{\partial z}\delta z\right)^2}
\]

Equation D.1

where \(x, \ldots, z\) are measured with uncertainties, \(\delta x, \ldots, \delta z\) and the measured values are used to compute a function \(q(x, \ldots, z)\) as long as the uncertainties involved are independent and random.

Furthermore, when a function is comprised of sums or differences, the uncertainties may be added in quadrature. This is simply the square root of the sum of the uncertainties squared. Similarly, when a function is comprised of products or quotients, the fractional uncertainties may be summed in quadrature\(^{41}\).

D.1.1 Moles

To calculate the number of moles absorbed or desorbed from a sample, Equation 3.1 was used:

\[
n = \frac{\Delta PV_{RES}}{zRT}
\]

Equation 3.1

The uncertainty in this calculation can be found as follows:
\[
\delta n = \left[ \frac{\partial n}{\partial P} \delta P + \frac{\partial n}{\partial V_{RES}} \delta V_{RES} + \left( \frac{\partial n}{\partial T} \delta T \right)^2 \right]^{1/2}
\]

\[
\delta n = \left[ \left( \frac{V}{RT} \delta P \right)^2 + \left( \frac{P}{RT} \delta V_{RES} \right)^2 + \left( -\frac{PV}{RT^2} \delta T \right)^2 \right]^{1/2}
\]

Equation D.2

The error associated with the compressibility factor is assumed to be negligible.

The temperature and volume uncertainty was taken as ±1 K and 4 cm³. The error associated with the pressure term is calculated differently.

During an experimental run, the reference and sample area are exposed to their respective reservoirs. If both the sample side and the reservoir side of the apparatus were exactly identical in volume, the differential pressure at the time these valves open would be zero. This situation, however, is not the case since the sample side and reservoir side are slightly different in volume. Since the volumes are not the same, a differential pressure is measured at the time the valves open. This pressure difference is not representative of absorption or desorption and must be accounted for. To account for this discrepancy, the starting differential pressure is noted and subtracted from subsequent measurements. Since this difference is used in the calculations, the uncertainty of the pressure sensor may not be used directly. The uncertainty is calculated as the pressure sensor uncertainty, 0.5171 kPa, summed in quadrature. This value was found to be 0.7313 kPa.

**D.1.2 Gravimetric Storage Capacity (Wt%)**

The weight percent value is also a measure of the amount of hydrogen a material can absorb and is the ratio of the amount of hydrogen held by the material in terms of
mass divided by the mass of the material plus the mass of the hydrogen. This value may be expressed as:

\[
\text{wt}\% = \frac{m_{H_2}}{m_{H_2} + m_{\text{metal}}} \times 100
\]

Equation D.3

The uncertainty for this calculation is:

\[
\delta \text{wt}\% = \left[ \left( \frac{\partial \text{wt}\%}{\partial m_{H_2}} \delta m_{H_2}\right)^2 + \left( \frac{\partial \text{wt}\%}{\partial m_{\text{metal}}} \delta m_{\text{metal}} \right)^2 \right]^{1/2} \cdot 100
\]

\[
\delta \text{wt}\% = \left[ \left( \frac{1}{m_{H_2} + m_{\text{metal}}} - \frac{m_{H_2}}{(m_{H_2} + m_{\text{metal}})^2} \delta m_{H_2}\right)^2 + \left( -\frac{m_{H_2}}{(m_{H_2} + m_{\text{metal}})^2} \delta m_{\text{metal}} \right)^2 \right]^{1/2} \cdot 100
\]

Equation D.4

In this situation, the error associated with the mass of the hydrogen was found by multiplying the error in the number of moles of hydrogen by the molar mass of gaseous hydrogen.

**D.1.3 PCT Experiment**

The PCT isotherms are calculated according to Equation 3.2 which is repeated below:

\[
n_{\text{tot}} = n_{\text{previous}} \pm \frac{\Delta PV_{RES}}{zRT}
\]

Equation 3.2
Since this is simply an addition or subtraction, the error calculated for total number of moles during each cycle’s step is simply the uncertainty of the previous steps summed in quadrature with the uncertainty associated with the current step. This expressed as:

\[
\delta n_{\text{tot}} = \left[ (\delta n_{\text{previous}})^2 + (\delta n)^2 \right]^{\frac{1}{2}}
\]

Equation D.5

where the uncertainty in the number of moles for the current step is calculated according to Equation D.2. Unfortunately, this leads to an ever increasing uncertainty throughout the entire PCT experiment.
### Appendix E

#### E.1 Water Volume Calibrations

The following table displays the results from the volume calibrations.

**Table E.1 Water Calibrated Volumes**

<table>
<thead>
<tr>
<th>Section</th>
<th>Run</th>
<th>Empty [g]</th>
<th>Filled [g]</th>
<th>Resistance [Ω]</th>
<th>Temperature [°C]</th>
<th>Density [kg·m⁻³]</th>
<th>Volume [cm³]</th>
<th>Error [cm³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calibration</td>
<td>1</td>
<td>166.22</td>
<td>192.08</td>
<td>107.6</td>
<td>19.175</td>
<td>998.37</td>
<td>25.8973</td>
<td>0.01299</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>166.22</td>
<td>192.09</td>
<td>107.7</td>
<td>19.425</td>
<td>998.32</td>
<td>25.9087</td>
<td>0.01300</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>166.22</td>
<td>191.99</td>
<td>107.9</td>
<td>19.925</td>
<td>998.21</td>
<td>25.8122</td>
<td>0.01295</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>166.22</td>
<td>192.15</td>
<td>107.7</td>
<td>19.425</td>
<td>998.32</td>
<td>25.9741</td>
<td>0.01303</td>
</tr>
<tr>
<td>Tube 1</td>
<td>1</td>
<td>112.2</td>
<td>120.4</td>
<td>107.5</td>
<td>18.923</td>
<td>998.42</td>
<td>8.2130</td>
<td>0.07094</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>112.2</td>
<td>120.7</td>
<td>108.8</td>
<td>22.205</td>
<td>997.72</td>
<td>8.5194</td>
<td>0.07100</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>112.2</td>
<td>120.7</td>
<td>108.8</td>
<td>22.205</td>
<td>997.72</td>
<td>8.5194</td>
<td>0.07100</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>112.2</td>
<td>120.6</td>
<td>108.8</td>
<td>22.205</td>
<td>997.72</td>
<td>8.4192</td>
<td>0.07100</td>
</tr>
<tr>
<td>Tube 2</td>
<td>1</td>
<td>112.8</td>
<td>121.0</td>
<td>107.5</td>
<td>18.923</td>
<td>998.42</td>
<td>8.2130</td>
<td>0.07094</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>112.9</td>
<td>121.4</td>
<td>109.1</td>
<td>22.205</td>
<td>997.72</td>
<td>8.5209</td>
<td>0.07101</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>112.9</td>
<td>121.4</td>
<td>109.1</td>
<td>22.205</td>
<td>997.72</td>
<td>8.2187</td>
<td>0.07099</td>
</tr>
<tr>
<td></td>
<td>4</td>
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<td>121.1</td>
<td>108.8</td>
<td>22.205</td>
<td>997.72</td>
<td>8.2187</td>
<td>0.07099</td>
</tr>
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<td>107.5</td>
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<td>111.4</td>
<td>107.9</td>
<td>22.205</td>
<td>997.72</td>
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<td>111.1</td>
<td>109.1</td>
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<td>997.72</td>
<td>4.3106</td>
<td>0.07092</td>
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<td>4</td>
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<td>111.0</td>
<td>108.8</td>
<td>22.205</td>
<td>997.72</td>
<td>4.0091</td>
<td>0.07090</td>
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<td>103.8</td>
<td>107.5</td>
<td>18.923</td>
<td>998.42</td>
<td>4.9078</td>
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<td>2</td>
<td>98.9</td>
<td>103.7</td>
<td>107.9</td>
<td>22.205</td>
<td>997.72</td>
<td>4.8086</td>
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<td>103.8</td>
<td>109.1</td>
<td>22.205</td>
<td>997.72</td>
<td>4.9121</td>
<td>0.07093</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>98.9</td>
<td>103.9</td>
<td>108.8</td>
<td>22.205</td>
<td>997.72</td>
<td>5.0114</td>
<td>0.07092</td>
</tr>
<tr>
<td>Sample</td>
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<td>13.688</td>
<td>N/A</td>
<td>N/A</td>
<td>998.00</td>
<td>0.5118</td>
<td>0.00071</td>
</tr>
<tr>
<td>Holder</td>
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<td>13.688</td>
<td>N/A</td>
<td>N/A</td>
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<td>0.5123</td>
<td>0.00071</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>13.177</td>
<td>13.688</td>
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<td>N/A</td>
<td>998.00</td>
<td>0.5119</td>
<td>0.00071</td>
</tr>
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<td>Reference</td>
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<td>13.788</td>
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<td>N/A</td>
<td>998.00</td>
<td>0.5222</td>
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<td>N/A</td>
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<td>N/A</td>
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<td>21.564</td>
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<td>3766.4</td>
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<td>22.333</td>
<td>997.69</td>
<td>981.76</td>
<td>0.86278</td>
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<td>997.69</td>
<td>982.06</td>
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<tr>
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<td>3806.8</td>
<td>108.9</td>
<td>22.846</td>
<td>997.57</td>
<td>989.29</td>
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<tr>
<td>Side Large</td>
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<td>2820.0</td>
<td>3807.7</td>
<td>108.9</td>
<td>22.846</td>
<td>997.57</td>
<td>990.17</td>
<td>0.86528</td>
</tr>
<tr>
<td>Volume</td>
<td>3</td>
<td>2820.5</td>
<td>3808.9</td>
<td>108.9</td>
<td>22.846</td>
<td>997.57</td>
<td>990.80</td>
<td>0.86548</td>
</tr>
</tbody>
</table>

The process used to calculate the different volumes was based on the density of water:
\[ V = \frac{m_{\text{full}} - m_{\text{empty}}}{\rho} \]

Equation E.1

where \( \rho \) is the density of the water used. The mass of the volume under question when full of water and when empty are represented by \( m_{\text{full}} \) and \( m_{\text{empty}} \) respectively. The density was calculated according to Equation 3.3, and an uncertainty value of 500 g \( \cdot \) m\(^{-3} \) was used. The uncertainty of the mass measurements was taken as 0.0005 g which is the accuracy of the scale used.

The uncertainty of this calculation can be expressed as:

\[
\partial V = \left[ \left( \frac{\partial V}{\partial m_{\text{full}}} \delta m_{\text{full}} \right)^2 + \left( \frac{\partial V}{\partial m_{\text{empty}}} \delta m_{\text{empty}} \right)^2 + \left( \frac{\partial V}{\partial \rho} \delta \rho \right)^2 \right]^{\frac{1}{2}}
\]

\[
\partial V = \left[ \left( \frac{1}{\rho} \delta m_{\text{full}} \right)^2 + \left( - \frac{1}{\rho} \delta m_{\text{empty}} \right)^2 + \left( - \frac{\left(m_{\text{full}} - m_{\text{empty}}\right)}{\rho^2} \delta \rho \right)^2 \right]^{\frac{1}{2}}
\]

Equation E.2

### E.2 Theoretical Volume Calibrations

Table E.2 displays the tube lengths, volumes, and error calculated for various components of the apparatus.

<table>
<thead>
<tr>
<th>Section Component</th>
<th>Number</th>
<th>Length [mm]</th>
<th>Total Volume [cm(^3)]</th>
<th>Total Error [cm(^3)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tube 5</td>
<td>1</td>
<td>390</td>
<td>6.4028</td>
<td>1.4005</td>
</tr>
<tr>
<td>Tube 7</td>
<td>1</td>
<td>139</td>
<td>2.2820</td>
<td>0.4992</td>
</tr>
<tr>
<td>Tube 9</td>
<td>1</td>
<td>427</td>
<td>7.0102</td>
<td>1.5333</td>
</tr>
<tr>
<td>Tube 11</td>
<td>1</td>
<td>160</td>
<td>2.6268</td>
<td>0.5746</td>
</tr>
<tr>
<td>Port Connector</td>
<td>2</td>
<td>N/A</td>
<td>0.7290</td>
<td>Negligible</td>
</tr>
<tr>
<td>Bellows Valve</td>
<td>1</td>
<td>N/A</td>
<td>0.9000</td>
<td>Negligible</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------------------------</td>
<td>---</td>
<td>---</td>
<td>-----</td>
<td>-----------</td>
</tr>
<tr>
<td>Bellows Valve</td>
<td>1</td>
<td>N/A</td>
<td>0.9000</td>
<td>Negligible</td>
</tr>
<tr>
<td>(2 halves)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Union</td>
<td>1</td>
<td>N/A</td>
<td>0.7480</td>
<td>Negligible</td>
</tr>
<tr>
<td>Pressure Transducer</td>
<td>1</td>
<td>N/A</td>
<td>0.9832</td>
<td>Negligible</td>
</tr>
<tr>
<td>Tube Adapter</td>
<td>2</td>
<td>N/A</td>
<td>1.2051</td>
<td>Negligible</td>
</tr>
<tr>
<td>Cylinder Small</td>
<td>1</td>
<td>N/A</td>
<td>75.0000</td>
<td>3.7500</td>
</tr>
<tr>
<td>Cylinder Large</td>
<td>1</td>
<td>N/A</td>
<td>1000.0000</td>
<td>50.0000</td>
</tr>
</tbody>
</table>

Note: This table displays only the sample side portion of the apparatus; however, theoretically the sample side and reference side should be approximately equal.

The uncertainty associated with each cylinder in the apparatus is 5% as stated in the Swagelok schematic. The uncertainty associated with volumes of the Swagelok components read from schematic was assumed negligible compared to the uncertainty associated with the cylinders. The volume for each tube length was calculated simply by:

\[ V = \frac{\pi}{4} D^2 L \]

Equation E.3

where L represents the length of the tube. D represents the diameter of the tube which was measured to be 4.572 mm for all tube lengths.

The uncertainty calculated for each measured tube length is calculated as follows:

\[ \delta V = \left[ \left( \frac{\partial V}{\partial D} \delta D \right)^2 + \left( \frac{\partial V}{\partial L} \delta L \right)^2 \right]^\frac{1}{2} \]

\[ \delta V = \left[ \left( \frac{\pi DL}{2} \delta D \right)^2 + \left( \frac{\pi D^2}{4} \delta L \right)^2 \right]^\frac{1}{2} \]

Equation E.4

An uncertainty of 0.5 mm for both the length and the diameter of each tube was used.
### E.3 Pressure Volume Calibrations

Table E.3 and Table E.4 show the results from the PCT apparatus pressure volume calibrations.

#### Table E.3  PCT Sample Side Apparatus Volumes

<table>
<thead>
<tr>
<th>Section</th>
<th>Run</th>
<th>Method</th>
<th>Starting Pressure [kPa]</th>
<th>Volume [cm³]</th>
<th>Error [cm³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample Reservoir</td>
<td>1-1</td>
<td>Forward</td>
<td>282</td>
<td>89.674</td>
<td>32.952</td>
</tr>
<tr>
<td>Sample Reservoir</td>
<td>1-2</td>
<td>Forward</td>
<td>287</td>
<td>90.516</td>
<td>32.276</td>
</tr>
<tr>
<td>Sample Reservoir</td>
<td>1-3</td>
<td>Forward</td>
<td>278</td>
<td>90.274</td>
<td>33.333</td>
</tr>
<tr>
<td>Sample Reservoir</td>
<td>1-4</td>
<td>Forward</td>
<td>283</td>
<td>89.984</td>
<td>33.014</td>
</tr>
<tr>
<td>Sample Reservoir</td>
<td>1-5</td>
<td>Forward</td>
<td>287</td>
<td>90.743</td>
<td>32.654</td>
</tr>
<tr>
<td>Sample Reservoir</td>
<td>2-1</td>
<td>Forward</td>
<td>Software Error Occurred</td>
<td>Software Error Occurred</td>
<td>Software Error Occurred</td>
</tr>
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#### Table E.4  PCT Reference Side Apparatus Volumes

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<tr>
<th>Section</th>
<th>Run</th>
<th>Method</th>
<th>Starting Pressure [kPa]</th>
<th>Volume [cm³]</th>
<th>Error [cm³]</th>
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<tr>
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<td>Reverse</td>
<td>707</td>
<td>90.613</td>
<td>12.947</td>
</tr>
</tbody>
</table>
The volumes are calculated based on a difference of pressures. The forward volume calculations were performed by:

\[
\begin{align*}
    n_3 &= n_x + n_c \\
    \frac{P_3 (V_x + V_c)}{z_3 RT_3} &= \frac{P_x V_x}{z_x RT_x} + \frac{P_c V_c}{z_c RT_c}
\end{align*}
\]

Equation E.5

noticing that temperature remains constant and rearranging leads to:

\[
V_x = \frac{P_x V_x z_x z_3 - P_c z_c z_x V_c}{P_3 z_c z_x - P_x z_c z_3}
\]

Equation E.6

where \( n, P, V, z, R, \) and \( T \) represent moles, pressure, volume, compressibility factor, universal gas constant, and temperature respectively. The subscript “3” denotes the properties when the calibration volume has been joined to the volume under observation. The subscript “x” and “c” represent the properties of the volume under question and of the calibration volume respectively.

Please note that the ideal gas law requires absolute pressures; however, the PCT apparatus uses gauge pressure transducers. Therefore, an average atmospheric pressure of 101.325 kPa has been added in the Labview software to all gauge pressure readings. The error associated with this addition has been considered negligible compared to the intrinsic error associated with the pressure sensors themselves.

The error associated with this forward volume calibration method is calculated by:
\[
\delta V_x = \left[ \left( \frac{\partial V_c}{\partial P_c} \delta P_c \right)^2 + \left( \frac{\partial V_c}{\partial P_x} \delta P_x \right)^2 + \left( \frac{\partial V_c}{\partial P_3} \delta P_3 \right)^2 + \left( \frac{\partial V_c}{\partial V_c} \delta V_x \right)^2 \right]^{1/2}
\]

\[
\delta V_x = \left[\left(\frac{V_c}{P_3 - P_x} \delta P_c \right)^2 + \left( \frac{P_c V_c - P_3 V_c}{(P_3 - P_x)^2} \delta P_x \right)^2 + \left( -\frac{V_c}{P_3 - P_x} - \frac{P_c V_c - P_3 V_c}{(P_3 - P_x)^2} \delta P_3 \right)^2 + \left( \frac{P_c - P_3}{P_3 - P_x} \delta V_c \right)^2 \right]^{1/2}
\]

Equation E.7

When calculating the larger volumes, a similar process is followed except that the volume of the reservoir must now be known. This leads to:

\[
n_3 = n_{x_{res}} + n_c
\]

\[
\frac{P_3 (V_x + V_c + V_{res})}{z_3 RT_3} = \frac{P_{res} (V_x + V_{res})}{z_{res} RT_{res}} + \frac{P_c V_c}{z_c RT_c}
\]

\[
V_x = \frac{P_{res} V_{res} z_c z_3 + P_c V_c z_{res} z_3 - P_3 z_c z_{res} V_{res} - P_3 z_c z_{res} V_c}{P_3 z_c z_{res} - P_{res} z_c z_3}
\]

Equation E.8

where \(V_x\) and \(V_{res}\) are the large volume under question and the reservoir volume respectively.

The error for this equation is calculated by:
The uncertainty of the gauge pressure transducers is stated as 0.5\% of span. These transducers range from vacuum to 100 bar. Therefore, the uncertainty is ±50 kPa. The uncertainty with the differential sensor is much more accurate since the span is smaller. The uncertainty of this sensor is 0.25\% of span (30 psi) or ±0.5171 kPa. Overall, uncertainty values for the reservoir volumes range from ±150 to 130 cm³, which is unacceptable. Worse still was the uncertainty associated with the large volume calculation. Therefore, the large volumes can not be calibrated using this difference of pressures method.

Since there is such a large uncertainty associated with the gauge pressure transducers, the differential sensor can be used to try to improve the error in the forward calibration method. The differential pressure sensor will predict the same pressure difference as the gauge sensor if only one side of the apparatus is calibrated at a time, and
both sides of the apparatus are at the same pressure before the calibration procedure. In
this situation, the calculations are:

\[
V_x = \frac{P_c V_c z_x z_3 - P_1 z_c z_x V_c}{P_3 z_c z_x - P_x z_c z_3}
\]

Equation E.6

and

\[
P_3 = P_x + P_{d2} - P_{d1}
\]

Equation E.10

where \(P_{d2}\) and \(P_{d1}\) are the differential pressure measurements after and before the

\[2\]

calibration volume is exposed to the volume under question. The uncertainty for this
calculation is:

\[
\delta V_x = \left[ \left( \frac{\partial V_x}{\partial P_c} \delta P_c \right)^2 + \left( \frac{\partial V_x}{\partial P_x} \delta P_x \right)^2 + \left( \frac{\partial V_x}{\partial P_{d2}} \delta P_{d2} \right)^2 + \left( \frac{\partial V_x}{\partial P_{d1}} \delta P_{d1} \right)^2 \right]^{\frac{1}{2}}
\]

\[\]

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\[
\delta V_x = \left[ \left( \frac{V_c}{P_{d2} - P_{d1}} \delta P_c \right)^2 + \left( \frac{V_c}{P_{d2} - P_{d1}} \delta P_x \right)^2 + \left( \frac{V_c}{P_{d2} - P_{d1}} \delta P_{d1} \right)^2 \right]^{\frac{1}{2}}
\]

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compared to the value calculated. To try to improve this uncertainty further, the reverse pressure calibration method was created as explained previously. The calculation for this method is almost exactly the same as for the forward method. The only difference is that a pressure decrease is measured instead of a pressure increase. Therefore, Equation E.10 becomes:

$$P_3 = P_x - P_{d2} - P_{d1}$$

Equation E.12

The error term remains almost the same as Equation E.11 except the sign of each $P_{d2}$ term is changed. The calculated result and magnitude of error remain the same approximately the same as the forward pressure calibration method.
Appendix F

F.1 Hybrid Reactor Pictures

Figure F.1 - Hybrid reactor in use with PCT apparatus

Figure F.2 - Close up of the sample and reference hybrid reactor
Appendix G

G.1 Hybrid Reactor Operating Calculations

From the hybrid reactor is displayed in Figure G.1, it can be seen that any heat produced by the NaBH₄ chemical reaction will either travel outwards to the external environment, or be carried with the fluids (NaBH₄ solution, hydrogen, or water vapour) exiting the reactor.

For simplicity, the heat transfer was assumed to:

- Heat the surrounding liquid fluid.
- Evaporate a small amount of water.
- Heat the surrounding copper and stainless steel walls.
- Transfer to the metal hydride through desorption reaction.
- Exit the reactor by fluid flow.
These assumptions neglect radiation from the hybrid reactor and heat transfer to the gas produced. Heat transfer from the external environment is also neglected. Heat was also assumed to transfer to the walls of the reactor, but not to the flanges, lid, or packed bed.

**G.1.1 Energy Transfer to Fluid**

The energy transferred to the surrounding solution was calculated as:

\[ Q_{sol} = \dot{m}C_{psol}\Delta T \cdot t \]  

Equation G.1

where \( \dot{m} \) is the flow rate of the solution (g·s\(^{-1}\)) and \( C_{psol} \) is the specific heat capacity of the solution (taken as 4.184 J·kg\(^{-1}\)K\(^{-1}\)). The fluid was assumed to be heated from 25 °C to 80 °C, and \( t \) represents the run time of the experiment. This value was calculated for all experimental runs.

**G.1.2 Energy of Evaporation**

The energy transfer involved during the evaporation of water was estimated using an average relative humidity for all experiments. It was assumed that throughout the experiment, a relative humidity of 80% existed.\(^{42}\)

\[ \phi = \frac{P_{H_2O}}{P_{sat}} \]

\[ \phi = \frac{\rho_{H_2O,v}}{\rho_{sat,v}} \]

Equation G.2
As shown in Equation G.2, the relative humidity is a ratio between the partial pressure of the water vapour and the saturation pressure of the water vapour at the vapour’s temperature. This expression can also be written in terms of density. At a temperature of 80 °C, water vapour has a saturation density of 0.29349 kg·m⁻³ and a heat of evaporation of 2308.8 kJ·kg⁻¹.

\[
\rho_{H_2O,v} = (0.29349)(0.8)
\]
\[
\rho_{H_2O,v} = 0.235
\]

Equation G.2

Throughout all of the experiments performed at a flow rate of 6 mL·min⁻¹, a gas production rate of 1.7 L·min⁻¹ was recorded. This represented a 0.2 L·min⁻¹ difference between the theoretical hydrogen production of about 1.5 L·min⁻¹. It was assumed that this difference was the amount of water vapour produced, and that this value was constant throughout all experiments. Under this assumption, it was possible to calculate the total mass of water produced, and therefore the heat contributing to vapourization.

\[
m_{H_2O,v} = \rho_{H_2O,v}\cdot\Delta t
\]
\[
m_{H_2O,v} = (0.235)(3.33\cdot10^{-6})(3600)
\]
\[
m_{H_2O,v} = 2.818\cdot10^{-3}
\]

Equation G.3

\[
Q_{evap} = m_{H_2O}\Delta H_{fg}
\]

Equation G.4

where \(Q_{evap}\) is the heat energy contributing to the evaporation of the water, \(m_{H_2O}\) is the mass of the water vapour, and \(\Delta H_{fg}\) is the heat of evaporation measured in kJ·kg⁻¹.

Using the equations above, the heat lost to evaporation was calculated for all experimental runs.
G.1.3 Energy Transfer to Reactor Walls

Prior to the fabrication of the hybrid reactor, the mass of all materials used was recorded. The mass of the copper and two stainless steel walls of the apparatus were 0.2016, 0.207, and 0.3846 kg respectively. The amount of heat energy transferred to each wall can be calculated in the exact same manor as Equation G.1, but without the run time included in the equation. The starting and ending temperatures of each wall were averaged. For example, the average temperature of the inner thermocouples was taken as the starting temperature of the copper tube wall and the inner stainless steel wall. Similarly, the outer thermocouples were used to take the temperature of the outer stainless steel wall. The same method was used to take the ending temperatures when the experimental run was finished. The specific heat capacity value of copper and stainless steel used was 385 and 500 kJ·kg⁻¹K⁻¹. A value of the energy transfer to each reactor wall was calculated for each experimental run.

G.1.4 Energy Transfer to the Metal Hydride

During the experimental runs which utilized the constant pressure desorption method, the metal hydride changed from a fully absorbed state to a fully desorbed state. Since the metal hydride released all of the possible hydrogen stored, the amount of energy transferred to the metal hydride is easily calculated.
Therefore, in each constant pressure desorption experiment, about 30.76 kJ of heat energy was transferred to the metal hydride. In the case of the kinetics experiment, the amount of desorption that occurred was measured directly. Although there is some experimental error associated with this measurement, this value was used to determine an estimate for the amount of energy transfer.

\[
Q_m = \Delta H_m \frac{m_m}{M_m}
\]

\[
Q_m = 28.52 \frac{466.36}{432.3725}
\]

\[
Q_m = 30.76
\]

Equation G.5

In the above example, it was assumed that 30% of the available hydrogen was desorbed from the metal hydride. Therefore, only 9.23 kJ were used in the desorption process. These calculations were performed for all experimental runs.

\[
Q_m = \Delta H_m \frac{m_m}{M_m} (\%_{\text{desorbed}})
\]

\[
Q_m = 28.52 \frac{466.36}{432.3725} (0.3)
\]

\[
Q_m = 9.23
\]

Equation G.6

In the above example, it was assumed that 30% of the available hydrogen was desorbed from the metal hydride. Therefore, only 9.23 kJ were used in the desorption process. These calculations were performed for all experimental runs.

**G.1.5 Heat Transfer Efficiency**

The heat transfer efficiency was measured as the amount of energy transferred to the metal hydride compared to the amount of energy generated by the NaBH₄ reaction. The calculation was as follows:
\[ \eta = \frac{Q_m}{\dot{n}_{NaBH_4} \Delta H_{\text{run}} t} \]

Equation G.7

where \( Q_m \) represents the theoretical amount of heat energy used by the metal hydride.

The molar flow rate of \( NaBH_4 \), the heat of reaction for \( NaBH_4 \), and the experimental run time are represented by \( \dot{n}_{NaBH_4} \), \( \Delta H_{\text{run}} \), and \( t \) respectively. An example calculation for a 6 mL·min\(^{-1}\) solution flow rate is as follows:

\[ \eta = \frac{30.76}{(2.8 \times 10^{-4})(217)(3600)} \times 100\% \]

\[ \eta = 14\% \]

Equation G.8

This calculation was also performed for each experiment.

**G.1.6 Summary**

The above calculations were performed for each hybrid experiment. The summary of these calculations is shown in Table G.1.

<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
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<th></th>
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<th></th>
</tr>
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<tbody>
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<td>7.6</td>
<td>30.8</td>
<td>14.0</td>
</tr>
</tbody>
</table>

Table G.1 displays the energy produced from the \( NaBH_4 \) reaction as well as all calculations of assumed energy transfer. Odd numbered runs were using the passive
temperature control desorption method. Pressure controlled desorption runs are labelled with even numbers. Heat transfer was more efficient during the pressure controlled desorption runs due to a larger amount of heat transfer to the metal hydride.