Mass and Heat Transfer in Intermetallic-Hydrogen Storage Tanks

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Doctor of Philosophy

September 2016
To my beloved parents

and

dear sister, Farnaz
STATEMENT

This work has not previously been submitted for a degree or diploma in any university. To the best of my knowledge and belief, the thesis contains no material previously published or written by another person except where due reference is made in the thesis itself.

Shahrzad Seyed Mohammadshahi
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ALL PAPERS INCLUDED ARE CO-AUTHORED

Acknowledgement of Papers included in this Thesis

Included in this thesis are papers in Chapters 2, 3 and 4 which are co-authored with other researchers. My contribution to each co-authored paper is outlined at the front of the relevant chapter. The bibliographic details and status for these papers including all authors are:

Chapter 2:


Chapter 3:


Chapter 4:


Appropriate acknowledgements of those who contributed to the research but did not qualify as authors are included in the papers.

(Signature)   (Date) 18/09/2016
Shahrzad Seyed Mohammadshahi

(Signature)   (Date) 18/09/2016
ABSTRACT

Hydrogen is a potential future energy carrier, but reliable storage of the hydrogen is required for widespread use. Metal-hydrides (MH) are suitable materials for safe, stable and long-term hydrogen storage applications such as off-grid and hybrid solar systems due to the ability to store hydrogen at moderate pressure and temperature. However, poor thermal properties of MH beds coupled with the need for managing the significant amount of heat generated during the absorption and desorption reactions, is a serious barrier for fast hydrogen uptake and release unless an efficient design for the MH tank and the heat exchange system is used. Appropriate design of the tank and thermal management systems as well as a suitable choice of material can improve the performance of the MH systems and make them more suitable for commercial use.

It is not usually practicable to build and test different MH tanks for large scale applications and explore the impact of different design and process parameters on the performance of the tanks. In contrast, mathematical models can be employed for examining various parameters, scenarios and used to predict the effect on the MH system without the cost of materials and manufacturing time. These models, however, must be accurate in order to reliably design large scale MH tanks and components and this accuracy can be achieved by refinement of the model’s parameters and equations based on practical systems. In turn, the accuracy of the model also needs to be validated through experimental data obtained from operating tank systems under different conditions.

This work presents an improved 3D mathematical model for large-scale MH tanks modified to include a number of practical features that allow the direct application of the model to a real system. This enhanced model was then validated by comparison to experimental results for a system undergoing significant compositional inhomogeneities.
The model described here has introduced new profiles for hydrogen in- and out-flow rates, empirical equations for material equilibrium pressure and effective thermal conductivity, modification of the kinetics equation using initial conditions matching hydrogen cycling situations and has investigated different approaches for thermal fluid temperature management. The accuracy of assuming hydrogen to be an ideal gas was also surveyed. The model was solved using COMSOL Multiphysics for a prototype intermetallic-hydrogen storage tank, designed to study the behaviour of MH beds under challenging operating conditions such as less than optimal thermal management systems.

An in-situ neutron diffraction measurement was conducted using a spatially-resolved diffractometer, ENGINX at Rutherford Appleton Laboratories, UK, for a medium scale $\text{LaNi}_5\cdot\text{D}_2$ system. The objective was to measure the spatial variation of bed composition after a rapid single injection of deuterium to approximately 50% hydride fraction. Although the compositional inhomogeneity had been predicted previously and observed qualitatively, mapping the spatial variation of the bed composition under these conditions had not been previously done. This provided unique data against which the MH model could be tested. The improved multiphysics model mentioned above was then adapted to match the experimental arrangement and the theoretical and experimental results were compared and analysed.

An experimental prototype system consisting of two MH tanks, gas handling systems and water circulation bath has been designed and simulated using the new model. This will be used in the future to test the improved model and further study the structural behaviour of MH beds during absorption and desorption under different conditions.
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<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau$</td>
<td>temperature, K</td>
</tr>
<tr>
<td>$P$</td>
<td>pressure, bar</td>
</tr>
<tr>
<td>$\rho$</td>
<td>density, kg/m$^3$</td>
</tr>
<tr>
<td>$\rho_{st}$</td>
<td>the total hydrogen density added to the tank, kg/m$^3$</td>
</tr>
<tr>
<td>$V$</td>
<td>velocity vector, m/s</td>
</tr>
<tr>
<td>$\Delta H$</td>
<td>enthalpy of formation, J/kg</td>
</tr>
<tr>
<td>$\Delta S$</td>
<td>entropy change, J/kg K</td>
</tr>
<tr>
<td>$E$</td>
<td>activation energy, J/kg</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Thermal conductivity, W/m K</td>
</tr>
<tr>
<td>$R_g$</td>
<td>universal gas constant, J/mol H$_2$ K</td>
</tr>
<tr>
<td>$C_p$</td>
<td>Specific heat capacity, J/kg K</td>
</tr>
<tr>
<td>$H_{mg}$</td>
<td>convection coefficient between solid and gas, W/m$^2$ K</td>
</tr>
<tr>
<td>$Q$</td>
<td>Heat flux (W)</td>
</tr>
<tr>
<td>$m$</td>
<td>hydrogen mass absorbed or desorbed, kg/m$^3$ s</td>
</tr>
<tr>
<td>$\mu$</td>
<td>viscosity, kg/m K</td>
</tr>
<tr>
<td>$d_p$</td>
<td>mean particle diameter, m</td>
</tr>
<tr>
<td>$V$</td>
<td>volume, m$^3$</td>
</tr>
<tr>
<td>$t_{inj}$</td>
<td>time of injection, s</td>
</tr>
<tr>
<td>$t$</td>
<td>time, s</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>porosity</td>
</tr>
<tr>
<td>$k$</td>
<td>permeability, m$^2$</td>
</tr>
<tr>
<td>$\phi_m$</td>
<td>hydrogen mass flow rate, (kg/m$^3$s)</td>
</tr>
<tr>
<td>$\phi_p$</td>
<td>hydrogen flow rate, (mol/m$^3$s)</td>
</tr>
<tr>
<td>$\eta^\prime$</td>
<td>maximum reacted fraction</td>
</tr>
<tr>
<td>$P_D$</td>
<td>downstream pressure, pa</td>
</tr>
<tr>
<td>$\left( \frac{H}{M} \right)$</td>
<td>hydrogen to metal ratio per formula unit</td>
</tr>
<tr>
<td>$\left( \frac{H}{M} \right)_{max}$</td>
<td>maximum hyrogen to metal ratio per formula unit at a certain temperature</td>
</tr>
<tr>
<td>$\left( \frac{H}{M} \right)_{sat}$</td>
<td>maximum hydrogen to metal ratio per formula unit at room temperature</td>
</tr>
<tr>
<td>$R$</td>
<td>reactor internal radius, m</td>
</tr>
<tr>
<td>$\eta$</td>
<td>reacted fraction</td>
</tr>
<tr>
<td>$E_p$</td>
<td>expansion coefficient</td>
</tr>
<tr>
<td>$n$</td>
<td>outward surface normal vector</td>
</tr>
<tr>
<td>$r_0$</td>
<td>radius of cooling tube, m</td>
</tr>
<tr>
<td>$h$</td>
<td>convective heat transfer coefficient, W/m$^2$K</td>
</tr>
<tr>
<td>$H(x)$</td>
<td>Heaviside step function</td>
</tr>
<tr>
<td>$t_m$</td>
<td>time for smoothing the Heaviside function</td>
</tr>
<tr>
<td>$l$</td>
<td>tank length, m</td>
</tr>
<tr>
<td>$Cv$</td>
<td>discharge coefficient</td>
</tr>
<tr>
<td>$A$</td>
<td>cross sectional area, m$^2$</td>
</tr>
<tr>
<td>$S$</td>
<td>fin spacing (m)</td>
</tr>
<tr>
<td>$\delta$</td>
<td>thickness (m)</td>
</tr>
</tbody>
</table>

### Subscripts

- $\mu$: viscosity, kg/m K
- $d$: desorption
- $eff$: effective
- $s$: solid phase
- $g$: gas phase
- $r$: radial
- $z$: axial
- $ref$: reference
- $Inj$: injection
- $eq$: equilibrium
- $i$: initial
- $f$: final
- $fl$: heat exchange fluid
CHAPTER ONE

Thesis Overview

1-1 Introduction
  1-1-1 Hydrogen
  1-1-2 MH properties
  1-1-3 MH tank models

1-2 Research scope

1-3 Thesis structure

1-4 List of publications and conference presentations

References
1-1 Introduction

Renewable energy is an alternative to fossil fuels to address global concerns over climate change [1]. A variety of natural sources of renewable energy such as tide, wave, sun and wind can be exploited to produce electricity and heat for households and industries as well as to power vehicles with effectively zero emission of air pollutants [2].

Nevertheless, due to the intermittent nature of these sources, safe, efficient and cost-effective energy storage is required to buffer the variation between supply and demand and provide a continuous supply for consumers [3].

Various technologies for energy storage (mechanical, electrochemical, chemical and electrical) are categorised in Table 1. More details about each method and their suitability for specific applications are available in other studies [4, 5].

Among these technologies, batteries and hydrogen have become more popular due to their versatility for mobile, portable and stationary applications of renewable energy [6].

Table 1-1- Electrical energy storage technologies [7-11]

<table>
<thead>
<tr>
<th>Mechanical</th>
<th>Electrochemical</th>
<th>Chemical</th>
<th>Thermal</th>
<th>Electrical</th>
</tr>
</thead>
<tbody>
<tr>
<td>•Pumped hydro (PHS)</td>
<td>•Flow Batteries (ex.: Zn-Br, Vanadium Redox)</td>
<td>•Hydrogen</td>
<td>•Phase change materials (PCM)</td>
<td>•Superconducting magnetic energy storage (SMES)</td>
</tr>
<tr>
<td>•Flyweel energy storage (FES)</td>
<td>•Secondary batteries (ex.: lead-acid, nickle-based, Sodium-sulfur, Li-based)</td>
<td>•Solid-state hydrogen storage</td>
<td>•Molten Salt</td>
<td>•Supercapacitor storage technologies</td>
</tr>
<tr>
<td>•Compressed air energy storage (CAES)</td>
<td></td>
<td>•Compressed gaseous hydrogen storage</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Batteries and hydrogen are sometimes viable alternatives in the same applications, for example battery and fuel-cell electric vehicles. Each storage modality has advantages and disadvantages in certain situations. This thesis is concerned with hydrogen storage, especially hydrogen stored in solid state materials. The goal of the project was to construct and test an advanced computational model of a solid state hydrogen storage canister. These are presently applied in submarines [12], merchant hydrogen storage and delivery [13, 14] and demonstration renewable energy systems [15].

1-1-1 Hydrogen

Hydrogen is an energy carrier that can be efficiently converted to electricity using fuel cells, producing water and heat [16]. Hydrogen is abundant in various compounds and can be produced using a variety of processes [17, 18] from fossil fuels [19, 20], biomass [21, 22] and biofuels, and also from water [23] through thermochemical water splitting [24, 25], photo catalysis [23], electrolysis [26] and photoelectrolysis [27]. In order to be sustainable and to reduce CO and CO₂ emissions, hydrogen needs to be produced using renewable sources such as biomass and water rather from fossil fuel sources [27-29].

In addition to conventional applications of hydrogen, which at present are largely in the petroleum and chemical industries for upgrading of fossil fuels (hydrocracking) and ammonia and methanol production [30], use in fuel cells for electricity generation is essential in order to expand clean energy applications in industries, households and transportation.

Hydrogen has higher mass energy density (120 kJg⁻¹) compared to carbon-based fuels such as gasoline (46.4 kJg⁻¹) [31, 32] , but exhibits low energy density per volume (volumetric energy density) and requires a larger space for storage at ambient
conditions even if compressed to high pressure (700 bar) or liquefied at cryogenic temperatures (253 K) [6]. For compression and liquefaction, the expense of maintaining the temperature and pressure as well as the higher safety risks associated with high pressure or very low temperature is an obstacle to widespread use.

However, solid-state hydrogen storage can achieve higher hydrogen volume density at more modest pressures and ambient temperatures which is safer and cheaper for long term use [33]. These materials, however, increase the mass of the storage systems reducing the gravimetric density. Different types of solid materials used for hydrogen storage applications are categorised in Figure 1-1.

![Figure 1-1: Different categories of solid materials for hydrogen storage](image)

The USA Department of Energy’s (DOE) gravimetric target for on-board hydrogen storage in light duty fuel-cell vehicles is a capacity of 5.5 wt% by 2020 and an ultimate capacity of 7.5 wt% [34]. Based on the lower heating value (120 kJg⁻¹), these
are equivalent to 1.8 kWhkg$^{-1}$ and 2.5 kWhkg$^{-1}$ hydrogen respectively. Lightweight materials including complex hydrides and physical adsorbents generally have higher gravimetric energy density compared to most metal alloy hydrides and are therefore better suited to mobile applications. Practical operating pressures and temperatures up to 85°C and 5 bar have also been considered by the DOE and these still are a critical obstacle in the way of extensive use of many of the potential materials [34].

Currently, all commercial fuel-cell vehicles, including buses, passenger cars and delivery vans rely on hydrogen gas storage at pressures up to 700 bar, because solid-state hydrogen storage at acceptable energy density has not been successfully commercialised.

For stationary applications of hydrogen storage such as hybrid and off-grid solar systems, weight is usually not the main issue. Instead cyclability, fast kinetics and practical thermodynamics are of greater importance. Many metal-hydrides (MH), have proven to be promising materials for this application [3] and some of these have been used in commercial hydrogen storage tanks [12, 13]. MH tanks may satisfy all the requirements of practical energy storage such as stability, safety, cost, long cycle life, fast charge and discharge rate and high energy density [3, 10]. Both material characteristics and tank design parameters play an important role in the performance of MH systems.

Hydrogen is a flammable gas and there is a risk of explosion when it forms a mixture with air, with the lower and upper explosive limits of 4 and 75 percent of hydrogen respectively at ambient conditions [35]). This is a serious threat when it is compressed to hundreds of bar which could release a large volume of H$_2$ uncontrollably in the case of rupture of the container. MH’s typically do not have these issues to the same degree because of reduced operating pressures. In addition, hydrogen from MH slows
or stops in the case of a rupture. This is because the initial release of some of the hydrogen causes a large drop in temperature due to the endothermic desorption reaction. The lower temperature can prevent further desorption until the material warms.

MH storage can be a more cost effective method compared to compressed hydrogen due to lower requirements for the pressure containment. Also, less space than compressed hydrogen is required due to the higher volumetric energy density. Figure 1-2 shows a comparison of the volumetric energy densities of the above mentioned hydrogen storage methods.

![Volumetric density of hydrogen storage methods](image)

Figure 1-2- Comparison of energy density of different means of hydrogen storage [36, 37]
1-1-2 MH properties:

MHs have been the subject of intensive research since the 1970's and are characterised by the following reversible reaction

\[ aM + \frac{b}{2}H_2 \leftrightarrow M_aH_b + \Delta H \]  

(1-1)

A significant group of metal-hydrides is the binary intermetallics, which are alloys composed of a metal element “A” with strong tendency to hydriding, such as La, Ca, Ti, Mg, Y, Zr, and “B”, a weakly hydriding metal element such as Ni, Fe, Mn, Co. AB, AB₂, A₂B and AB₅ are common families of intermetallic compounds.

In simple ternary hydrides (AₓBᵧHₜ), Pressure-Composition-Temperature (PCT) isotherms indicate the thermodynamic equilibrium of MH system pressure in transition between α phase (a weak solid solution) and β phase (the hydride) at a fixed temperature. This is often expressed as equilibrium pressure versus hydrogen concentration in the form of hydrogen to metal ratio (H/M), reacted fraction or storage capacity (wt%) as shown in Figure 1-3. When the host alloy starts to dissolve hydrogen, the pressure increases until the first nuclei of β phase is formed. The pressure tends to plateau while α and β phase coexist and sharply increases after the pure β phase is reached [38]. The inverse phase transition from β to α occurs at lower desorption equilibrium pressure. The difference between the equilibrium absorption and desorption pressures is termed hysteresis. Hysteresis is an inherent characteristic of metal-hydrides and varies among different MH.

Although the origin of hysteresis is not completely clear, its effect on thermodynamic and kinetics properties of the MH during hydrogen release and uptake as well as its interaction with other mass and heat transfer throughout the bed complicates MH bed
systems [39]. The slope of the plateau, the plateau pressure and the degree of hysteresis depend on the nature of the material [40, 41] as well as the system temperature.

The thermodynamic properties and hydrogen capacity of an intermetallic can be modified through substitution of metal elements into the “A” and “B” components [42, 43]. Alternatively a variation of B/A stoichiometry [40] is also possible. This enables the tailoring of intermetallic properties to suit the requirements of fuel cell operating temperature and pressure conditions (0-100°C and 1-10 bar typically), as well as Ni-MH batteries which operate at sub-bar pressures.

Figures 1-3 (a) and (b) show the PCT isotherms of LaNi$_5$ and the modified hydride LaNi$_{4.7}$Al$_{0.3}$ at 80°C; lower plateau pressure and higher plateau slope can be observed after modification. More examples of the compositional modification and references are given in the review paper [44] in chapter 2.
During cycling it is possible for the intermetallic alloy to become partially amorphous, decompose into separate metals or hydrides or form a stable hydride that does not desorb [46]. Typically, this reduces the capacity for the next cycle of absorption and desorption. A good material will be able to be cycled thousands of times. Investigations of different compositions in order to modify the hydrogen absorption/desorption characteristics metal-hydrides and increase their capacity are ongoing [47-49].

Many AB₅’s have good cyclability and resistance to gas impurities compared with other intermetallic compounds. These properties make AB₅’s promising candidates to satisfy the requirements of efficient hydrogen storage systems. Among the AB₅ family, LaNi₅ has been extensively studied and the thermodynamics and physical properties, including thermal conductivity are well-known. Good knowledge of the physical properties makes this material an excellent choice as a model hydrogen absorber, despite being too expensive to be commercially used in large scale hydrogen storage vessels for stationary applications [50, 51]. Therefore, multi-substituted AB₅’s based on LaNi₅ are used because of their long cycle life, high volume density,
relatively fast kinetics and low operating pressure and temperature [46, 52, 53]. A lower-cost variation uses mischmetal (naturally occurring mix of Ce+La+Nd+Pr) instead of La. Often the Ni is substituted with (Ni+Al+Mn+Co+) to tailor properties such as pressure and temperature to specific requirements of fuel cells and electrolysers. For example, La_{1-x}Mg_xNi_5, La_{1+x}Mg_{2-x}Ni_9, La_{1-x}Ce_xNi_5 [42, 54, 55] and LaNi_{5-x}Al_x [56] have different sorption characteristics and sometimes higher hydrogen capacity and cyclability.

**1-1-3 MH tanks models:**

Metal alloy as a storage medium for hydrogen is usually used in the form of a powder and is considered as a packed bed for all the calculations. The reaction between metal and hydrogen releases significant heat in absorption and requires a similar amount of energy to discharge hydrogen. If the required heat is not supplied/removed the reactions and as a result hydrogen flow in and out of the tank will be stopped.

Since MH packed beds typically suffer from poor thermal conductivity, an efficient heat exchange system to manage the considerable heat power of the reaction is essential [37]. Therefore, in addition to research on materials to promote the capacity and effective thermal conductivity, the performance of tanks and cooling systems needs to be investigated in order to find optimum tank designs, in particular for medium to large scales.

Design and testing of many different MH tanks and heat exchange systems in pilot studies is expensive and time-consuming. However, modelling provides the possibility of examining different geometrical and operating parameters to investigate their effect on the tank performance and to optimise the design with minimal cost and delay.
Due to the complexity of the fundamental interaction between hydrogen and metal alloys, which is further complicated by thermal management, several assumptions and approximations are typically made to simplify these models and reduce the computation time [44]. However, in order to achieve more precise and reliable results, accurate equations and values for properties and conditions of real MH systems need to be employed.

Conversely, experimental data from a real MH bed under different conditions must be available to validate any new model.
1-2 Research Scope

Among the numerous models developed for MH tank systems [57-62], a comprehensive 3D multiphysics model for a sodium alanate tank has been presented by Hardy and Anton [63, 64]. This model was able to be generalised for all cylindrical MH tanks and is also applicable for large scale systems. However, some of the practical features of MH material characteristics and tank operating conditions including hysteresis, bed volume changes during absorption/desorption, and pressure-dependence of effective thermal conductivity as well as parameters such as hydrogen flow to and from the tank and practical initial conditions were neglected or simplified.

In this study, therefore, an improved model [44, 65], based on the Hardy and Anton model, has been developed to include parameters that influence practical MH systems. The compressibility factor of hydrogen gas was considered instead of the simplified hypothesis of hydrogen as an ideal gas. Practical initial and boundary conditions, hydrogen inlet and out flow rate are also adjustable in the model. An equation was fitted to PCT experimental data and used in the model in order to accurately estimate the equilibrium pressure of the MH bed for all the compositions and operating temperatures. An empirical equation for the pressure dependence of the effective thermal conductivity based on previous experimental data [66] was introduced. Moreover, various temperature configurations were investigated: the effects of a fixed coolant inlet temperature for both absorption and desorption versus a cycled coolant temperature for energy cost reduction hydrogen cycling time were compared.

Most of the available experimental data have been derived from small scale metal hydrogen storage systems under specific conditions such as constant volume or constant pressure [59, 67-69]. This can be used to verify models under similar situations, however, these cannot always be used to verify the above mentioned
models which have been developed for large scale systems with dynamic hydrogen inlet and outlet flow.

A prototype intermetallic-hydrogen system consisting of two pressure tanks with the storage capacity of ~1.5 kg hydrogen each, gas handling and cooling circulation baths has been designed. This will be used in a subsequent project to test the model developed in this project. 100 kg each of two different AB₅ intermetallics, LaNi₅ and a material designed for large-scale storage (the Sir Samuel Griffith Centre at Griffith University) [15], have been chosen for the tanks, allowing for study and comparison of their performances at the same time as well as eliminating the need for an extra hydrogen reservoir. The model presented here specifically caters for these tanks, which explains the use of LaNi₅ in the model. However, the model is capable of being run with different materials properties and under different conditions.

A comprehensive model, in addition to predicting averaged values of operating conditions such as temperature, pressure and hydrogen content, must be able to predict local values. Macroscopic compositional inhomogeneities of MH beds have been reported in previous studies [70, 71] which arise due to the complex interaction of MH hysteresis, exothermic reaction between metal and hydrogen and poor effective thermal conductivity of the MH bed. This can be used to test the strength of the models to predict the local value of hydride reacted fractions provided quantitative data exist. For this study, an in-situ neutron diffraction measurement was conducted in a medium scale LaNi₅ sample cell to map the α/β phase proportions. A 3D multiphysics model based on the experimental conditions was developed and solved using COMSOL. The experimental and model results were compared and analysed.

The commercial alloy used in the Sir Samuel Griffith Centre has a different stoichiometry to LaNi₅, but many of the same characteristics which are shared by the
AB₅ family. The project models LaNi₅ and the smaller scale experiment tests the model for the same material, but the larger scale experiment is designed to have both LaNi₅ and the commercial AB₅ (in different tanks). This allows for the results of the model to be compared to the commercial material while still retaining the reference with LaNi₅.
1-3 Thesis structure

The research presented in this thesis is divided into five chapters. This chapter introduces metal-hydrides as potential materials for stationary and portable hydrogen storage applications. The necessity of modelling to the design and implementation of metal-hydride tanks is also discussed.

Chapter 2 reviews the mathematical models of metal-hydride systems for hydrogen storage applications. Different aspects of the models such as assumptions, governing equations, physical properties and equations, initial and boundary conditions which have been used in previous models are reviewed and discussed. This is presented as a published review paper with an added introduction.

Chapter 3 describes the improved metal-hydride model, the purpose of which was to accurately describe a practical large-scale metal-hydrogen tank. The model was solved by COMSOL Multiphysics 4.3a. Two papers were published based on the model; the first details the developments made to the model and the second describes the results of the application of this model, investigating areas such as the temperature of the thermal management system, the injection rate and amount of hydrogen.

In Chapter 4, experimental results from an in-situ neutron diffraction measurement study of a small sample of LaNi$_5$ were used to test the ability of the FEM calculations to predict the spatial inhomogeneities of the hydrogen concentration over the bed. This is presented as an unpublished paper.

The instrumentation of prototype intermetallic hydrogen storage system comprises two identical pressure vessels, gas handling and circulation bath are given in chapter 5. This system has been designed and constructed to investigate the distribution of mass and heat throughout the MH bed during absorption and desorption. This will
assist in the verification of improved models of MH tanks as well as to understand MH bed behaviours in large-scale hydrogen storage systems.

Finally, a summary, conclusion and suggested future work are given.
1-4 List of publications and presentations

Journal papers


Conferences


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CHAPTER TWO

Mathematical Modelling of Metal–Hydride Systems for Hydrogen Storage Applications: A Review

2-1 Introduction

References

2-1 Introduction

With the absorption of hydrogen, the storage material undergoes a change in density (typically expanding by 10-25%) and releases energy due to the exothermic reaction. Similarly, during desorption, the material cools and increases in density. Since the rate at which the reaction with hydrogen takes place is both pressure and temperature dependent, the reaction process can be quite complicated. The heat of reaction is substantial, with enthalpies of \(~30 \text{ kJ/mol} \ \text{H}_2\) for \(\text{LaNi}_5\). The heat generated during hydrogen absorption must be removed or the reaction will slow or even reverse. Similarly, heat must be provided during desorption for the release of hydrogen to continue. Despite high thermal conductivity of the metal alloys, MH beds are porous and suffer from poor thermal properties due to low contact area between particles of the solid phase and low thermal conductivity of hydrogen gas.

As fast hydrogen uptake and release is required for efficient hydrogen energy storage, thermal management is a crucial part in the design of MH tanks and an effective heat exchanger is necessary for the development of practical MH systems.

Building a variety of experimental tank systems to evaluate the performance with different thermal management and under different conditions is practically infeasible. With modelling, however, the effect of different parameters such as the physical size and configuration of the tank and the thermal management system as well as different MH materials can all be examined. Many MH models have been presented since the 1990’s, in which different geometries and configurations of MH tanks and heat exchange systems have been investigated [1-4]. These studies focussed on finding and optimising efficient thermal management systems to improve the performance of the hydrogen cycling. A discussion of the evolution of design parameters for MH containers and the heating/cooling systems is given in the following review paper [5], among which internal cooling with the aid of fins have been shown to be an efficient method.
These systems are typically connected to a circulation bath which can be set at different temperatures for controlling absorption and desorption temperatures.

The governing equations, which originate from the conservation laws for energy, mass and momentum, need to be specific to the properties of the MH materials used and system operating conditions.

In order to simplify these equations, a number of assumptions and approximations are typically used. The simplifications may be employed to make the computations tractable or to allow the application of the model to more than one material. Assumptions about properties of the material are sometimes required where particular properties are unknown. Finding suitable simplifications that do not reduce the accuracy of the results has also been a focus of the study.

An example of a controversial simplification is using a constant value for the effective thermal conductivity, which changes as a function of the material’s temperature and reacted fraction as well as the hydrogen pressure and temperature. Another simplification is the use of a generic van ‘t Hoff equation for the derivation of the equilibrium pressure as a function of uptake and temperature.

The Computational Fluid Dynamics (CFD) methods, finite difference method (FDM), finite volume method (FVM) and finite element method (FEM), have all been used to solve the equations in various models. A commercial software package, COMSOL, which is based on FEM has facilitated the solving of difficult partial differential equations, and this has been mostly used in recent MH model studies.

In addition to the design parameters of MH tanks and heat exchange systems, process variables have a major impact on the performance of MH systems. These parameters have been extensively studied [1, 3, 4, 6] and include inlet hydrogen temperature, pressure, initial hydrogen to metal ratio, thermal fluid temperature and flow rate.
The following review paper, published in the International Journal of Hydrogen Energy, details the development of different models, the variation in equations, assumptions, boundary and initial conditions.

This survey shows that in addition to work on testing different physical and process parameters to improve the performance of heat transfer systems of MH tanks, increasing the accuracy of models deserves more consideration. This will in turn help models to reliably predict operating conditions for practical large scale designs.
References

STATEMENT OF CONTRIBUTION TO CO-AUTHORED PUBLISHED PAPER

This chapter includes a co-authored paper. The bibliographic details of the co-authored published paper, including all authors, are:

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Appropriate acknowledgements of those who contributed to the research but did not qualify as authors are included in the paper.

My contribution to the paper involved:

1) Literature review
2) Collection of information
3) Manuscript preparation

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2-2 Review paper: A review of mathematical modelling of metal-hydride systems for hydrogen storage applications,
Shahrzad S. Mohammadshahi, Evan MacA. Gray and Colin J. Webb,
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A review of mathematical modelling of metal-hydride systems for hydrogen storage applications

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Abstract
Metal-hydrides have been of great interest as one of the most promising materials for hydrogen storage applications. For widespread use, the most appropriate container and thermal management systems to minimise the time of absorption and desorption and maximise the amount of stored hydrogen must be designed. In recent years, many attempts have been made to identify the relationship between different operating and design variables and the resultant performance of metal-hydride systems. In this review, features of mathematical models of metal-hydride reactors including the assumptions, different applied equations and solution methods which have been developed in previous studies are presented. The evolution of the reactor geometries and configurations of cooling systems as well as different effective factors of metal-hydride performance are also discussed.

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Introduction
There is an increasing awareness of the adverse effects of greenhouse gas emissions on global warming and climate change due to the use of fossil fuels. Hydrogen is an appropriate alternative to conventional fuels because of its natural abundance and high energy density or heating value per unit mass as well as being environmentally friendly [1]. Widespread uptake of hydrogen energy has yet not occurred because of difficulties with storage since the gas has low energy density per unit volume requiring a large space to be stored at ambient conditions. Methods to address this problem include compressed gas at high pressure (700 bar) or liquid at cryogenic temperatures (20 K), however, both of these methods entail additional costs due to high pressure containment or maintenance of cryogenic temperatures [2].

Metal-hydrides (MH) are able to store relatively large amounts of hydrogen in a solid phase with safety and long-term stability. This class of solid-state materials has advantageous features for hydrogen storage and has been the subject of intensive research since the 1970’s [3]. Metal-hydrides are characterised by the following reversible reaction.

$$xM + \frac{y}{2}H_2 \rightarrow M_xH_y + \Delta H$$

where $\Delta H$ is the heat of the reaction.
The necessity of modelling

Designing a practical metal-hydride storage system with respect to the different aspects of thermodynamics, kinetics and mass and energy transport requires credible modelling that is in a good agreement with the conditions experienced. Mathematical modelling is a useful tool to identify and predict the state of the metal-hydride during absorption and desorption as well as to determine the relationship between different effective factors with the aim of finding the best performance of the MH storage system.

Many models for one-dimensional [4–7], two-dimensional [8–12] and three-dimensional [13–16] systems have been developed and used to determine transport properties, equilibrium conditions and reaction kinetics of metal-hydride systems. The three-dimensional form of the model requires significantly more time and computing capacity to run and is often only used to investigate those effects that the two dimensional models cannot [15].

Many variables such as the inlet temperature, pressure and hydrogen concentration and flow rate as well as reactor geometry, thermal management system configuration and operating conditions have a significant impact on the performance of MH tanks. Cycling time and the amount of hydrogen to be stored are the main parameters used to measure the overall performance of a hydrogen storage system. However, temperature and pressure evolution as a function of time and space, gas velocity, pressure, temperature and hydrogen concentration distribution in the bed are also necessary to identify the behaviour of MH systems. To reduce the complexity of the model and to reduce computer processing time, assumptions and simplifications are frequently made.

There are a number of review papers specifically about MH reactors and thermal management systems [3, 17, 18] but these are primarily focussed on experimental and technical aspects of the tank and cooling system designs. This paper presents the different theoretical points of view for mathematical modelling of MH tanks including the various assumptions and simplifications made, variables and equations used as well as the different boundary and initial conditions and numerical methods used to resolve the governing equations. The majority of the important geometrical and operational parameters of the tank and thermal management system which have been considered in previous studies are discussed here.

Storage materials

While the metal hydride material used to store the hydrogen typically does not determine the fundamental equations used to model the storage system, details of properties of the storage material are required in some equations to accurately model aspects such as thermal conductivity and the thermodynamics and kinetics of the interaction of the material with hydrogen.

The material used may be a simple metal, such as magnesium, an intermetallic or alloy, including Mg2Ni and the AB5 alloys (of which LaNi5 is the archetypal intermetallic) and AB2 alloys, and the complex hydrides such as alanates (especially NaAlH4) and borohydrides, such as Mg(BH4)2. Each of these material classes has advantages and disadvantages. Simple, light metals have moderate gravimetric hydrogen capacities but often have high enthalpy of creation of the hydride, necessitating high temperatures for hydrogen release. Intermetallics can significantly lower the thermodynamics, but...
Intermetallics

Intermetallics have proven to be practical hydrogen storage alloys. The simplest intermetallics are binary phases, often represented as A\textsubscript{x}B\textsubscript{y}. Those which form ternary hydride phases are of interest in hydrogen storage studies. It has been found that good prospective hydrogen storage materials are often formed where “A” is a metal which readily forms a hydride such as La, Ca, Ti, Y, Zr and “B” represents a metal which does not hydride or only weakly hydrides such as Ni, Fe, Mn, Co, Cr, V. Common intermetallics for hydrogen storage include AB, AB\textsubscript{2}, A\textsubscript{2}B and AB\textsubscript{5} materials [19]. LaNi\textsubscript{5} is a classic intermetallic of the AB\textsubscript{5} family. Partial substitution for both the A and B metals is possible and this can be used to tailor the temperature and pressure properties of the material. Intermetallics have the advantage that most can be modified by inclusion of another metal or modification of the relative proportions of elements to tailor the characteristics in order to meet the fuel cell requirements of 0–100 °C and 1–10 bar or other requirements depending on the application. For example, in LaNi\textsubscript{5}, La is often replaced by mischmetal (Mm), a naturally occurring mix of rare earth elements, which is cheaper to produce due to the cost of separating the similar large mass elements [20], or lighter metals such as magnesium and cerium (La\textsubscript{1-x}MgxNi\textsubscript{5}, La\textsubscript{1-x}MgxNi\textsubscript{3} and La\textsubscript{1-x}Ce\textsubscript{x}Ni\textsubscript{5} [21–23]). Different compositions such as substitution for the “B” metal can dramatically change the absorption/desorption characteristics and this is used, for example, in nickel–metal hydride batteries, substituting various metals including Al, Co and Mn for some of the Ni [24,25].

MH systems are pressure and temperature dependent since the thermodynamic conditions vary according to the solid phase structural and thermo-physical properties. Thus, characterisation of this thermodynamic behaviour is of paramount importance to MH studies. A Pressure-Composition-Temperature (PCT) or isotherm, as shown in Fig. 1, is the relationship between hydrogen pressure in thermodynamic equilibrium and hydrogen concentration, often expressed as a ratio of hydrogen to metal (H/M) at a certain temperature [26]. The slope of the isotherm plateau and the hysteresis are inherent characteristics and vary among different metal-hydrides [27]. These also depend on experimental variables such as pressure, temperature and mass flow rate [26,28].

Hysteresis, defined as the difference between equilibrium pressures in hydrogen absorption and desorption, complicates the analysis [24,29]. The plateau pressure is the equilibrium pressure of the metal-hydride in the mid-range of transformation from α-solid solution to β-hydride phase [30]. Changing the elements of either A or B can change the hydriding characteristics of metal-hydrides [25,31–36]. For example, a LaNi\textsubscript{5} isotherm at 23 °C (as shown in Fig. 1) has a hysteresis of ca 1 bar and negligible plateau slope at an absorption plateau pressure of 2–3 bar while LaNi\textsubscript{4.7}Al\textsubscript{0.3} has large hysteresis and a sloping plateau [26].

Because of decrepitation in the first few cycles [37], after repeated hydrogen cycling the material consists of a fine powder which usually has very poor thermal properties. Since hydrogen absorption and desorption are exothermic and endothermic reactions respectively, if heat is not removed from or added to the system appropriately, the reaction will stop or slow down [2]. The amount of heat required is determined by the enthalpy of the reaction. Hence the reaction kinetics is strongly affected by the heat transfer rate and so thermal management is vital in the design of tanks for MH systems. Enhancing heat transfer is one of the main challenges in metal-hydride storage system design [38].

Mathematical modelling

The preliminary steps of a mathematical model are to represent the problem and define appropriate assumptions to simplify the governing equations and enable them to be solved either analytically or numerically.

Preliminary assumptions

The assumptions listed below are often considered in the modelling of the MH systems:

1. The equation of state for an ideal gas is appropriate for hydrogen,
2. the compression work and viscous dissipation is negligible,
3. radiative heat transfer is negligible,
4. the tortuosity and dispersion terms can be modelled as diffusive fluxes,
5. both the gas and solid have the same temperature (local thermal equilibrium),

![Fig. 1 – Pressure-composition-temperature (PCT) graph of LaNi\textsubscript{5}–H\textsubscript{2} system at 23 °C.](image-url)
6 the effect of pressure variation (heat transfer by mass convection) is neglected and
7 the dependence of equilibrium pressure on hydrogen concentration can be neglected.

Some of these are general and commonly used such as the ideal gas approximation and ignoring radiative heat transfer [10,39–41], while others are controversial such as local thermal equilibrium, neglecting pressure variation and dependence of equilibrium pressure on hydrogen concentration. A number of studies have been performed to evaluate the accuracy of these assumptions or approximations [39,41,42]. Applying different assumptions leads to different governing equations and sometimes different results.

The microscopic energy, mass and momentum balance equations are obtained from substitution of relevant fundamental physical, mechanical and thermodynamic laws in the appropriate conservation laws [43]. These are converted to the macroscopic governing equations using an averaging procedure over a volume to represent the physical reality of the system by the mathematical model [44]. A schematic representing the averaging volume of the tank bed is shown in Fig. 2.

The expression for averaging a microscopic quantity (ηi) over a volume is given by:

$$\eta_i' = \frac{1}{V_i} \int \eta_i d\omega$$

where $\omega$ is the averaging volume, η denotes properties such as temperature (T), pressure (P) and density (ρ) and i designates the phases present (usually the solid and the gas).

Heat flow

Because of the strong temperature dependence of the hydriding and dehydriding processes, determining and analysing the temperature profile is essential. For this purpose, energy balance for the MH porous media is obtained from substituting relevant microscopic heat transfer equations for the pore-scale conservation of energy law which is an extension of the first law of classical thermodynamics [45].

The general equation of change for internal energy is given by:

$$\frac{\partial U}{\partial t} + \rho \nabla \cdot (U \mathbf{v}) = -\nabla \cdot (\nabla U) + Q - P(\nabla \cdot \mathbf{v}) - \psi_{viscous}$$

where $U$ and $\mathbf{v}$ are the internal energy between two equilibrium states and fluid velocity respectively, $\rho$ is the density, Q is the heat added to or removed from the system through convection or internal sources such as reactions and $\psi$ is heat transferred by conduction. The terms $P(\nabla \cdot \mathbf{v})$ and $\psi_{viscous}$ are compression work and viscous dissipation respectively which are usually neglected.

In order to convert Eq. (3) to the usual form of energy equation as a function of temperature, $U$ can be rewritten as:

$$U = H - P/\rho$$

where $H$ is the enthalpy.

Substituting Eq. (4) into Eq. (3) and using the substantial (material) derivative gives:

$$\frac{DH}{DT} = -(-\nabla \cdot \mathbf{q}) + Q + \frac{DP}{DT}$$

Enthalpy is expressed as a function of temperature and pressure:

$$\frac{DH}{DT} = C_p \frac{DT}{DT} + \left(1 + \frac{T}{\rho} \frac{d\rho}{dT}\right) \frac{DP}{DT}$$

where $C_p$ is the specific heat capacity.

Therefore, by substituting Eq. (6) into Eq. (5), the energy equation is obtained:

$$\rho \C_p \frac{\partial T}{\partial T} + \mathbf{V} \cdot \mathbf{I} = \lambda \nabla^2 T + Q \frac{\partial \ln \rho}{\partial T} \left(\frac{\partial P}{\partial T} + \mathbf{V} \cdot \mathbf{V}\right)$$

where $\frac{\partial \ln \rho}{\partial T} = -1$ for an ideal gas.

Energy balance can be expressed for the gas and solid phases separately for a geometry with cylindrical symmetry and with the assumption of neglecting pressure variation [41,42]:

$$\rho \C_g \frac{\partial T_g}{\partial T} = \epsilon \lambda_g \nabla^2 T_g - \rho_g \C_g \mathbf{V} \cdot \nabla \mathbf{V} + H_m \left(T_g^3 - T_g^2\right) A - m \C_p \left(T_g^3 - T_g^2\right)$$

(1 - $\epsilon$) $\rho_s \C_s \frac{\partial T_s}{\partial T} = \lambda_s \nabla^2 T_s - H_m \left(T_s^3 - T_s^2\right) A - m \left(\frac{dH}{dT} + \C_p \left(T_s^3 - T_s^2\right)\right)$

where “g” and “s” designate the gas and solid phases respectively (as discussed in Preliminary assumptions), A is the solid–gas exchange area, $\lambda$ is the thermal conductivity and m is the amount of absorbed or desorbed hydrogen per unit volume and unit time. $\epsilon$ is the porosity of the MH bed and $H_m$ is the interphase heat transfer coefficient between gas and solid.

There are several empirical equations have been developed for the interphase heat transfer coefficient which relate the Nusselt number (Nu) to the Reynolds (Re) and Prandtl (Pr) numbers [46]:

One of the commonly used equations for packed beds [47,48] is the relation presented by Gunn [49]:

$$H_m = \frac{\lambda_g}{d_p} \left[7 - 10e + 5e^2\right] \left(1 + 0.7Re^{0.2}Pr^{1/3}\right) + (1.33 - 2.40e) + 1.20e^2\Re^{0.7}Pr^{1/3}$$

where $d_p$ is the average metal-hydride particle diameter. Jenni and Nasrallah [41] used the correlation presented by Saez and McCoy [50].

$$H_m = \frac{\lambda_g}{d_p} \left(2 + 1.1Re^{0.6}Pr^{1/3}\right)$$

Fig. 2 – Averaging volume for a porous medium with solid and gas phases.
The mechanisms of heat transfer for both phases include heat conduction ($\kappa \nabla^2 T$), natural convection between gas and solid ($H_{gi}(\nabla^2 T_s - \nabla^2 T_g)$) and the changes in molecular energy ($mC_p(T_s - T_i)$). Heat transfer due to gas movement ($\rho C_{pg} \nabla \cdot \nabla T_g$) is taken into account in Eq. (8) and the enthalpy changes of the hydriding and dehydriding reactions ($m\Delta H$) are applied in Eq. (9).

The local thermal equilibrium hypothesis has been employed in nearly all theoretical studies for MH systems. Under this assumption the temperature of the gas and solid storage bed are regarded as equal throughout the bed volume. By applying this assumption, Eqs. (8) and (9) can be combined to give a single equation for the energy balance.

$$\left(\rho C_p\right)_g \frac{\partial T}{\partial t} = \frac{\partial}{\partial t} \left( \lambda_A \nabla^2 T - \rho_l C_{pg} \nabla \cdot \nabla T + m(\Delta H + T(C_{pg} - C_p)) \right)$$  \hspace{1cm} (12)

Where

$$\left(\rho C_p\right)_g = \rho_l C_{pg} + (1 - \varepsilon)\rho_l C_{ps}$$  \hspace{1cm} (13)

The accuracy of the assumed thermal equilibrium has been evaluated by Jemni and Nasrallah [39,41]. They showed the difference between $T_s$ obtained from Eq. (9) compared with the calculated $T$ from Eq. (12) is negligible as was the difference between $T_g$ and $T_s$. Although the difference near the cooling walls was higher than that in other parts of MH bed (1 K), this assumption was generally found to be valid. This hypothesis (local thermal equilibrium between a moving fluid and a solid bed) has also been investigated and validated by other researchers such as Quintard and Whitaker [51,52].

Either Eqs. (8),(9) or (12) express the energy balance in a porous medium which contains a homogenous mixture of hydrogen gas and metal-hydride. However, in some studies the volume has been divided into two sections: first, an expansion volume (the volume of the tank not occupied by MH) and second, a porous medium (homogenous mixture of gas and MH bed). In the latter case energy conservation for the expansion volume was taken into consideration in addition to that of the porous medium [40,53]. The expression of energy balance for the expansion volume is:

$$\rho_g C_{pg} \frac{\partial T_g}{\partial t} = \lambda_g \nabla^2 T_g - \rho_l C_{pg} \nabla \cdot \nabla T + \nabla \cdot \nabla P + \frac{\partial P}{\partial t}$$  \hspace{1cm} (14)

This equation originates from the conservation of energy as discussed above (Eqs. (3)–(7)).

In these studies where the total volume is fixed, the effect of the proportion of the expansion volume to the whole reactor volume ($H_g/H$) on the MH performance in a vertical cylinder with external cooling/heating bath was examined [40,53]. The results showed that by increasing this ratio, total hydrogen mass absorbed and desorbed and also the fluid velocity increases. But the reaction rate decreases because of increasing thermal resistance [54]. For the desorption it can be explained that increasing the ratio ($H_g/H$) causes the relative increase in pressure with hydrogen release to be reduced (as the gas volume is larger) keeping it below equilibrium pressure and as a result facilitating the desorption of more hydrogen [40]. Likewise, for absorption the larger expansion volume maintains a higher pressure than equilibrium pressure as the absorption proceeds. It is worth pointing out that the effect of changing ($H_g/H$) on the hydrogen uptake and discharge processes is less in higher volume vessels, because the influence of the expansion volume on the total pressure of the system becomes less significant [40,53]. It can be concluded that the effect of the expansion volume can be neglected in the calculations of large scale systems and is not as relevant for systems where hydrogen is removed or added during absorption and desorption.

The effect of pressure variation on thermal transport was included in some studies [15,40,55] by applying the following equation for the energy balance of the MH system (see Eq. (7)).

$$\left(\rho C_p\right)_g \frac{\partial T}{\partial t} = \lambda_g \nabla^2 T - \nabla \cdot \left( \rho_l C_{pg} \nabla T \right) + \varepsilon \nabla \cdot \nabla P + \frac{\partial P}{\partial t} + m\Delta H$$  \hspace{1cm} (15)

Where $\lambda_g$ is the effective thermal conductivity of the MH bed. The effective thermal conductivity of a porous media depends on various factors such as the thermal conductivity of both solid and fluid and the amount of each phase as well as structural properties of the porous media that affect the available paths for heat diffusion and the similarity of the thermal conductivity between the gas and solid that makes it difficult to estimate exact relations for porous media [56]. Many early research works have been conducted to find $\lambda_g$ for different general porous media experimentally and theoretically [57–59]. Subsequently, a number of experiments and theoretical studies have also been performed to determine $\lambda_g$ for MH systems [37,60–66]. Pons and Dantzer [67] and Jemni et al. [68] conducted experimental studies to determine $\lambda_g$ for LaNi$_5$–H$_2$ systems. They reported values of $\lambda_g$ for LaNi$_5$–H$_2$ as 0.1–2.1 W/mK as a function of pressure from 0.01 to 10 bar [67]. As the operating pressure of LaNi$_5$–H$_2$ system is 1–10 bar the average value of $\lambda_g$ for this pressure range obtained by Pons and Dantzer is applicable. Goodell [61] also obtained 1.32 W/mK. In previous modelling studies different values had been used including 1.32 [40,53,69] and 1.6 [8,11,70,71]. Values for LaNi$_5$–H$_2$ effective thermal conductivity from other sources include 1.087 W/mK [68], 0.466 W/mK [72] and 1.2 W/mK [41]. All of those values lie within the range Pons and Dantzer presented. Because there is a range of experimental values and most modelling studies have chosen to implement the effective thermal conductivity as a constant, there is considerable variation in the value of the constant chosen. In fact, the effective thermal conductivity of MH beds varies during absorption and desorption due to the dependence on porosity and thermal conductivity of the solid bed material, (both of which depend on the degree of hydriding) and the gas thermal conductivity (which is pressure sensitive). Sometimes this is simply modelled as a function of pressure. More recently, some MH studies have used empirical equations [73,74] or a range as a function of pressure through interpolation [75] in the model for greater accuracy.

Alternatively, $\lambda_g$ can be estimated analytically from:

$$\lambda_g = \varepsilon \lambda_A + (1 - \varepsilon)\lambda_s$$  \hspace{1cm} (16)

where $\lambda_s$ and $\lambda_A$ are the thermal conductivity of the metal alloy powder and the hydrogen gas respectively at a specific pressure.

Another commonly-used assumption for simplification of the modelling of MH tanks is to neglect the effect of gas movement on heat transfer through the bed. This allows the heat transfer by mass convection term ($\rho_l C_{pg} \nabla \cdot \nabla T$) to be
eliminated from Eqs. (8), (12) and (15). This model is termed conductive compared with convective models [39, 41, 76, 77]. As the gas velocity has a direct relationship with the pressure gradient in porous media (discussed later), this assumption implies that the effect of pressure variation is neglected. In order to determine the validity of this assumption, Jemni and Nasrallah [41] solved Eq. (12) with and without taking into account the mass convection term and demonstrated that the difference in the temperatures obtained was less than 1%. It was concluded that neglecting the role of mass convection in heat transfer between hydrogen and solid and, as a result, its effect on MH performance, is a valid approximation [39, 41].

**Mass balance**

To identify hydrogen concentration distribution in the MH bed and its evolution as a function of time, it is necessary to include mass balance. The equation of continuity that is obtained from the conservation of mass is expressed by:

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0
\]

(17)

The mass balance for the gas (hydrogen) is:

\[
\rho \frac{\partial \rho_g}{\partial t} + \frac{1}{\partial t} \left( \rho_g u_g \right) + \frac{\partial}{\partial z} \left( \rho_g^0 u_g ^0 \right) = -m
\]

(18)

And the mass balance for the solid (metal/hydride) is:

\[
(1 - \epsilon) \frac{\partial \rho_s}{\partial t} = m
\]

(19)

where \(m\) is the amount of absorbed or desorbed hydrogen per unit volume and unit time and this indicates the reaction rate for absorption and desorption.

**Equilibrium properties and reaction kinetics**

\(m\) is defined based on the rate law for hydrogen uptake and discharge reactions and shows the relationship between the reaction rate and species concentrations. To determine such a relationship for each system, experimental works are needed [78]. Supper et al. [79] and Suda et al. [80] conducted experiments for hydriding some intermetallics such as LaNi5 and MmNi5. The following relations were based on those results to include the reaction rate law for hydrogen uptake and discharge reactions. For the LaNi5 system the values of absorption and desorption reaction rate \((C_a, C_d)\) are 59.187 s\(^{-1}\), 9.57 s\(^{-1}\) and absorption/desorption activation energies \((E_a, E_d)\) are 21.170 kJ/mol H\(_2\), 16.420 kJ/mol H\(_2\) respectively [80].

\[P_{eq} = \text{the equilibrium pressure of the MH system and it can be observed in Eqs. (20) and (21) that it plays a significant role in both absorption and desorption processes. The difference between the equilibrium pressure and the system pressure is the driving force of the sorption processes. As can be seen from Eq. (20), lower equilibrium pressure for the same system pressure causes increased hydrogen absorption and faster formation rate and similarly a higher equilibrium pressure for the same system pressure enhances the desorption (Eq. (21)). So, because of the direct relationship between temperature and equilibrium pressure, cooling the system during absorption and heating during desorption, helps to increase the reaction rates. Therefore, in addition to the importance of thermal management in MH tank design to achieve the most appropriate \(P_{eq}\), using the most accurate expression for \(P_{eq}\) is also necessary [76, 82].

The van’t Hoff equation relates equilibrium pressure \((P_{eq})\) to the absolute temperature \((T)\) of the hydride, the change in enthalpy \((\Delta H)\) and entropy \((\Delta S)\) at a particular uptake (H/M) which is usually taken to be central along the plateau. The values of the change in enthalpy and entropy are a constant for a particular material provided the same reference point (in this case the same H/M value) is used. This has been applied by many researchers e.g. Refs. [14, 15, 83, 84].

\[\ln P_{eq} = \frac{\Delta H}{R g T} - \frac{\Delta S}{R g}
\]

(22)

However, at different H/M values, different values for the entropy \(\Delta S\) necessitate a modification to the van’t Hoff equation in order to express the dependence of equilibrium pressure on the hydrogen to metal ratio (H/M). The determination of the precise equilibrium pressure is then given by Ref. [39].

\[P_{eq} = f(H/M)\exp \left[ \frac{\Delta H}{R g \left( 1 - \frac{1}{T_0} \right)} \right]
\]

(23)

where \(f(H/M)\) is the equilibrium pressure at the constant temperature \(T_0\). This has been presented in the form of different functions. Nishizaki et al. [85] presented a relation for a PCT based on experimental data that not only relates \(P_{eq}\) to both the hydrogen concentration and temperature but also takes into account plateau features such as hysteresis and the slope:

\[\ln P_{eq} = \frac{\Delta H}{R g T} + (\phi \Delta H) \tan \left[ \frac{\phi \Delta H}{\phi \Delta H} \right] \frac{\Delta S}{\Delta S}
\]

(24)

where \(\phi, \Delta S\) and \(\Delta S\) are the slope factor, slope constant and hysteresis factor, respectively. These are different for different metal-hydrides, for example, the values for LaNi5 are reported as 0.038, 0 and 0.137 respectively [85]. The “+” sign indicates absorption and the “−” sign desorption.

Pons and Dantzer [67] believed that the isotherm expressed in Eq. (24) does not fit the experimental data at the phase boundaries and proposed the following equation.
\[
\ln P_e = \frac{dH}{R_g T} \frac{dS}{H/M} + A_{0/d} \left( \frac{H}{M} \right) + B_{0/d} \left( \frac{H}{M} \right)^3 \left[ \tan \left( \frac{\pi}{2} \left( \frac{H}{H_{\text{max}}} \right) \right) \right] - C_{0/d} \left( \frac{H}{H_{\text{max}}} \right)^3
\]

where \( A, B, C \) are coefficients determined by fitting experimental isotherms for LaNi\(_x\)H\(_y\) at 297.7 K and \( a \) and \( d \) denote absorption and desorption, respectively.

Later, Jerni et al. [39,41,86,87] obtained a polynomial form with different orders (\( n = 5, 7 \) or 9) for \( f[H/M] \) from fitting experimental data and presented this as an equation for the equilibrium pressure.

\[
P_e = \sum_{i=1}^{n} b_i \left( \frac{H}{M} \right)^{1/2} \exp \left( \frac{dH}{R_g T} (1 - \frac{1}{T_{\text{max}}}) \right)
\]

The coefficient \( b_i \) has different values for absorption and desorption and also for different hydrides. Jerni et al. [41,42,68] obtained values for LaNi\(_5\) and Dhaou et al. [86] determined values for LaNi\(_5\), LaNi\(_{4.75}\)Fe\(_{0.25}\) and LaNi\(_{4.85}\)Al\(_{0.15}\).

Another expression for equilibrium pressure as a function of both hydrogen concentration and temperature was proposed by Wijayanta et al. [76].

\[
P_e = \sum_{i=1}^{n} b_i \left( \frac{H}{M} \right)^{1-\varepsilon} \left( \frac{1}{1 - \varepsilon} \right) D_{ij}\epsilon^{i-1}
\]

where \( n = 4 \) in the plateau region and \( 6 \) in other regions respectively and \( l = 4 \). The accuracy of this expression was compared with the van ‘t Hoff equation, Eq. (26) and experimental results. The results showed that the trends of the temperature evolution and hydriding rate obtained by different mentioned PCT models are similar under both uniform and variable pressure conditions. The results from the calculations with the van ‘t Hoff equation deviated more from the experimental data especially under variable pressure conditions [76]. In another comparison between the van ‘t Hoff and Eq. (26) using a fifth-order polynomial, the error in temperature distribution calculated by the van ‘t Hoff equation could not be neglected in particular for the desorption process [39]. Hence, a number of different equations have been used in an attempt to accurately model the equilibrium pressure as a function of hydrogen content and temperature as well as for different materials, such as Sm\(_2\)Fe\(_7\) [88], MnNi\(_{6.4}\)Al\(_{0.4}\) [70] and LaNi\(_{4.75}\)Fe\(_{0.25}\) and LaNi\(_{4.85}\)Al\(_{0.15}\) [86].

**Momentum balance**

In addition to heat and mass transfer in MH reactors, momentum transport needs to be included. The velocity (\( \vec{v} \)) indicates the hydrodynamic condition of the system in which one of the phases is fluid. To measure gas velocity in the MH beds as porous media, estimated correlations for the gas velocity and pressure distribution in the packed bed can be used [45].

Darcy’s law which has been used in most MH studies [39,41,76,83] was proposed to empirically describe the motion of the fluid as it flows slowly through a granular media [45]:

\[
\vec{v} = \frac{k \nabla P}{\mu}
\]

where \( \mu \) is dynamic viscosity of the gas at the system working temperature and \( P \) is pressure drop of the gas which is the driving force of the mass flow rate [17]. The permeability \( k \) is defined by Kozeny-Carman’s equation as:

\[
k = \frac{1}{5} \frac{\epsilon^3}{(1 - \epsilon)^2} \frac{1}{a_s}
\]

where \( d_p \) and \( \epsilon \) are the mean particle diameter and porosity in the packed bed, respectively and are related to each other [45] by

\[
d_p = \frac{6(1 - \epsilon)}{a_s}
\]

where \( a_s \) is the specific surface area of the bed, i.e. the wetted surface of the volume of the bed [45].

The initial diameter for LaNi\(_5\) particles was reported to be 150 \( \mu \)m decreasing to 10 \( \mu \)m due to pulverisation [19,76]. Different values of permeability have been reported in different studies. Examples for LaNi\(_5\) include 10\(^{-8}\) m\(^2\) [40,41] and 10\(^{-12}\) m\(^2\) [39,83]. In this context, porosity is defined as:

\[
\epsilon = 1 - \frac{\rho_s}{\rho_e}
\]

where \( \rho_s \) is the density of the solid and \( \rho_e \) is the effective density of the powder, which depends on the degree of compression.

For example, the porosity of LaNi\(_5\) is typically taken to be 0.5 [40,53,83]. In one experimental study it was calculated to be 0.63 by considering the metal density (\( \rho_m \)), the mass of powder in the tank and the volume occupied by the particles themselves [68]. A porosity less than 0.4 may induce deformation of the reactor vessel as the hydride is formed [37].

Although it is considered as constant in most modelling studies, porosity is variable during the reactions because the crystal lattice expands during hydriding.

Wijayanta et al. [76] used the following equation to include changes in porosity as a function of reacted fraction.

\[
\epsilon = 1 - (1 - \epsilon_0) (1 - \epsilon_0) + (1 - \epsilon_0)^2 - \epsilon_0^3
\]

where \( E_p \), \( \zeta \) and \( \epsilon_0 \) are the expansion coefficient, the reacted fraction and the initial porosity respectively.

Another correlation function used to describe the fluid flow in a porous medium is the Blake-Kozeny equation as used by Hardy and Anton [14,15] for a sodium alanate system.

\[
\vec{v} = \frac{d_p^2 \epsilon^3}{150 \mu (1 - \epsilon)^3} (\nabla P)
\]

The Blake-Kozeny equation treats the packed bed as a bundle of tubes. Hydrodynamic calculations such as the friction factor of single straight tubes are modified and related to the pressure drop due to passing fluid through a straight conduit of uniform cross section [45]. This equation is appropriate for systems with a porosity of up to 0.5, and therefore is applicable to metal-hydride systems whose porosity is in this range [45].
The law of conservation of momentum of the gas in a system (from which the equation of motion or Navier-Stokes equation under the assumptions of constant density and viscosity as well as Newtonian fluids is derived), has also been used to describe the motion of gas in a MH packed bed [9,53,89]. The expressions for both r and z directions are:

\[
\frac{\partial}{\partial t} \vec{\rho} \vec{u} = - (\nabla \cdot \vec{u} \cdot \vec{u}) - \nabla P - \nabla \cdot \vec{\tau} + \rho \vec{g}
\]  

r-direction:

\[
\frac{\partial u_r}{\partial t} = \frac{\partial P}{\partial r} + \mu \left( \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial u_r}{\partial r} \right) \right) + \rho \left( \frac{\partial u_r}{\partial r} + u_r \frac{\partial u_r}{\partial z} \right) + S_r
\]  

z-direction:

\[
\frac{\partial u_z}{\partial t} = \frac{\partial P}{\partial z} \left( \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial u_z}{\partial r} \right) \right) + \rho \left( \frac{\partial u_z}{\partial r} + u_r \frac{\partial u_z}{\partial z} \right) + S_z
\]  

\[S_r, S_z\) represents flow in a porous medium and is obtained from Darcy's law.

Boundary and initial conditions

After choosing the governing equations it is necessary to specify appropriate boundary and initial conditions based on the shape and the operating conditions of the reactor and the associated cooling system. This typically includes the Neumann condition (outward normal derivative of variables), Drichlet conditions (the condition of dependent variables at various points in space and time), and symmetry boundaries in such systems depending on the cooling system configuration.

Initial conditions are typically taken as identical throughout the whole system. The initial pressure is often chosen to be equal to the equilibrium pressure at the initial temperature \(T_i\). The initial gas velocity in the directions \(r\) and \(z\) is taken to be zero and it is assumed that the gas is static [40–42].

\[
P(r, z, 0) = P_0 \quad T(r, z, 0) = T_0
\]

Solution methods

The mathematical models described above are typically solved by one of the computational fluid dynamics (CFD) methods. CFD methods are applied to solve the governing equations obtained from systems with fluid motion. This method converts the partial differential equations (PDE) to a system of algebraic equations or ordinary differential equations (ODE) [90,91].

Finite Difference Method (FDM), Finite Element Method (FEM) and Finite Volume Method (FVM), are three standard CFD methods to solve PDE’s based on discretisation (converting the governing partial differential equations to a system of algebraic equations or ordinary differential equations). FDM applies the Taylor series to discretise the derivatives of dependent variables at various points in space and time [69,87].

FEM and FVM use integral formulations to discretise the domain to a finite number of sub-domains. This provides the flexibility to deal with complex geometries. Moreover, these are able to accommodate discontinuous sources since smoothness and regularity are not prerequisites. For this reason, these methods have advantages compared to FDM. FVM is a variation of FEM that has been a popular method in MH studies [40,69,81,87] because of the advantage of good conservation properties (insuring the flux conservation), greater flexibility, simplicity of discretisation of complicated domains and improved stability of the numerical solutions [90]. Control Volume- FDM (CV- FDM) also has these merits [39,41,42]. In the control volume method, the discretised space is considered as a set of subregions, instead of integration and derivatives based on a set of points in those methods without control volume [91,92].

FEM, as opposed to FVM, is able to handle Neumann boundary conditions without requiring any modification to the equations. In addition, the calculation for each element is done independently of the neighbouring elements while in the other two methods (FVM and FDM) the equations for each point are dependent on neighboring points [93]. Hence, FEM methods which consider a control volume around each node (CV-FEM) have advantages over FVM [40,53,81].

In recent years using CFD commercial software based on the FEM has facilitated solving PDE’s. Fluent, FEMLAB and COMSOL are examples of such software packages. COMSOL multiphysics is one of the application modes of the COMSOL software that has the ability to simultaneously solve more
than one physics mode and has become a popular tool to solve the governing equations of MH systems since these involve a combination of mass, heat and momentum transport coupled with a reaction [10,11,13,15,83].

Summary of previous studies

In the 1980s, a number of mathematical models including one-dimensional conductive bed [4–6] and two-dimensional [94] models were presented for metal-hydrogen storage systems. Although these were basic and included many simplifications in order to be solved by the available tools, they were the basis for future studies. Later, gas movement (mass convection) in heat transport throughout the bed was included in the energy balance calculations by Choi and Mills [95] presenting a convective model taking into consideration gas movement and determining the gas velocity by Darcy’s law.

Jemni and Nasrallah [39,41,42,68] conducted a number of theoretical and experimental works on MH systems in the 1990s. They performed two-dimensional mathematical models and solved them, mostly using CV-FDM, to investigate the impact of parameters such as initial pressure and temperature and also the geometrical features of the vessel such as height to radius (h/R) on both absorption and desorption processes. The bulk of their work has been devoted to evaluation of the preliminary assumptions applied in previous works. The shape of the reactor used was a small vertical cylinder with external cooling. The modified van’t Hoff equation for the equilibrium pressure fitted to experimental results with an order-five polynomial was used in their calculations. They also presented modified expressions for reaction kinetics and examined them experimentally in a reactor containing a small amount of LaNi5 (2.6 g). Based on their results there was good agreement with the theoretical and experimental data in absorption while some differences could be observed in the desorption case, attributed to uncertainty in the pressure gauge. Another equation for equilibrium pressure with a ninth order polynomial was employed in their calculations. The dimensions of the MH tank were higher than the previous studies (length 475 mm, internal radius 300 mm). However, the height to the radius (h/R) ratio was in the effective range which had been proposed by Askri et al. [40,53].

Hardy and Anton [14,15] constructed 2- and 3-dimensional models for a cylindrical hydrogen storage tank containing sodium alanate with a shell and tube type heat exchanger using COMSOL Multiphysics. Although this model is comprehensive, some realistic features such as hysteresis and the volume expansion of MH during the absorption were not taken into account and the system geometries required optimisation. Bhouri et al. [99] used Hardy and Anton’s results to investigate the effect of fin thickness, number and configuration of cooling tubes on the hydriding and dehydriding time on that system. Their intention was to maximise charging and discharging rates and minimise volume and weight fraction of the cooling system to the bed in order to achieve better system gravimetric and volumetric capacity. They also revealed the importance of the role of fins for metal-hydrogen tanks by determination of hydrogen sorption rates which were poorer in the absence of fins. Garrison et al. [55] optimised the geometry of cooling systems with longitudinal and transverse fins based on maximising gravimetric capacity of the hydrogen or minimizing the volume and dimensions of heat exchanger elements using the Nelder-Mead methods of built-in MATLAB routines. They concentrated on the hydrogen capacity based on the whole system weight including the heat exchanger.

Some researchers have used analytical methods for analysis and optimisation of the various parameters. Yang et al. [100,101] defined analytical formula, mass controlled reaction rate and heat controlled reaction rate, to evaluate the system performance. They compared the obtained results with the numerical results which were found to be in agreement. Nyamsi et al. [83] also presented an analytical model for a
cylindrical MH tank containing LaNi₅ to find the optimum fin dimensions using MATLAB built-in routines based on maximizing the effectiveness of the fins. Then they used the derived results in their numerical calculations with the COMSOL software package to see the effect of optimal fin design on the hydriding characteristics.

Raju et al. [102,103] presented numerical studies on a sodium alanate system to optimise the geometrical parameters of both the container and exchanger using a COMSOL-MATLAB interface for three different designs, first a shell and tube type heat exchanger with sodium alanate in the tubes, secondly an internally helical heat exchanger and, thirdly, a shell and tube type heat exchanger with sodium alanate in the shell. Their modelling focused on the highest amount of hydrogen absorbed in a certain time (10.5 min which is 40% of refueling rate of the DOE 2010 goals).

Many efforts have been made to improve the basic MH mathematical models to obtain more realistic results. For this purpose, correlations were added to the numerical MH calculations or new parameters and definitions have been presented or reformulated. Minko et al. [104,105] focussed on finding accurate values of permeability (k), interphase heat transfer coefficient (Hₚₑ), effective thermal conductivity (λₑ) and porosity (ε) for ordered and random packing of spherical MH particles by developing a direct numerical simulation. Three different packing structures, simple cubic packing, body-centred cubic packing and face-centred cubic packing as well as random packing with sets of particle distributions and spheres of equal diameter with different porosity were considered in their work to determine corresponding values of Hₚₑ, k and λₑ. These correlations and values were used in the mathematical model of the MH storage tank. Yang et al. [106] proposed mass boundary conditions (flow coefficient) to determine hydrogen outlet flow and investigated the sensitivity to different parameters such as bed pressure, bed initial temperature and convective heat transfer coefficient. They also compared the effect of two types of internal heat exchange systems (electrical and convective heating) on the hydrogen outlet flow rate and found significant differences.

Discussion

Tank and thermal management system design

The geometry and configuration of MH containers which have evolved over years of study is an important factor in the heat transfer in the MH bed [9,40,41,53,81,107]. Many research works have been devoted to optimisation of the design parameters of MH tanks and the heat exchanging systems by methods such as increasing the surface area and temperature difference between hydride bed and cooling fluid. These are discussed below.

Primitive tank designs exchanged the required heat externally by the mechanism of natural convection with the surrounding air [9,39,40,53] or with a liquid circulating around the tank in coils or a cooling bath [13,41,68,76]. Subsequently, internal heat exchange via the concentric cylindrical tube [11,13] or spiral tubes in which liquid flows [97,103,108] was used. Changing the shape of the tanks [9,81], using external fins around the tanks [10,69,81,109], multiplication of the number of exchanging tubes [11,13,102,110,111], using elliptical tubes instead of circular ones [112] have also been considered to increase the contact surface area and hence the rate of heat transfer [18].

Four different configurations of heat exchange systems for a cylindrical MH tank were numerically modelled by Askri et al. [81]. These included:

1. Exchanging the heat with surrounding air by natural convection
2. Exchanging the heat with the surrounding air by fins
3. Internal concentric cooling system circulation fluid
4. Internal concentric fin – equipped cooling system with circulation fluid

It was concluded that a concentric tube in which cooling/heating fluid flows equipped by transverse fins is the most efficient design in terms of achieving low hydriding and dehydriding times. Subsequent designs typically employed internal heat exchange by finned tubes [14,81,83] or combination of coils inside and external use of water [87]. Hardy and Anton [14,15], who carried out a comprehensive research on hydrogen storage in metal-hydride system, utilised a symmetrical cylinder with internal finned tubes.

The ratio of height to radius (H/R) is a geometrical parameter which affects the rate of energy and mass transport throughout the bed. If the value of (H/R) is much higher or lower than a certain amount, mass and heat transport occurs in only one dimension (either the r-direction or the z-direction). Askri et al. [40,41,53] determined a critical value for (H/R) of 2 at which MH tank has the least capacity. They believed this minimum point is due to the transition from one-dimensional energy and mass transport to a two-dimensional system (from r to z direction). It was observed that for H/R < 2, heat and mass transfer and, as a result, the amount of absorbed hydrogen are significantly enhanced. Likewise, for values higher than 2 the absorption increases but with a slower rate.

The thermal mass of the wall or wall heat transfer coefficient is a convective heat transfer coefficient which was also considered as one of the effective factors of heat transfer in MH tanks. Measurements indicated that this is large enough so as not to be a limiting factor for heat transfer in the pressure vessel [67]. A 2-dimensional model was solved with and without taking into account the thermal mass of the wall by Askri et al. [81] and the results of hydriding rate and time evolution of temperature showed little difference between two cases. They also concluded that the material of the tank does not influence the hydriding process.

In addition to the geometry and the material of the MH reservoir, studies have been devoted to design and optimisation of the thermal management systems. Internal fins are important components to enhance heat transfer rate in the MH bed and many aspects of fin design have been investigated. Optimizing fin geometric parameters (thickness, spacing and length) based on maximizing the gravimetric
capacity of the hydrogen was performed using Nelder-Mead methods [55]. Maximizing both volumetric and gravimetric capacity by an automated Matlab-COMSOL integration was also performed [99,103]. A built-in Matlab optimiser tool was employed by Nyamsi et al. [83] to improve the energy efficiency of the system. Fin materials have also been studied to find the effect of fin conductivity on storage time. It was concluded that it does not have a significant effect on the process [81,83,113].

**Process variables**

Inlet pressure and initial hydrogen to metal atomic ratio (H/M) are critical process variables in MH tank models that impact on the hydriding rate and total amount of hydrogen absorbed and desorbed [9,12,42,53]. Based on previous results, the temperature evolution and hydriding rate are in direct proportion to the inlet pressure while the temperature gradient through the bed is inversely related [9,41,53,54].

As the reaction kinetics are determined by the difference between the supply pressure and the equilibrium pressure, maintaining the pressure of charging higher than equilibrium pressure reduces charging times and allows for the maximum stored mass of hydrogen [114]. Temperature is a key factor which can accelerate or retard the reaction rate due to the effect on the equilibrium pressure. This must be managed by an effective cooling system. Cooling the hydride bed reduces the equilibrium pressure and as a result the driving force of absorption will increase, for a given gas pressure.

In addition, the effect of the operating conditions of the heat exchange fluid, including the temperature and flow rate, on the hydriding process, have been considered [30,97,115]. Operating conditions for thermal management systems for MH tanks are determined based on the amount of required heat for the exothermic and endothermic reactions [3,96]. A lower fluid temperature leads to reduced hydriding time for absorption but does not affect the total stored hydrogen [12,97].

The effect of the initial hydrogen to metal ratio (H/M)₀ on desorption in LaNi₅—H₂ system has been investigated [39]. It was found that changing the amount of (H/M)₀ between 5.4 and 6 has a significant effect on the amount of hydrogen desorbed and the system pressure whereas a decrease in the amount below 5.4 did not make a significant difference in the results. They proposed that this occurs because of the high sensitivity of the equilibrium pressure to hydrogen concentration at H/M values close to 6. Later, Mellouli, et al. [97] investigated the effect of this factor on absorption and found increasing the initial hydrogen amount leads to an increase in the amount of absorbed hydrogen.

**Practical applications and experimental validation**

Although some of the papers reviewed here have compared modelling results with experimental data, much of this is performed with small MH prototype cells and the limited number of working, large-scale metal-hydride tank systems prevents adequate validation of modelling results. Askri et al. [12] compared calculated with measured bed temperature results as a function of time with constant inlet pressure as well as experimental and calculated pressure as a function of time for the case of constant volume. Their results are shown in Fig. 3 (from Ref. [12]). Bao et al. [13] also used a constant volume to compare the results of their model with experimental results for the average reacted fraction as a function of time. These results are shown in Fig. 4 (from Ref. [13]).

There is a need for large-scale experimental systems which can provide sufficient data (pressure and spatial variation of temperature) as a function of time during the process of absorption and desorption.

An area of MH tank modelling that has not been well investigated is the requirement of some systems that hydrogen flow may need to be switched from in-flow (supply for storage) to outflow (perhaps for customers at a hydrogen re-fuelling station) abruptly at random intervals according to demand. Under these conditions, time to reach full capacity is not an appropriate optimisation variable as hydrogen is stored and discharged without the tank necessarily reaching full capacity. A model which considers hydrogen mass flow as a variable input/output quantity that can be mapped to data from a real system is required to accurately describe such a system.

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Fig. 3 – Comparison of experimental data and modelling results for time-evolution of bed temperature under constant-pressure conditions and system pressure in constant-volume for a MH system containing less than 0.5 kg of LaNi₅. (Reproduced with permission from Ref. [12]).
Fig. 4 – Comparison of experimental data and modelling results for time-evolution of reacted fraction for a MH system containing less than 0.5 kg of LaNi₅. (Reproduced with permission from Ref. [13]).

Conclusions

Modelling of the hydrogen flow, heat flow and capacity of metal-hydride tank systems as a function of heat exchange systems, tank geometries and the availability and use of hydrogen is an invaluable aid in the design of better systems. Characteristics of the metal–hydrogen interaction such as hysteresis and the dependence of sorption on temperature coupled with the exo- and endo-thermic reactions of absorption and desorption respectively, result in complex spatial distributions of MH capacity and temperature and the modelling of this necessitates sophisticated software using carefully chosen and articulated modelling equations.

The models reviewed in this paper have investigated the effect of thermal management improvements such as internal heat exchange systems, coils and fins (together with fin arrangement, number, thickness and material) and various tank geometries with the aim of optimizing storage capacity and efficiency. The modelling equations have been tested to examine the validity of various approximations and simplifications that reduce the calculations to manageable running times. Some of these, such as treating hydrogen as an ideal gas, assuming local thermal equilibrium and ignoring heat transfer by mass convection have been validated under normal operating conditions, whereas others, such as ignoring the effect of hydrogen capacity on equilibrium pressure are still problematic. Other approximations still need to be investigated in order to have realistic mathematical models that accurately model real tank systems.

References


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Addendum

Eqn (21), p3475 of the Review paper should be:

\[ m_d = C_d \exp\left(-\frac{E_d}{R_s T}\right) \left(\frac{P_s}{P_{eqd}}\right) \rho_s \]
CHAPTER THREE

An Improved Model for Metal-Hydrogen Storage Tanks

3-1 Introduction

References


3-1- Introduction

Most of the previous mathematical models for MH systems have been developed for small scale prototypes and under conditions of constant volume or constant pressure. A few, such as the model of Hardy and Anton [1, 2] were more comprehensive and applicable for large scale systems. Some important practical features of MH systems were, however, neglected in these models and the work here addresses this gap between theoretical models and practical implementations of large scale MH tanks. A 3D mathematical model based on the work of Hardy and Anton has been developed for a large scale intermetallic-hydrogen storage system which can be generalised to all physically similar MH tanks. The included paper, published in the International Journal of Hydrogen Energy contains the details of this model, but the modifications as well as the reason for the improvements are summarised here.

In an example complete MH system, an electrical source, such as a solar array or wind turbine produces electricity which can be used directly or, if it is excess to demand, used in an electrolyser to produce hydrogen. The hydrogen flows to the MH storage tank and is subsequently used in a fuel cell to generate electricity when demand is higher than supply. In order to emulate such a situation in a model of a MH tank, a mathematical function for the inflow of hydrogen and an empirical equation for the outlet flow rate were introduced to the mass balance equation. This improvement enables the model to adjust the time and amount of hydrogen injection and investigate the effects of these parameters on hydriding rate. Dehydriding performance also can be examined via a discharge coefficient.

The inflow and outflow terms have been directly added to the hydrogen mass conservation in gas phase as an external hydrogen source [3, 4], which flows into and out of the tank during absorption and desorption, respectively. In the Hardy and Anton model, hydrogen flow rate is implemented as a mass boundary condition and occurs as the difference between constant
injection pressure and local bed pressure. The drawback of this method is that the rate and amount of input hydrogen cannot be adjusted as operational parameters.

MH beds are typically treated as a packed bed in model calculations. For example, in order to estimate the effective thermal conductivity of a MH bed, various models and equations applicable to general packed beds [5] have been used. However, MH’s are more complicated than simple packed beds due to the interstitial diffusion of hydrogen inside the particles and the direct effect of hydrogen absorption on the morphology and particle size, affecting in turn the contact area of the particles. After about the first 10 cycles, particle size reduction stops and as a result little change in porosity due to pulverisation would occur [6]. For this reason, pulverisation is not considered in the model as it is not a long term effect. The effective thermal conductivity is also highly pressure-dependent due to the Knudsen effect [6] and this dependence causes the effective thermal conductivity to vary by more than one order of magnitude during hydrogen cycling. Due to the interaction of these factors, estimation of the effective thermal conductivity of the MH beds is difficult. That has led to quite different values of effective thermal conductivity for the same material being used in different MH models. Examples for the LaNi₅–H₂ system have been given in the review paper in chapter 2 [7].

The effective thermal conductivity of a MH powder has a direct impact on the temperature distribution over the bed and plays a critical role in determining the kinetic rate of exothermic and endothermic reactions between the metal and hydrogen in absorption and desorption respectively. Models results are, therefore, highly sensitive to this parameter.

Hence, in order to achieve more accurate results, the effective thermal conductivity should not be considered as a constant [6]. Experimental data obtained by Pons and Dantzer [8] for the effective thermal conductivity of LaNi₅-H₂ as a function of pressure up to 10 bar were fitted to an empirical equation, extrapolated to 100 bar and used in the revised model.
The difference between the hydrogen gas pressure and the equilibrium pressure of the bed provides the driving force for the desorption and absorption reactions. Model results are therefore quite sensitive to the detailed terms of the PCT isotherm equation, necessitating an accurate equation within the model. The generic van ‘t Hoff equation, which does not include the dependence of the equilibrium pressure on the bed composition, has been the most commonly used equation in published models [9-11]. A number of modified equations have also been suggested and used in MH models [12-15]. Equations proposed for LaNi₅ in previous studies have been given in the review in chapter 2 [7] and are quite varied. This led to the conclusion that more investigation was required in this part.

Isotherms for LaNi₅ were measured using a commercial Sieverts instrument at four temperatures. An empirical equation for equilibrium pressure with different coefficients for absorption and desorption was fitted to the experimental data.

During absorption, the difference between the maximum and the current hydrogen uptake at any time gives a driving force due to concentration difference in the reaction kinetics equation for LaNi₅–H₂ developed by Mayer et al. [16]. In previous studies [11, 12, 17, 18], the maximum hydrogen to metal ratio has been taken as constant and equal to the saturated hydrogen to metal ratio at room temperature. However, experimentally, this varies with temperature and the relationship can be determined from the PCT curves for different temperatures. In order to increase the accuracy of the kinetics calculations this modification was also applied to the model.

The usual assumptions about thermal and physical properties of the bed include pressure and temperature independence of the effective thermal conductivity and porosity (See for example, Hardy and Anton [1]) have been avoided by using equations for effective thermal conductivity based on experimental results.
The assumption of hydrogen as an ideal gas was evaluated; compressibility factors of hydrogen gas for pressures and temperatures of 0–100 bar and 260–400 Kelvin respectively were taken from NIST REFPROP [19] database and used in the model for calculations of hydrogen pressure. Comparison of hydriding characteristics achieved from the assumptions of hydrogen as a non-ideal and ideal gas showed that the ideal gas law is a reasonable approximation for the LaNi\textsubscript{5}-H\textsubscript{2} system below 100 bar at about 300 K.

The model was used to examine the effect of varying a number of the parameters introduced. This is detailed in the attached paper, “An improved model for metal-hydrogen storage tanks – Part 2: Model results” [20], published in the International Journal of Hydrogen Energy. A summary of the main points is made below.

The improved model was specifically employed for modelling a large scale prototype intermetallic hydrogen storage tank (about 1.5 kg hydrogen capacity). Physically, a cylindrical tank was chosen with an internal cooling system equipped with a number of fins with a fin separation of 93 mm. Studies have indicated that the best thermal management systems for metal hydride beds are those where no material is more than 10 mm from a heat sink/source (refer to the calculations in chapter 5 of this thesis and [1]). However, poor thermal management has been deliberately adopted for the tank in order to achieve inhomogeneous mass and heat distribution over the bed for advanced and realistic testing of the models and for further experimental studies.

Impractical initial conditions for both absorption and desorption have been chosen in the majority of previous studies [12, 14, 21]. For example, the initial pressure for absorption was usually considered to be tens of bars with a corresponding initial reacted fraction of zero. For desorption, a fully hydried bed under sub-bar hydrogen pressure was taken to be the initial conditions; neither of these is possible in practice. The ability of this model to inject and release hydrogen in a controlled fashion allowed a range of input and output flow rates and
amounts to be compared, together with the effect on maximum pressure reached and cycle times, which can be set from a few minutes to several hours.

To avoid exceeding the working pressure of the vessel during injection at a controlled rate, the duration of hydrogen injection needs to be quite long. The long injection time condition was also applied for comparison of the two methods of setting the heat exchange fluid temperature, and the injection amount of hydrogen. Due to slow and constant injection of hydrogen and the fast kinetics of LaNi$_5$ hydriding, an approximately linear profile for the evolution of the reacted fraction over time can be expected (as seen in Fig. 7 of the modeling paper-part 1).

In this study, initial conditions were defined so as to match the practical conditions of hydrogen uptake-release cycling. In practical MH tanks the initial conditions for absorption and desorption are the final values from the previous process, meaning that these vary for each cycle depending on the balance between consumption and loading of hydrogen to the tank.

The adiabatic boundary conditions were defined according to the experimental system, for which the model will be applied in the longer term (Chapter 5). Specifically, the tank is thermally isolated from the environment with appropriate insulation, emulating an adiabatic boundary at the walls of the tank. This can be changed according to different thermal designs for different tank systems.

As the thermal management is critical to the operation of the MH system, two different approaches for control of the thermal fluid temperature were investigated; fixed fluid temperature for both absorption and desorption and a fluid temperature which is changed depending on the whether the tank is absorbing or desorbing. Three fixed temperatures, 293, 303 and 313 K, were used for both absorption and desorption and their effects on the
hydrogen cycling rates were compared. According to the results, thermal fluid supplied at a constant 313 K accelerated the endothermic desorption reaction and gave a lower final reacted fraction.

In comparison, switching the fluid temperature between cold and hot for absorption and desorption respectively showed that cycled temperatures accelerated both the exothermic and endothermic reactions and so led to slightly higher hydriding and dehydriding rates. However, the model indicated that the difference between switching the coolant temperature and a fixed coolant temperature in terms of the effect on hydrogen cycling rate was relatively small. In practical systems, the energy cost of cycling the temperatures with the advantages of marginally higher performance would need to be evaluated.

In the cycled temperature approach, it takes time to change the temperature of the fluid based on the thermal mass and heating/cooling power of the physical system, which has taken into consideration in the model. The effect of those temperatures and hence the fluid temperature is varied as a parameter of the model, not as a fixed boundary condition which is what has been typically used in other models.

This work emphasises the use of practical parameters and conditions for MH tank model to increase the accuracy of prediction and to enable it accommodate realistic operating conditions for reliable test and optimization of real MH systems.
References

STATEMENT OF CONTRIBUTION TO CO-AUTHORED PUBLISHED PAPER

This chapter includes a co-authored paper. The bibliographic details of the co-authored published paper, including all authors, are:


Appropriate acknowledgements of those who contributed to the research but did not qualify as authors are included in the paper.

My contribution to the paper involved:

1) Development of the model  
2) Calculations and analysis of the results  
3) Manuscript preparation

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3-2 Modelling paper 1: An improved model for metal-hydrogen storage tanks- Part1: Model development,
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An improved model for metal-hydrogen storage tanks – Part 1: Model development

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ABSTRACT

The complexity of the metal-hydrogen interaction and the critical role of thermal management in a metal-hydride storage tank necessitate comprehensive mathematical modelling before a suitable design can be chosen and subsequently implemented. Existing models have been analysed and integrated into an enhanced model which incorporates several features more suited to practical applications using an intermetallic metal-hydride tank. These include matching initial conditions of the model to physically achievable experimental conditions, the ability to vary the cooling system fluid temperature and realistic modelling of hydrogen injection and extraction from the tank as well as incorporating the non-ideal gas equation and modifying the equilibrium pressure and effective thermal conducting equation based on experimental data.

Introduction

Metal-hydrides [1], ranging from simple light-weight metal-hydrides such as magnesium hydride to intermetallics, such as LaNi₅, and the complex hydrides including borohydrides and alanates [2-4], are suitable for applications in hydrogen storage systems [5-8]. While some are more appropriate for stationary applications due to low gravimetric densities and others more suitable to portable applications despite issues with cyclability or degradation, most potential hydrogen storage materials have poor thermal properties [9]. As the hydrogen absorption and release is exothermic and endothermic respectively, low thermal conductivity exacerbates the problem of removing and supplying heat and this slows or halts the hydriding/dehydriding processes [10]. It is therefore necessary to design the most appropriate container (tank) and thermal control systems to supply and remove the heat of reaction between the metal and hydrogen. Mathematical modelling is a useful tool to identify and predict the state of the metal-hydride during absorption and desorption. Mathematical modelling is useful to identify and predict the state of the metal-hydride during absorption and desorption. Mathematical modelling is useful to identify and predict the state of the metal-hydride during absorption and desorption. Mathematical modelling is useful to identify and predict the state of the metal-hydride during absorption and desorption.
In this work, the effect of different rates and amounts of hydrogen injection into the tank (during absorption) and hydrogen extraction (during desorption) was explored by...
modelling the H₂ mass input to the tank. Injection and removal rates are considered in view of the practical consideration of supply of the H₂ to the tank during absorption and external storage or use of the H₂ during desorption.

Another enhancement incorporated into this model is that the heat exchange fluid temperature can be varied. This provides the possibility to study the effect of varying the coolant temperature depending on whether the hydride is absorbing (say from an electrolyser, with enthalpy removal to the surroundings) or desorbing (say to a fuel cell with enthalpy captured from the fuel cell cooling circuit). This enables a comparison with constant heat exchange fluid temperature in terms of energy costs and the performance of the metal-hydride system.

Finally, the conditions necessary to model a continuously cycling tank system were determined by iterating to a solution that leaves the system in the same state at the end of desorption as it was at the beginning of absorption. These developments represent an attempt to improve the current state of metal-hydride tank modelling in a way that facilitates comparison with future experimental results.

**More accurate equations for thermal conductivity and equilibrium pressure**

Empirical equations were fitted for the effective thermal conductivity as a function of pressure using the experimental data of Pons and Dantzer [32] and for the equilibrium pressure of the LaNi₅–H₂ system based on the experimental data obtained from a commercial Sieverts instrument. To accurately model H₂ absorption/desorption in an intermetallic below the critical temperature, the equation of the absorption reaction kinetics was modified by introducing the maximum reacted fraction as a function of temperature.

**The model**

A three-dimensional mathematical model based on the work of Hardy and Anton [22,23], was developed for intermetallic-hydride cylindrical systems which can also be used for all metal-hydride tanks with modifications to those equations specific to the hydrogen absorbing material. This model was solved by COMSOL Multiphysics 4.3 specifically for the LaNi₅–H₂ system.

**Geometry and thermal management system**

The tank geometry and physical design, together with that of the thermal management system were chosen based on previous studies [22,27]. A horizontally-mounted, axially symmetric, cylindrical tank containing 100 kg LaNi₅ was employed. A schematic of the metal-hydride pressure vessel and the volume modelled are shown in Fig. 1. The cylindrical symmetry simplifies the model. Full-scale dimensions (tank volume 0.03 m³) are deliberately used to match practical considerations for future experimental works. A temperature-controlled circulating bath is used to circulate the heat exchange fluid through the heat exchange system in order to add and remove heat to and from the tank during desorption and absorption. The heat exchange system inside the metal-hydride bed consists of two concentric tubes for the fluid inlet and outlet equipped with eleven transverse copper fins to enhance the heat distribution through the bed. The length of the fins are 97 mm, the thickness of nine fins are 3 mm and the two at either end are 1.5 mm thick, insulated by PTFE in order to make the bed seem infinitely long (i.e. remove the end effect). The fins define notionally identical cells. The hydrogen inlet/outlet port is implemented at one end of the horizontal tank. It is worth noting that this physical system was chosen to match an experimental design to investigate of temperature gradients and compositional inhomogeneity throughout the bed – not for best heat performance.

**Absorption–desorption model**

In most previous studies [16,19,25,26], the modelling of absorption starts with the initial conditions of high pressure, however, this cannot be physically realised. In this study, the hydrogen is injected into the tank during the absorption cycle. While in practice this might be supplied from an electrolyser (for a production and storage system) or a re-fuelling station (for a vehicle tank) this is modelled as a hydrogen mass pulse input which can be varied with regard to time duration and total hydrogen injected. Hydrogen discharge during the desorption process is modelled as flow through an aperture for as long as the tank hydrogen pressure is greater than a fixed external pressure. This approximates hydrogen supply to another tank or a fuel cell via a pressure regulator.

To maximize heat transport from the metal-hydride bed to the thermal fluid and vice-versa, it may be advantageous to cycle the temperature of the thermal fluid from some set low temperature during absorption to a set higher temperature during desorption. Obviously this comes at a cost of additional equipment and maintenance as well as an energy cost of temperature cycling the thermal fluid, but may correspond to real conditions in some applications. This model allows for the investigation of temperature cycling or fixed temperature thermal fluid by modelling the system variables (pressure, temperature, hydrogen capacity of the metal) for different temperature ranges of cycled thermal fluid.

In many practical applications of hydrogen storage, the process of desorption begins immediately after absorption has finished. For example, a vehicle will begin to use the hydrogen in the tank as soon as the tank has been refilled. For all the modelling results presented here, the initial conditions for desorption have been taken as the final conditions of the absorption process. In addition, many practical systems may reinitiate the absorption process immediately desorption has concluded and this has also been incorporated in the modelling presented here. The overall result is a model of a tank absorption–desorption cycle for which the conditions at the end of the cycle can be the same as the conditions at the start of the cycle and so it can model an infinitely repeating cycle of absorption and desorption, as in metal-hydride heat pump.

**Mathematical model**

The model used in this study follows on from the work of Hardy and Anton [22,23] modified to study hydriding and
dehydriding processes inside an axially symmetric cylindrical pressure vessel. The macroscopic governing equations are obtained from averaging the microscopic energy, mass and momentum balance equations over a volume. These are formulated using substitution of relevant fundamental physical, mechanical and thermodynamic laws in the appropriate conservation laws [33,34]. Because of the symmetry conditions of the metal-hydride tank, the computation region of the tank was chosen as half of the space between two fins, starting from a centre of one fin, over half of the internal diameter of the tank. This is shown in Fig. 1.

The assumptions listed below are normally employed in metal-hydride tank models [21] and have also been used in this model:

- The compression work and viscous dissipation are negligible
- Gas pressure distributes promptly in the system
- Radiative heat transfer is negligible
- The tortuosity and dispersion terms can be modelled as diffusive fluxes
- Both gas and solid have the same temperature (local thermal equilibrium)
- Thermal and physical properties of the bed are not dependent on bed temperature or concentration in the bed

**Heat balance**

The energy equation for the metal-hydride bed taking into consideration gas pressure variation is expressed as:

\[
(rC_p)_{eff} \frac{\partial T}{\partial t} = \lambda_{eff} \nabla^2 T - \nabla \cdot (\rho_j C_{jj} \nabla T) - \frac{\partial m}{\partial t} \left( \nabla \cdot (\rho_j \nabla P) - \frac{\partial P}{\partial t} \right) \pm \dot{m} \Delta H
\]

(1)

\[
(rC_p)_{eff} = \varepsilon r_{pp} C_{pp} + (1 - \varepsilon) \rho_s C_{ps}
\]

(2)

where \(m\) is the amount of absorbed or desorbed hydrogen per unit volume and unit time and is therefore the reaction rate of absorption and desorption. The “+” sign indicates absorption and the “−” sign desorption. \(\varepsilon\) is the porosity of the metal powder bed which is variable and must be considered a function of reacted fraction [31]:

\[
\varepsilon = \varepsilon_p (1 - \varepsilon_i) / (\eta) + \varepsilon_i
\]

(3)

where \(\varepsilon_i, \varepsilon_p\) and \(\eta\) are initial porosity, expansion coefficient and reacted fraction respectively.

\(\lambda_{eff}\) is the effective thermal conductivity of metal-hydride bed; As the thermal conductivity of a porous medium is pressure dependent due to the Knudsen effect, this should be implemented as a function of pressure in the calculations [35].

Previous models [27,36,37], have regarded this as a constant despite sensitivity to the bed pressure being shown in early research [32,35,38,39]. However, the effect of different values
of the effective thermal conductivity on the performance of metal-hydride beds has been investigated [24].

Pons and Dantzer [32] presented experimental data analysed by the Zehner, Bauer and Schlunder method (one of the models used to predict thermal conductivity in packed beds [40]) for the effective thermal conductivity of the LaNi5–H2 system as a function of pressure up to 10 bar. This was used here by fitting their data (extrapolated to 100 bar by assuming the Knudsen effect) to Eq. (4):

$$\lambda_{\text{eff}} = \frac{B_1 \rho B_2}{\varepsilon + B_3}$$

(4)

where $B_1$, $B_2$, and $B_3$ are the fitting coefficients and were determined to be 0.70316, 2.12923, and 0.73648, respectively by a least squares fit.

*Momentum equation*

Gas movement throughout the bed is expressed by the Blake-Kozeny's equation [41], assuming that the bed is in the laminar condition:

$$\overline{\nu} = -\frac{\partial^2 \rho g}{150 \mu} \left( \frac{V}{\rho g} \right) \rho \overline{\nu} (\nabla \overline{\nu})$$

(5)

where $\mu$ is dynamic viscosity of the gas at the system working temperature and $d_p$ is the mean particle diameter.

*Mass balance*

The equation of continuity is normally used to express the hydrogen gas balance in the metal-hydride bed [21,42]:

$$\varepsilon \frac{\partial \rho g}{\partial t} + \nabla \cdot \rho g \overline{\nu} = \pm \dot{m}$$

(6)

In the gas phase, the density varies due to the addition and removal of hydrogen owing to the reaction with metal during desorption and absorption respectively, as well as through an external source such as electrolyser or fuel cell which should be included in the equation. Incorporating the mass flow in and out of the tank explicitly gives the mass conservation equations for the gas and solid phases:

Gas:

$$\varepsilon \frac{\partial \rho g}{\partial t} + \nabla \cdot \rho g \overline{\nu} = \pm \dot{m}$$

(7)

Solid:

$$\frac{(1 - \varepsilon) \partial \rho g}{\partial t} = \pm \dot{m}$$

(8)

where $\dot{m}$ is the hydrogen flow rate per unit volume (kg/m³ s):

$$\dot{m} = \dot{\phi}_{g, \text{in}} \frac{\dot{V}}{V}$$

(9)

where $\dot{\phi}_{g, \text{in}}$ and $V$ are mass flow rate (kg/s) and total tank volume respectively. With this model enhancement, different profiles for hydrogen injection during absorption ($\dot{\phi}_{g, \text{in}}$) and hydrogen extraction during desorption ($\dot{\phi}_{g, \text{out}}$) can be employed.

For verification of the model, the absorption flow rate, $\dot{\phi}_{g, \text{in}}$ was modelled by a smoothed trapezoidal function:

$$\dot{\phi}_{g, \text{in}} = \frac{\rho g_{\text{in}}}{t_{\text{inj}}} \times \left[ H(t - t_{\text{inj}}/2, t_{\text{inj}}/2) - H(t - t_{\text{inj}} - t_{\text{inj}}/2, t_{\text{inj}}/2) \right]$$

(10)

where $H(x, y)$ is a smoothed Heaviside step function (implemented as the function ‘flc2hs’ in COMSOL):

$$H(x, y) = \begin{cases} 0 & (x < -y) \\ \frac{1}{2} + \frac{x}{15} - \frac{3}{16} \left( \frac{x}{y} \right) - \frac{5}{8} \left( \frac{x}{y} \right)^2 + \frac{15}{16} & (-y \leq x \leq y) \\ 1 & (x > y) \end{cases}$$

where $t_{\text{inj}}$, and $t_{\text{inj}}$ are time for smoothing the function and time of injection respectively. The maximum injection rate is $\rho g_{\text{in}}/t_{\text{inj}}$ which is determined from specifying both the maximum amount of hydrogen injected ($\rho g V$) and the time of injection.

Fig. 2 shows the hydrogen flow rate into the metal-hydride tank representing hydrogen flow produced by a supplier such as an electrolyser in a real hydrogen cycling systems. A range of injection rates for the hydrogen flow for which the total amount of hydrogen injected (the area under the curve of flow against time) is the same in each case, so the maximum flow rate is higher for shorter injection time.

For desorption, hydrogen extraction from the vessel is modelled here as a flow rate proportional to the pressure difference between the bed and a constant external pressure (0.1 bar). The cross sectional area at the outlet can be set by a valve that determines hydrogen outlet flowrate. Based on the mass balance of the discharge of a compressible gas from a container in adiabatic condition, the density change of the gas relates to the pressure difference [43]:

$$\dot{\phi}_{g, \text{out}} = \frac{k}{V} \sqrt{\frac{\rho g}{P}} (P - P_0)$$

(11)

where $k = C_{g1} A$ and $C_{g1}$ and $A$ are the discharge coefficient and gas outlet cross sectional area respectively.

An experiment was performed investigating pressure changes during hydrogen discharge from a gas container in order to determine an experimental value for the coefficient $K$ and to confirm the accuracy of Eq. (11) for the hydrogen outlet flowrate. The experimental and theoretical results shown in Fig. 3 demonstrate the validity of this equation in representing the mass flow rate in this model. The estimated value of $C_{g1} A$ from the experimental data is $2.89 \times 10^{-7}$ m² which is dependent on the valve or outlet pipe size and larger values were used in this model (see Section Hydrogen outlet flow rate).

*Equilibrium pressure*

The equilibrium pressure, $P_{eq}$, is a critical parameter in metal-hydride studies since the difference between the equilibrium and the system pressure is the driving force of the sorption processes. Different equations for the equilibrium pressure of LaNi5–H2 system have been previously presented, based on the modification of the van’t Hoff equation to include both temperature and hydrogen concentration as independent variables [44]. Previous numerical studies of the LaNi5–H2 system have used either Jenni and Nasrallah’s equations [16,17] or Nishizaki’s equation [21,45]. However, due to high
sensitivity of the model to the $P_{\text{eq}}$ equation, independent experiments were performed on LaNi$_5$ using a commercial Sieverts instrument (Hiden Isochema HTP1) for LaNi$_5$ at temperatures 293, 313, 353 and 373 K.

An empirical expression was fitted to the experimental data

$$P_{\text{eq}} = \left[ C_0 C_3 \eta^2 + C_2 \eta + e^{C_1 (\eta - C_4)} \right] \exp \left( -K \left( \frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \right)$$

where $C_0$ to $C_5$ are the fit coefficients which differ for absorption and desorption cycles and are given in Table 1 together with the $R^2$ coefficient of determination. Fig. 4 shows the results of the experimental data and the empirical equations obtained by fitting Eq. (12) to the data for absorption (Fig. 4(a)) and desorption (Fig. 4(b)). These are in reasonable agreement.

As can be seen in Fig. 4(b) there is a change in the plateau slope of experimental data at 100 °C which has influenced the manner of fitting the isotherm equation compared with the two other isotherms at lower temperatures. This may be caused by the occurrence of $\gamma$-LaNi$_5$H$_x$ ($x \approx 3$) in the mechanism of $\alpha$ to $\beta$ phase transformation which has been
reported in previous research for LaNi$_5$ at temperatures above 80 °C [46].

Reaction kinetics
The reaction kinetic equations of LaNi$_5$ developed by Mayer et al. [12] are:

$$
\dot{m}_a = C_a \exp \left( -\frac{E_a}{R \cdot T} \right) \ln \left( \frac{P}{P_{eq,a}} \right) \left( \frac{H}{M} \right) - \left( \frac{H}{M} \right)_{max}
$$

(13)

for absorption and

$$
\dot{m}_d = C_d \exp \left( -\frac{E_d}{R \cdot T} \right) \frac{P - P_{eq,d}}{P_{eq,d}} \left( \frac{H}{M} \right)
$$

(14)

for desorption, where $C_a$, $C_d$ and $E_a$, $E_d$ are rate constants and activation energies typically for diffusion respectively. These equations were used in this model with values for the constants taken from the literature for LaNi$_5$ (shown in Table 2). $(H/M)$ is the hydrogen to metal ratio at any time during the hydriding processes and $(H/M)_{max}$ is the maximum amount of hydrogen stored in the metal alloy. $(H/M)_{max}$ varies with temperature as can be seen in Fig. 4, however, it has always been treated as a constant in previous studies [22,23,26–28].

In Eq. (13) the reaction kinetics for absorption depends on the pressure drive determined by the difference between the gas pressure and the equilibrium pressure. However, it is important to use the appropriate maximum uptake, $(H/M)_{max}$

| Table 1 – The coefficients of the PCT equations. |
|----------------|----------------|----------------|----------------|----------------|----------------|----------------|--------|---------|
|                | $C_0$          | $C_1$          | $C_2$          | $C_3$          | $C_4$          | $C_5$          | $K$     | $R^2$   |
| Absorption     | 3.218          | 1139           | 2.3445         | 1.383          | 36.311         | 0.84022        | 3291    | 0.931   |
| Desorption     | 2.427          | 23,924         | 3.5749         | 1.481          | 31.833         | 0.82688        | 3093    | 0.989   |

Fig. 4 – Equilibrium pressure as a function of reacted fraction (experimental and theoretical PCT curve) (a) absorption (b) desorption.
for the temperature at which the absorption takes place. In this model, the temperature dependence of \((\theta/M)_{\text{max}}\) is taken into account.

The maximum amount of hydrogen that can be stored in one \(\text{LaNi}_5\) formula unit at room temperature is 6.6 atoms of hydrogen (saturation) which is denoted \((\theta/M)_{\text{sat}}\).

Eqs. (13) and (14) can be rewritten as a function of reacted fraction:

\[
\frac{d\eta}{dt} = \frac{C_d}{(1 - \epsilon)} \exp\left(- \frac{E_d}{R_g T}\right) \ln \left(\frac{P_{\text{eq}}}{P}\right) (\eta' - \eta) \tag{15}
\]

\[
\frac{d\eta'}{dt} = \frac{C_d}{(1 - \epsilon)} \exp\left(- \frac{E_d}{R_g T}\right) \left(\frac{P - P_{\text{eq}}}{P_{\text{eq}}}\right) (\eta') \tag{16}
\]

\[
\dot{m} = \frac{d\eta}{\left(\frac{\theta}{M}\right)_{\text{max}}} \rho \epsilon (1 - \epsilon) \tag{17}
\]

where \(\eta\) and \(\eta'\) are the reacted fraction and maximum reacted fraction (a function of temperature) respectively:

\[
\eta = \frac{\left(\frac{\theta}{M}\right)}{\left(\frac{\theta}{M}\right)_{\text{sat}}} \tag{18}
\]

\[
\eta' = \frac{\left(\frac{\theta}{M}\right)_{\text{sat}}}{\left(\frac{\theta}{M}\right)_{\text{max}}} \tag{19}
\]

From the experimental data shown in Fig. 4, a linear relation between \(\eta'\) and temperature was obtained:

\[
\eta' = -0.0009T(K) + 1.2411 \tag{20}
\]

Initial and boundary conditions

It is assumed that temperature and pressure are initially uniform throughout the bed for both absorption and desorption. The values of the initial conditions for each process are equal to the final conditions of the previous process. When hydrogen has finished discharging the desorption is considered to be complete and absorption starts from the end of that desorption state.

Initial conditions

Absorption:

\[
P(r, z, 0) = P_{\text{id}}, \quad T(r, z, 0) = T_{\text{id}} = T_{\text{f,d}} \tag{21}
\]

Desorption:

\[
P(r, z, 0) = P_{\text{id}} = P_{\text{f,d}}, \quad T(r, z, 0) = T_{\text{id}} = T_{\text{f,s}} \tag{22}
\]

Boundary conditions

The tank is in adiabatic conditions with the surrounding atmosphere:

\[
\frac{\partial T(R, z, t)}{\partial r} = 0, \quad \frac{\partial T(r, 0, t)}{\partial z} = 0, \quad \frac{\partial T(r, l, t)}{\partial z} = 0 \tag{23}
\]

Convective heat flux with the heat exchange fluid:

\[
r = r_0 - \lambda_{\text{eff}} \nabla T \cdot \vec{n} = h_T (T - T_f), \quad -k_p \nabla T_{\text{fin}} \cdot \vec{n} = h_T (T_{\text{fin}} - T_f) \tag{24}
\]

where it is also assumed that

\[
T_{\text{fin}} = T_{\text{bed}} = T
\]

where \(h_T\) and \(T_f\) are the convective heat transfer coefficient and temperature of the heat exchange fluid respectively. \(\vec{n}\) is the normal vector to the corresponding wall.

Ideal and non-ideal gas

In all published models of metal-hydride storage systems known to the authors, hydrogen has been considered as an ideal gas. However, at the operating conditions of pressure and temperature, the compressibility of hydrogen should not be neglected without justification. For example, the compressibility, \(Z = PV/nRT\) of hydrogen at 100 bar and 300 K is 1.0598. In this model, values of the compressibility obtained from the NIST REFPROP [47] database were applied to the model using an interpolation function. A comparison was made between the hydriding characteristics assuming hydrogen as a non-ideal and ideal gas.

Summary of model features

The purpose of the extensions to the equations and variables used in the governing equations which constitute the mathematical models of metal-hydride systems is to bring the results of the theoretical and experimental studies closer in order to allow valid comparisons.

Because of the fact that in a real hydrogen storage tank, hydrogen will flow in and out at finite rates, two functions were defined to model hydrogen inlet and outlet flow rates. These relations were added to the mass conservation governing equation (Eq. (7)).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravimetric capacity (GC) wt%</td>
<td>1.5</td>
</tr>
<tr>
<td>(\Delta H_a) kJ/mol</td>
<td>30.1</td>
</tr>
<tr>
<td>(\Delta H_b) kJ/mol</td>
<td>30.0</td>
</tr>
<tr>
<td>(\Delta S_a) J/mole K</td>
<td>110.9</td>
</tr>
<tr>
<td>(\Delta S_b) J/mole K</td>
<td>110.6</td>
</tr>
<tr>
<td>Density, (\rho), Kg/m³</td>
<td>8400</td>
</tr>
<tr>
<td>Initial porosity, (\epsilon_0)</td>
<td>0.5</td>
</tr>
<tr>
<td>Permeability, (k), m²</td>
<td>(10^{-12})</td>
</tr>
<tr>
<td>Specific heat capacity, (C_p), J/kg K</td>
<td>419</td>
</tr>
<tr>
<td>(C_{p,a}) s⁻¹</td>
<td>59.187</td>
</tr>
<tr>
<td>(C_{p,b}) s⁻¹</td>
<td>9.57</td>
</tr>
<tr>
<td>(E_{\text{ps}}) kJ/mole H₂</td>
<td>21.170</td>
</tr>
<tr>
<td>(E_{\text{pa}}) kJ/mole H₂</td>
<td>16.420</td>
</tr>
<tr>
<td>(SC_v) m³</td>
<td>(2.89 \times 10^{-7})</td>
</tr>
<tr>
<td>(T_{\text{ref}}), K</td>
<td>313</td>
</tr>
<tr>
<td>(P_0) (Downstream pressure), bar</td>
<td>0.1</td>
</tr>
</tbody>
</table>
In this model, the temperature of the heat exchange fluid can be varied during the absorption/desorption cycle. This is modelled to allow for the thermal mass of the heat exchange system as well as the heating/cooling power of the system. This is not the same as models in which the temperature can be set to different values for different executions of the model to examine the relative effect of different heat exchange temperature settings, but allows for the simulation of a single heat exchange system which can be used for both absorption and desorption at different temperatures. From a practical viewpoint, a single heat exchanger has a lower initial setup cost, but possibly higher running costs heating and cooling the fluid mass each cycle. In addition to also modelling the thermal system as separate heat exchangers for absorption and desorption, this model permits a comparison of changing the temperature of the heat exchange fluid for absorption and desorption versus maintaining the same temperature for both charging and discharging. This allows for analysis of the different heat exchange conditions from the point of view of energy evaluation and system performance.

The dependence of the effective thermal conductivity of the metal-hydride bed with pressure was taken into consideration by employing an empirical relationship based on Fons and Dantzer's experimental results for LaNi5 [48].

Experimental data from FCT measurements on LaNi5–H2 for different temperature were used to construct an empirical equation for the equilibrium pressure as a function of reacted fraction and temperature. Moreover, based on these data, the maximum reacted fraction as a function of temperature was determined and used in the equation of reaction kinetics of absorption.

**Choice of physical system**

The heat, momentum and mass balance equations in the model above are general equations appropriate for most tank systems. This model incorporates the thermodynamics and kinetics of the hydrogen storage material through the subsequent Eqs. (12) and (20) and, in this case, these are tailored for the intermetallic LaNi5; although these are readily substituted by equations suitable for other materials. LaNi5 was chosen as a test material as it has been extensively studied and the necessary parameters such as thermodynamics, kinetics and thermal conductivity are known. While this material may not be a suitable candidate for a commercial hydrogen storage system (although variations on this AB5 material are used), it allows for comparative modelling without uncertainties about the material’s characteristics.

Similarly, in order to test the model, a physical tank system must be specified. A cylindrically symmetric tank with fin-based thermal management was chosen to match an experimental system being developed. The relatively large size (100 kg hydride storage with 1.5 kg H2 capacity) demonstrates realistic modelling of larger systems. While there are more efficient thermal management systems, such as a compound of spiral-coils and fins [26,49], several cooling tubes [50] and a combination of external fluid jackets and a central tube with longitudinal fins [51], the use of fins is quite common [27,52] and so the model represents a popular class of storage tanks. The experimental system upon which the physical system for testing this model is based, is designed to have poor thermal exchanged in order to explore, both experimentally and in the modelling, the effect of spatial temperature variations. The choice of tank design, including the pressure and temperature maximum ratings, will have consequences for how the system is used, for example, the chosen tank which is physically large with poor thermal management, necessitates a slow ingress of hydrogen during absorption and a controlled flow rate (eg from an electrolyser) in order to avoid exceeding the maximum pressure rating. Different applications, for example metal hydride compressors and fuel cell supply will have different requirements on the flow of hydrogen and therefore will require different designs to suit those requirements.

### Initial results

For the purpose of testing the model, calculations were performed for a limited number of initial conditions and injection rates. A full description of results of this model is given in part 2 [30].

The model was executed with parameter values appropriate for 100 kg of LaNi5 in a tank of volume 0.03 m3 using a fixed thermal fluid temperature. Results for modelling ideal vs non-ideal gas, a range of injection rates and discharge coefficients are shown below.

Results were obtained with the assumption of considering hydrogen as a non-ideal and an ideal gas and compared.

**Ideal vs non-ideal gas**

Pressure calculations assuming hydrogen to be an ideal gas as well as a non-ideal gas were compared to determine if it is necessary to consider the compressibility of hydrogen in the pressure and temperature ranges appropriate to this tank system namely 0–100 bar and 260–400 K. The time-evolution of the bed pressure and the difference between system pressure and equilibrium pressure as a function of time for both calculations are presented in Figs. 5 and 6. For high pressures a small difference can be seen. There was no difference between the results of hydriding rates and time-evolution of the average of bed temperature.

These results were obtained with the coolant temperature of 303 K and a total amount of H2 of 1.65 kg injected in 5 h.

**Hydrogen injection time**

Hydrogen inlet flow rate during absorption influences system pressure and temperature and, as a result, the hydriding rate. In order to investigate these effects, modelling results were obtained with different hydrogen flow rates made by injection of the same mass of hydrogen over different time intervals. Fig. 7 shows rate of reaction for different injection times of 5 h, 10 h, 15 h and 20 h.

The duration of the hydrogen injection times above demonstrates the consequences of a large scale tank with a relatively poor thermal management system and the reality of a maximum pressure rating. As the hydrogen is injected, the material absorbs some of that hydrogen causing the bed
temperature to rise due to the exothermic reaction. Without adequate heat removal, the higher temperature reduces the reaction rate and therefore more of the hydrogen inflow remains in the gas phase. The minimum time chosen (5 h) to inject sufficient hydrogen to fully hydrogenate the metal-hydride bed (1.65 kg) was the fastest injection rate that did not cause the tank pressure to exceed 100 bar. This compares favourably with the model developed by Muthukumar et al. [21] in which the charging time for 150 kg of MnNi$_4$Al$_{0.4}$ was about 3 h, using a more efficient thermal management system which included 20 cooling tubes inside the bed. Smaller tank systems with efficient thermal management will have much faster charging times [49,53,54]. For example, Visaria and Mudawar [52] describe a 2.65 kg Ti$_{1.1}$CrMn system with a charging time of less than 5 min.

**Fig. 5** – The effect of considering hydrogen as ideal and non-ideal gas on the result of system pressure—inset shows detail.

**Fig. 6** – The effect of considering hydrogen as ideal and non-ideal gas on the result of the difference between pressure and equilibrium pressure.
Hydrogen outlet flow rate

Hydrogen outlet flow provided by the metal-hydride tank for the next step of hydrogen cycling, (in practice a fuel cell or another tank) is modelled as proportional to the difference between system and downstream pressures. The constant of proportionality is the discharge coefficient which depends on the size of the aperture and can be varied experimentally by opening a valve for example. Fig. 8 shows the impact of this coefficient on the hydrogen outlet flow rate.

It can be seen that the higher discharge coefficient markedly affects the reduction of the gas pressure in the tank until the equilibrium pressure of the bed is reached. After this, the outflow of gas is determined largely by the kinetics and heat management system.

Figs. 9 and 10 show the effect of the discharge coefficient on desorption rate and changes in the average bed temperature over time. As expected a larger discharge coefficient helps desorption complete more rapidly. Although the temperature excursion is greater due to the faster release/absorption of heat, because the reaction finishes earlier, the temperature has more time to recover, leading to an overall superior cycle.

Conclusions

A number of enhancements were made to the conventional mathematical model of metal-hydride tank systems to enable the model to more accurately predict experimental configurations.

To demonstrate the model, initial conditions were chosen to satisfy the practical conditions of hydrogen absorption–desorption cycling, empirical equations were determined for the effective thermal conductivity and equilibrium pressure of the LaNi₅. The relationship between the maximum reacted fraction and temperature was also obtained to modify the reaction kinetic equation of absorption.

In addition, two profiles for hydrogen inlet and outlet flow rate were presented and used in the mass balance equation. This enhancement provides the model with the ability of investigation of both different times of hydrogen injection into the tank influencing hydriding rate and the effect of discharge coefficients on dehydriding performance. Since it is not possible experimentally to start absorption under conditions of high pressure and zero reacted fraction, this also permits the comparison of the model with experimental results. The reality of introducing the hydrogen during absorption and removing the hydrogen during desorption

Fig. 7 – Hydriding rate with different injection times (see Fig. 2 for injection profile).

Fig. 8 – Hydrogen outlet flow rate with different discharge coefficients (see Fig. 3 for the profile of outlet flow) – inset shows detail.
necessitates also impacts on the overall performance of the hydrogen cycling.

The assumption of hydrogen being considered as an ideal gas, which has been usually used in the metal-hydride models was also evaluated. It was found that an ideal gas law is a reasonable approximation for the LaNi$_5$–H$_2$ system to 100 bar and 300 K.

In order to demonstrate some sample results of the model, hydrogen cycling characteristics such as reaction rate and average bed temperature changes over time were given at different times of injection and different discharge coefficients. It was shown that although the shorter times of injection and higher discharge coefficients lead to faster reaction rate, there are some restrictions for the system in terms of operating pressure and thermal management system which will be discussed in detail in the second part of this paper.

Acknowledgements

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REFERENCES


STATEMENT OF CONTRIBUTION TO CO-AUTHORED PUBLISHED PAPER

This chapter includes a co-authored paper. The bibliographic details of the co-authored published paper, including all authors, are:


Appropriate acknowledgements of those who contributed to the research but did not qualify as authors are included in the paper.

My contribution to the paper involved:

1) Development of the model
2) Calculations and analysis of the results
3) Manuscript preparation

(Signature) (Date) 18/09/2016

Name of student: Shahrzad Seyed Mohammadshahi

(Signature) (Date) 18/09/2016

Corresponding author of paper: Colin Jim Webb

(Signature) (Date) 18/09/2016

Supervisor: Colin Jim Webb
3-3 Modelling paper 2: An improved model for metal-hydrogen storage tanks- Part2: Model results,
Shahrzad S. Mohammadshahi, Tim Gould, Evan MacA. Gray and Colin J. Webb,
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An improved model for metal-hydrogen storage tanks – Part 2: Model results

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Abstract
An enhanced 3-D numerical model, described in Part 1 [1] of this two part work, has been employed to study a metal-hydrogen storage system. In this manuscript we investigate the effect of varying the hydrogen in-flow rate and total amount of hydrogen inserted on the time taken to absorb/store the hydrogen and the temperature excursions. In addition, the ability to vary the temperature of the thermal management fluid has been used to examine the relative effect of a fixed fluid temperature and one which is hotter for desorption and colder for absorption.

It was found that a shorter time and a greater amount of hydrogen injection to the tank leads to a higher driving pressure and, as a result, higher rate of absorption. This must be moderated by constraints such as the pressure rating of the tank. Furthermore, compared to using the same constant temperature thermal fluid for absorption and desorption, switching the fluid temperature between 283 K for absorption and 343 K for desorption leads to faster hydrogen cycling and more complete hydrogen desorption in the tank. However, a constant fluid temperature of 313 K gives a reasonable performance over the same time duration, without the additional energy expenditure associated with switching the fluid temperature.

Introduction
Hydrogen storage devices must balance a number of competing factors and limitations for optimal performance. Good design will aim to optimise factors like storage yield and energy cost under standard operating conditions. Ideally the optimisation of these parameters can be carried out on a computer, saving time and money in the design process. However, this optimisation is only useful if the mathematical models are sufficiently accurate.

Improvement of mathematical models of metal-hydride storage systems enables the emulation of experimental variables of real systems more accurately and reliably. In this study, an enhanced three-dimensional multiphysics model of a metal-hydride tank, described in Part 1 [1], was used to explore the effects of hydrogen injection time and temperature cycling on system performance. This corresponds to the practical realities that hydrogen supply and withdrawal cannot be instantaneous, and thermal management may be unpractical at high supply or withdrawal rates.

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Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>T</td>
<td>temperature, K</td>
</tr>
<tr>
<td>P</td>
<td>pressure, bar</td>
</tr>
<tr>
<td>ρ</td>
<td>density, kg/m³</td>
</tr>
<tr>
<td>ρ₀ₜ</td>
<td>the total hydrogen density added to the tank, kg/m³</td>
</tr>
<tr>
<td>u</td>
<td>velocity vector, m/s</td>
</tr>
<tr>
<td>ΔH</td>
<td>enthalpy of formation, J/kg</td>
</tr>
<tr>
<td>ΔS</td>
<td>entropy change, J/kg K</td>
</tr>
<tr>
<td>E</td>
<td>activation energy, J/kg</td>
</tr>
<tr>
<td>λ</td>
<td>thermal conductivity, W/m K</td>
</tr>
<tr>
<td>R_g</td>
<td>universal gas constant, J/mol K</td>
</tr>
<tr>
<td>C_p</td>
<td>specific heat capacity, J/kg K</td>
</tr>
<tr>
<td>Hgs</td>
<td>convective coefficient between solid and gas, W/m² K</td>
</tr>
<tr>
<td>m</td>
<td>hydrogen mass absorbed or desorbed, kg/m³ s</td>
</tr>
<tr>
<td>d_p</td>
<td>mean particle diameter, m</td>
</tr>
<tr>
<td>V</td>
<td>volume, m³</td>
</tr>
<tr>
<td>tᵢnj</td>
<td>time of injection, s</td>
</tr>
<tr>
<td>t</td>
<td>time, s</td>
</tr>
<tr>
<td>ε</td>
<td>porosity</td>
</tr>
<tr>
<td>k</td>
<td>permeability, m²</td>
</tr>
<tr>
<td>φ_m</td>
<td>hydrogen mass flow rate, (kg/m³ s)</td>
</tr>
<tr>
<td>φ_e</td>
<td>hydrogen flow rate, (mol/m³ s)</td>
</tr>
<tr>
<td>Hᶠ_max</td>
<td>maximum hydrogen to metal ratio per formula unit at a certain temperature</td>
</tr>
<tr>
<td>Hᶠ</td>
<td>hydrogen to metal ratio per formula unit</td>
</tr>
<tr>
<td>Hᶠₑₜ</td>
<td>maximum hydrogen to metal ratio per formula unit at room temperature</td>
</tr>
<tr>
<td>P₀ₜ</td>
<td>downstream pressure, pa</td>
</tr>
<tr>
<td>η'</td>
<td>maximum reacted fraction</td>
</tr>
<tr>
<td>η</td>
<td>reacted fraction</td>
</tr>
<tr>
<td>E_p</td>
<td>expansion coefficient</td>
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<tr>
<td>ħ</td>
<td>convective heat transfer coefficient, W/m² K</td>
</tr>
<tr>
<td>H(x)</td>
<td>Heaviside step function</td>
</tr>
<tr>
<td>t_sm</td>
<td>time for smoothing the Heaviside function</td>
</tr>
<tr>
<td>l</td>
<td>tank length, m</td>
</tr>
<tr>
<td>Cᵥ</td>
<td>discharge coefficient</td>
</tr>
<tr>
<td>A</td>
<td>cross sectional area, m²</td>
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Subscripts

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tr>
<td>a</td>
<td>absorption</td>
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<tr>
<td>d</td>
<td>desorption</td>
</tr>
<tr>
<td>eff</td>
<td>effective</td>
</tr>
<tr>
<td>g</td>
<td>gas phase</td>
</tr>
<tr>
<td>r</td>
<td>radial</td>
</tr>
<tr>
<td>s</td>
<td>solid phase</td>
</tr>
<tr>
<td>t</td>
<td>time for smoothing the Heaviside function</td>
</tr>
<tr>
<td>refs</td>
<td>reference</td>
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<tr>
<td>eq</td>
<td>equilibrium</td>
</tr>
<tr>
<td>i</td>
<td>initial</td>
</tr>
<tr>
<td>f</td>
<td>final</td>
</tr>
<tr>
<td>fl</td>
<td>heat exchange fluid</td>
</tr>
</tbody>
</table>

Most of the recent studies [2–8] of metal-hydride systems have been devoted to the optimum designs of heat transfer systems in order to increase the performance of the metal-hydride storage tanks. There has been less concentration on developing models suited to the simulation of practical systems, but it is important to consider all realistic factors which affect a system’s smooth running.

Minko et al. [9,10] made additions to the basic mathematical model of a LaNi₅–H₂ bed for the calculation of the effective thermal conductivity and the bed porosity. A correlation for the hydrogen outlet flow rate was used in the model by Yang et al. [11]. Some improvements, including introducing realistic geometry and using validated parameters in the model, were made by Xiao et al. [12]. However, some aspects of a practical system, such as injection of hydrogen and a comparison of fixed-temperature vs variable temperature cooling systems have not previously been studied.

In the first part of this paper [1], a number of assumptions were tested and improvements made to the usual models. The usual assumption of a metal-hydride system model, which is the treatment of hydrogen as an ideal gas, was examined and found to be a justifiable simplification for pressures up to about 100 bar and at temperatures around 300 K. Experimental data for LaNi₅ were used to develop an empirical equation for equilibrium pressure as a function of reacted fraction and temperature. The maximum reacted fraction was also calculated as a function of temperature, in line with experimental observations.

Experimental data for effective thermal conductivity from Pons and Dantzer’s study [13] were fitted and used in this model. Hydrogen in-flow and out-flow were modelled to represent realistic conditions and the thermal fluid temperature could be varied according to whether the bed was absorbing or desorbing [1].

These modifications align the model more closely with experimental conditions as well as enabling the investigation of experimental parameters such as hydrogen inlet and outlet flowrate, the amount of hydrogen injected into or withdrawn from the tank, and facilitate an investigation of the effects of varying the thermal management fluid.

The model

A three-dimensional mathematical model [1] based on the work of Hardy and Anton [14,15] was applied to a horizontally-mounted, axially symmetric, cylindrical tank containing 100 kg LaNi₅ with a hydrogen capacity of 1.5 kg. The thermal management system consisted of a system of fins embedded in the hydride bed with concentric tubes for inlet and outlet of the temperature controlled fluid. The model was solved by COMSOL Multiphysics 4.3 specifically for the LaNi₅–H₂ system but can also be used for all metal-hydride tanks by adapting those equations which depend on the material used for H₂ storage.
The details of tank geometries, mathematical models, the modifications applied to the governing equations, the equilibrium pressure and also reaction kinetic equations of the MH mathematical model have been fully described in the first part of this paper [1]. This physical system used to demonstrate the model was chosen to approximate an experimental system being developed. As the aim of the experimental design is to study the effect of poor or limited thermal management and the constraints of pressure and temperature ratings, this is quite deliberately not an example of the best possible thermal management, but a model of a real system using a popular fin-based thermal management design.

### Results and discussion

#### Initial conditions for repeated cycling

In practical hydrogen storage each absorption or desorption phase starts with the final conditions of the previous tank state. In order to replicate real world conditions of cycling between pre-set states of absorption and desorption, the final values of these parameters after the completion of the absorption phase were used as the initial conditions for the desorption phase. To implement these constraints with the model, the final conditions were used as the initial conditions for the next approximation, iterating until these initial parameters were the same as the final condition. All the results presented here were obtained by this method.

If less H₂ is added, absorption will cease once the pressure of H₂ on the metal bed decreases below the absorption equilibrium pressure at the current temperature and H/M value, leading to incomplete hydrogenation of the bed. For LaNi₅, the equilibrium pressure at 300K is 2–3 bar, so a practical tank system will always have this pressure upon completion of the absorption phase and hence at the start of desorption.

Similarly, if the desorption phase runs to completion, the pressure in the tank must be lower than the desorption equilibrium pressure at the current temperature and H/M value. This will typically be close to zero. Hence the absorption phase must start with the injection of H₂ and the absorption begins as soon as the pressure in the tank is above the equilibrium pressure. So it is not practically possible to have a high pressure of H₂ as an initial condition for the absorption phase. To model a real tank, a model of H₂ injection is necessary.

#### Hydrogen injection

The implementation of an injection profile in time for introducing hydrogen into the tank from an external source during absorption, allows for the time duration and the total amount of added hydrogen to be varied. In the first part of this series [1] a smoothed heaviside step function was employed to synthesize a pulse of hydrogen supplied to the tank and, on the other hand, for desorption, hydrogen out-flow was considered proportional to the difference between the tank pressure and an external pressure (0.1 bar) based on the mass balance of the discharge of a compressible gas from a container in adiabatic condition (the details of these calculations are given in part 1 of this series).

**Injection time**

To achieve full absorption it is necessary to inject enough H₂ to fully hydride the bed at the current temperature and still provide a gas pressure at or above the equilibrium pressure. In this case, for the tank size modelled, 150 g hydrogen above what was required to fully charge the 100 kg LaNi₅ was injected to the tank, a total of 1.65 kg. This results in a non-zero pressure at the end of the absorption and therefore at the start of the desorption.

**Fig. 1(a)** shows the effect of varying the rate of injection from 5 h to 20 h on the hydrogen uptake by the storage material. As expected, the more slowly the hydrogen is injected the longer it takes to reach maximum capacity. The total amount of hydrogen injected is sufficient to fully charge the storage material.

For this study of the injected hydrogen, the inlet temperature of the tank coolant was maintained at 303 K. As shown in **Fig. 1(b)** the bed temperature starts at 266.97 K (this is chosen to match the bed temperature at the end of the previous desorption step), rises with the exothermic absorption to a peak which corresponds to enthalpy generation and then cools under the effect of the thermal fluid.

Although a higher hydriding rate can be achievable by faster hydrogen injection, bed pressure increases rapidly with the hydrogen input and needs to be maintained below the design pressure of the tank. The pressure variations over time for different times of injection are shown in **Fig. 1(c)**. The relatively slow charging time is a consequence of the chosen physical tank parameters, in particular the size of the storage and the design of the thermal management system. Poor thermal management reduces the reaction rate as the bed temperature rises and consequently the injected hydrogen increases the gas pressure rather than converting to the hydride. The pressure rating of the vessel then imposes a limit on how quickly the hydrogen can be injected.

**Injection amount**

The amount of hydrogen injected was varied between 1.45 kg and 1.65 kg. For this study the injection time was maintained at 10 h and the heat exchange fluid temperature was fixed at 303K.

As shown in **Fig. 2(a)**, although 1.5 kg is the maximum capacity of 100 kg of LaNi₅, it is not enough to complete the absorption since sufficient driving pressure (difference between system pressure and equilibrium pressure) will not be supplied.

**Fig. 2(b)** shows average bed temperature for different amounts of hydrogen injected. For 1.65 kg this is slightly higher whereas the average temperatures for 1.5 and 1.45 kg injections are similar since the rate of hydriding for both are also similar.

**Fig. 2(c)** shows the changes in bed pressure over time for different amount of injected hydrogen. As can be seen only 10% increase in injected hydrogen leads to a much greater
Fig. 1 — Effect of different injection times on (a) hydrogen absorption rate (b) time-evolution of average bed temperature and (c) time-evolution of bed pressure. (d) shows the profile of the hydrogen inlet flow rate.
driving pressure which should be taken into account when designing the tank.

Effect of the heat exchange fluid temperature on the hydrogen cycling

In previous studies [16,17] in order to maintain the required temperature for the reactions cold and hot fluid temperatures typically ~293 K and ~313 K have usually been used for absorption and desorption processes respectively. In the present work two different methods of controlling the thermal fluid temperatures were compared: fixed fluid temperature for both absorption and desorption and variable fluid temperature: switching between high and low temperatures alternatively according to whether the sample is desorbing or absorbing.

As discussed in Section “Injection time”, the amount of hydrogen required to complete absorption was taken as 1.65 kg. This hydrogen was injected over 10 h as a compromise between rapid hydrogenation and reduced pressure and temperature excursions.

Absorption is influenced by hydrogen flow rate to a greater extent than coolant temperature, unlike desorption which

Fig. 2 – Effect of injected amount of hydrogen on (a) hydrogen cycling rate (b) average bed temperature (c) bed pressure. The hydrogen was injected over 10 h.
shows little dependence. As desorption completes with different reacted fraction amounts by employing different coolant temperatures, the reacted fraction initial condition varies for the absorption cycle. Hence to keep the total inserted amount of hydrogen at the tank and the time of injection at 1.65 kg and 10 h respectively, hydrogen flow rates were varied slightly in these calculations.

Fixed heat exchange fluid temperature
The sensitivity of hydrogen cycling to the fluid temperature, where the final thermal fluid temperature is constant for both absorption and desorption, was investigated by examining three different fixed temperatures, 293, 303 and 313 K. Fig. 3(a) shows the result of running the model for these fixed temperatures where a cycling time of 11 h was used for both absorption and desorption. A full absorption/desorption cycle is shown in the figure. In each case, the start and final conditions of pressure, temperature and reacted fraction were matched by iterating successive approximations.

1.65 kg of hydrogen injected over 10 h produces near full absorption before the desorption cycle starts. The highest temperature (313 K) preferentially facilitates desorption which produces a final value for the reacted fraction lower than the fluid temperatures. Since this is used as the initial condition, the absorption cycle for that temperature also starts from a lower reacted fraction – which is an advantage for the absorption process.

Fig. 3 – Effect of coolant temperature on (a) hydriding and dehydriding rate (b) the time-evolution of average bed temperature.
Fluid temperatures higher than 313 K accelerate desorption but decrease hydrogen storage capacity due to reduced absorption in the set time. Similarly, temperatures colder than 293 K adversely affect the dehydridding rate and hence the start and final reacted fraction.

Fig. 3(b) shows the variation of the average bed temperature by time for these fixed thermal temperatures. The choice of fixed temperature for the thermal fluid is a compromise between the kinetic rates of the absorption cycle and the desorption cycle. As can be seen in Fig. 3(b) showing the average bed temperature as a function of time, the higher thermal fluid temperature leads to higher temperatures during absorption due to slower removal of the heat generated by the exothermic reaction. With a fixed time for the cycle, this could lead to incomplete absorption and hence a lower effective tank capacity. For 313 K, because the temperature of the bed at the end of absorption is slightly higher (325 K, cf 300 K for the 293 K thermal fluid case), the maximum absorption possible is slightly lower, which can be seen in Fig. 3(a). However, for desorption, the 313 K fluid provides faster heat supply to the endothermic reaction and the desorption proceeds to a lower reacted fraction in the available time. This provides a better overall storage factor than the lower fixed temperature thermal fluid condition (303 K or 293 K).

Cycled heat exchange fluid temperature
Switching the fluid temperature between two set temperatures for absorption and desorption may facilitate faster absorption and desorption. If the thermal fluid temperature is decreased during absorption and increased during desorption, heat exchange during the exothermic and endothermic reactions could be facilitated. An additional system cost of heating and cooling the thermal fluid mass is also incurred. Depending on the coolant flow rate and the set temperatures for each process, it takes time for the bath to reach the target temperatures. Two different temperature ranges were considered, 283–313 K and 283–343 K to determine the effect on the bed thermal conditions and the overall capacity.

For the modelling presented here, the heating and cooling capacity was taken to be 2000 W, resulting in a time to heat/cool the fluid from 8 to 16 min which was small compared to the cycle times for absorption and desorption. Fig. 4(a) and (b) show simultaneous changes of average bed temperature and

Fig. 4 – Cycled heat exchange fluid temperature and average temperature of the bed for (a) 313–283 K and (b) 343–283 K.
temperature of cycled heat exchange fluid varying from 283 K to 313 K and 343 K respectively. Note that the model has been run repeatedly to iterate to the same initial and final conditions. This is done by choosing an initial condition and modelling both absorption and desorption cycles for a set time which is sufficient for both cycles to complete. The final conditions (pressure and temperature) at the end of the desorption cycle are then used as new initial conditions for absorption and the model is run again. This process is repeated until it iterates to a consistent set of conditions such that the end of desorption matches the start of absorption and the cycling could in principle be run indefinitely.

Hydrogen cycling rates obtained with these two cycled fluid temperatures and the fixed fluid temperature 313 K, are compared in Fig. 5. Comparing the two cycled temperature ranges 313–283 K and 343–283 K, it can be seen that the range with the higher temperature excursion causes a higher dehydriding rate and a more complete desorption (98%) while the lower temperature range leaves the tank with a higher amount of hydrogen in the bed (due to only 93% of full desorption). This, in turn, starts the absorption with a higher initial hydrogen reacted fraction. To take the time of injection of 10 h and 1.65 kg of the total amount of hydrogen, lower flow rates were considered for higher initial amounts of hydrogen. So, cycling the fluid temperature leads to greater capacity but requires a significant excursion in temperature which has an associated energy cost.

Fig. 5 also shows the effect of fixed temperature at 313 K for comparison purposes. While the fixed 313 K fluid temperature is slightly poorer in terms of capacity and absorption–desorption cycle time, the economic advantages of the simpler system at quite moderate temperature may justify the choice of fixed temperature for a practical tank system.

Conclusions

The three-dimensional multiphysics model presented in part 1 of this series [1] was applied to a real metal-hydride storage tank. The properties of LaNi5 were used for the calculations. This model was developed to be able to examine the effects of hydrogen flow rate adjustable by the time and the total amount of hydrogen injected to the tank.

As in a real system, absorption and desorption may start with different conditions in terms of the amount of hydrogen, pressure and temperature depending on the state at the end of the previous process. In this work, the initial conditions for desorption were defined as the conditions at the end of the time allotted for absorption (and vice versa). With this capability, the model can simulate continuous cycling.

The impact of two different approaches to heat exchange, cycled and fixed temperature, on the performance of hydrogen cycling were studied. The results showed that varying of the temperature of circulating bath leads to more complete and faster hydrogen cycling but the effect was small. The energy costs imposed on the system by changing the circulating fluid temperature would need to be taken into consideration and weighed up against the benefits of mildly higher performance of the hydrogen cycling.

Perhaps most importantly, this work highlights the importance of considering operating-like conditions in the injection and removal of both hydrogen and heat when testing system designs. An optimal system under one set of injection or bath conditions may be sub-optimal under another. Only by including these effects in the model can optimisation strategies be relied upon for the improvement of storage devices.

![Diagram](image.png)

**Fig. 5** — Comparison of hydrogen cycling at cycled fluid temperature (313–283 K), fixed temperature (313 K) and cycled fluid temperature (343–283 K).
REFERENCES


CHAPTER FOUR

Experimental and Theoretical Study of Compositional Inhomogeneities in LaNi$_5$D$_x$ owing to Temperature Gradients and Pressure Hysteresis, Investigated using Resolved In-situ Neutron Diffraction

4-1 Introduction

References

4-1 Introduction

The necessity to develop reliable and comprehensive models for the design and optimisation of experimental and commercial MH tanks has been discussed in the preceding chapters. A good test of these models is to predict unusual states of the MH beds during absorption and desorption. Such states arise from the complex interaction of hydrogen pressure and temperature of the MH bed, together with properties such as hysteresis. For this purpose, suitable experimental data obtained under unique operating conditions are needed for thorough testing.

As discussed in chapter 2, the hysteresis and the plateau slope of a pressure-composition isotherm are intrinsic properties of the metal-hydrogen system and these vary among different metals. For example, the archetypal AB₅, LaNi₅, has a relatively high hysteresis and a relatively flat plateau pressure.

Although metal alloys have relatively high thermal conductivity, their use in the form of powder leads to poor thermal properties of the MH beds due to low contact area between the particles. In addition, the particle size of the metal decreases further due to decrepitation, resulting from the expansion of the unit cell during hydriding together with the brittleness of the alloy particles. This occurs in the first few cycles of hydriding and dehydriding. The change in the size and morphology of the particles leads to reduction in the contact area and this exacerbates the heat conduction problem.

The difference between hydrogen pressure and equilibrium pressure drives the sorption reaction. As the equilibrium pressure of the MH bed has a direct relationship with temperature, an increase in the bed temperature, which can be external or due to the exothermic absorption reaction, decreases the hydriding rate for the same hydrogen pressure. If the temperature is sufficiently high, the bed can start to desorb hydrogen.
For temperatures below the critical point, the equilibrium pressure for absorption in LaNi$_5$ and most intermetallics is higher than the equilibrium pressure for desorption at the same uptake fraction. This hysteresis means that both pressure and temperature excursions are not reversible.

Significant heat produced due to absorption following the initial contact of the metal alloy with a large amount of hydrogen causes a sharp temperature rise in the sample. The poor effective thermal conductivity prevents those parts which are furthest away from a heat exchange system (such as the walls of the container or fins) from cooling, resulting in temperature gradients over the MH bed. As both the absorption and desorption plateau pressures increase with increasing temperature, the cooler parts will absorb more hydrogen while the higher temperature MH further away from the cooling system will have reduced absorption or even desorb. This causes significant inhomogeneities in the reacted fraction over the bed, which can persist once thermal equilibrium is reached.

For a material with no hysteresis, as the temperature starts to equilibrate, the previously warmer parts with lower hydride fraction begin to absorb as the desorption equilibrium pressure drops below the current hydrogen pressure. This removes hydrogen from the gas phase, reducing the pressure, which in turn causes the higher hydride fraction parts of the material to desorb. Therefore, as the temperature equilibrates, so does the relative proportion of metal to metal-hydride, leading to a homogeneous medium.

However, for a MH material with high hysteresis, the equilibrium pressure of desorption is significantly lower than that of absorption at the same temperature. This means the system pressure must drop substantially before the hydride desorbs. The parts which are initially cooler with higher concentration of H$_2$ do not release hydrogen; consequently there is insufficient hydrogen in the gas phase for the parts with lower concentration of hydrogen to absorb despite having cooled.
The first indication of this was the experiments of Pons and Dantzer [1] where LaNi$_5$ was subjected to a brief temperature excursion. A coarse difference between the temperatures of two parts of a small MH bed was found, one in the centre of the bed and another near the heat sink. The composition state of the two points was inferred through a diagram of temperature versus hydrogen concentration, from which the hysteresis effect on the temperature and hydrogen content of the two positions could be determined. The coupling between temperature and composition gradient due to the exothermic absorption together with hysteresis was later discussed by Gray et al. [2]. Such behaviour can be attributed due to the large-aliquot effect, which is the consequence of fast injection of a large amount of hydrogen into the sample and the consequent temperature excursions as described above.

Subsequently, this was observed by Kisi and Gray [3] using in-situ X-ray diffraction and neutron diffraction (ND) measurements of the surface of a sample of LaNi$_5$-hydride and in the bulk of LaNi$_5$-deuteride respectively. These data are, however, qualitative; for testing the MH models quantitative data are needed. ND is suitable for structural studies of hydrides - in particular for bulk materials due to high penetration depth. Neutrons can deeply penetrate the materials usually used in the fabrication of the pressure cells as well as the hydrogen absorbing material itself.

In this experiment, an in-situ Neutron Diffraction (ND) measurement has been conducted using a time of flight spatially-resolved neutron diffractometer, ENGIN-X, at the ISIS pulsed neutron source (Rutherford Appleton Laboratory, UK). Deuterium was used instead of hydrogen due to the large incoherent scattering from hydrogen.

Deuterium prepared in a known reference volume at a selected pressure was allowed in to a sample cell containing LaNi$_5$. The amount of hydrogen was pre-set to ensure an overall average hydride reacted fraction of 50% in the bed. To accentuate the large-aliquot effect, the
pressure step was applied to the sample as fast as possible to achieve a significant temperature gradient.

The bottom and top of the aluminium cell were equipped with copper heat sinks with water circulated through them from a constant temperature bath to supply and remove the heat of desorption and absorption. The fluid temperature was maintained at 23 °C.

Neutron diffraction patterns were taken starting several hours after the initial absorption, to ensure that thermal equilibrium had been reached. Small volumes in different locations of the sample were scanned in order to map the spatial phase distribution. The volume detected was adjusted through the dimensions of the horizontal and vertical neutron beam slits and the detector collimators. The collimation was selected to define as small a gauge volume as possible but still have sufficient neutron counts for high resolution patterns. The cell was translated in both the axial and radial directions. The measurements were taken incrementally starting at bottom of the cell and proceeding in steps up to the highest possible point without the neutron beam striking the bolts at the top of the sample cell. The axial measurements were repeated at three radial points, near the wall of the cell, approximately the halfway along the radius and at the centre of the cell. Five radial scans were taken between the edge and the centre as high as possible, in the middle and near bottom of the cell.

The phase proportions were determined quantitatively by Rietveld refinement of the diffraction pattern for each position in the sample, which represents the average structural state over the volume of that voxel. The phases are easily distinguished because parameters of metal-hydride phases with different hydrogen contents are generally different due to the volume expansion of the particles absorption of deuterium.

As expected, it was found that the LaNi$_5$ near the walls of the cell materials underwent a significant reaction and those parts far from the walls remained at a low reacted fraction even
after thermal equilibration (many hours). In particular, the centre of the cell, which was furthest from any cell wall, was observed to have a very low reacted fraction.

The model described in Chap 3 was modified to suit this experimental arrangement. The modification consisted of removing hydrogen flow rate from the mass balance equation and assuming high initial hydrogen pressure. The geometry was also changed to suit the sample cell. This model was then solved using COMSOL Multiphysics. These conditions simulate the experimental situation as the total amount of deuterium available at relatively high pressure was almost instantly applied to the sample.

Pressure drop, average reacted fraction and temperature of the centre of the cell calculated by the model were compared with the experimental measurements, and showed a satisfactory agreement. This agreement was obtained using a variable effective thermal conductivity, as introduced in the modelling paper [ref]. Most previous models presented in the literature common use a constant effective thermal conductivity for LaNi₅ (as described in the review paper in chapter 2 [4]). Repeating the modelling with a constant effective thermal conductivity gave a significant difference between calculated and experimental results, resulting in a much poorer fit.

The spatial distribution of phase proportions in the axial and radial directions obtained from the ND measurements was also compared with the model predictions. The model generally emulated the experiment well, although there were some differences which may be attributed to very high thermal gradients or the presence of the gamma phase which is not considered by the model.

The model could not predict the higher absorption at the top of the cell, (the entrance of the hydrogen), over the absorption at the bottom of the cell. This can be explained by the absence of the mass flow rate in the model and shows the importance of considering this parameter.
References


STATEMENT OF CONTRIBUTION TO CO-AUTHORED PUBLISHED PAPER

This chapter includes a co-authored paper. The bibliographic details of the co-authored published paper, including all authors, are:

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My contribution to the paper involved:

1) Take part in the experiment
2) Development of the model
3) Preparation of the results in a comparable form
4) Collaborate in manuscript preparation

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4-2 Neutron paper: Experimental and theoretical study of compositional inhomogeneities in LaNi$_5$D$_x$ owing to temperature gradients and pressure hysteresis, investigated using resolved in-situ neutron diffraction,

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Experimental and theoretical study of compositional inhomogeneities in LaNi$_5$D$_x$ owing to temperature gradients and pressure hysteresis, investigated using spatially resolved in-situ neutron diffraction

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An in-situ neutron investigation of the spatial variation in hydride composition of LaNi$_5$ after a single absorption pressure step was performed. Compositional inhomogeneities are formed due to the strong temperature gradients created by the rapid absorption process coupled with the pressure and temperature hysteresis of the metal–hydrogen interaction. The hydride fraction of LaNi$_5$ in a cylindrical cell was mapped using the ENGIN-X stress/strain instrument and quantitative phase analysis performed using the Rietveld technique. The material was observed to preferentially absorb hydrogen close to the edges of the cell where heat transfer out of the material was more efficient. This spatial variation was maintained even after thermal equilibration. The experimental results are compared to predictions of a 3D multiphysics model solved by the software package COMSOL. The good agreement achieved demonstrates the suitability of this model for optimisation of metal hydride tank systems.

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Introduction

The increasing development of renewable energy supply systems, with an inherent sporadic output which is often dependent on weather conditions, such as photovoltaic and wind energy, requires the development of energy storage systems [1]. A hydrogen-based storage system has the potential to store excess energy as hydrogen during high output periods and supply energy when the direct output drops below demand with the use of fuel cells [2–4]. To do this, the hydrogen must be stored until required.

Hydrogen storage research has been extensive, with a focus on vehicular applications [2,5,6]. For stationary applications however, such as smoothing the intermittent supply of renewable energy sources, requirements such as high gravimetric and volumetric capacities are less important [7]. Solid state hydrogen storage in hydrides and complex
Hydrides at moderate pressures is a safer and often cheaper and more convenient storage system than pressurised or liquefied gas, and a number of metal hydride (MH) tank systems have been built or proposed [4,8–10].

Hydrogen absorption by metal hydrides is an exothermic reaction, in some cases with quite large formation enthalpies [11]. As the temperature of the metal hydride bed rises, so does the equilibrium pressure of the material, necessitating higher pressures to maintain the absorption process, or removal of the heat to allow absorption at the initial applied pressure. The converse applies during desorption where the material cools and requires the addition of heat to maintain the release of hydrogen [12]. Thus for practical storage tanks, heat management is a significant issue and there have been many types of heat management systems designed for MH storage tanks [13–17].

The development and testing of new tank heating/cooling systems, particularly for medium to large scale tanks, is expensive and modelling offers a way to explore novel designs as well as to optimise parameters for a particular design. It is therefore important that such models accurately predict the pressure, temperature and reacted hydride fraction, both spatially and temporally. Testing the models under different operating conditions where the outcomes have been experimentally observed is a crucial part of the continuing improvement of MH tank models.

If sufficient hydrogen to hydride a significant fraction of the metal alloy in a MH tank is released into the tank over a short time interval, then during the hydrogen absorption the heat released in the exothermic reaction, coupled with the typically poor effective thermal conductivity of the metal hydride powder, leads to temperature gradients in the MH bed [18]. Although an active cooling system may be in effect, only those parts of the bed closest to the heat exchange system are effectively cooled. Any cooled, unreacted metal will absorb hydrogen faster than hotter regions due to the lower equilibrium pressure, leading to greater absorption where the material is actively cooled and corresponding less absorption where the material is at a higher temperature. Consequently, there will be a spatial variation of the reacted fraction (f, the proportion of the bed that is hydride) throughout the tank [18,19].

In the absence of hysteresis, and provided the isotherm exhibits a relatively flat plateau, as the material proceeds to thermal equilibrium the low reacted fraction areas will release some hydrogen and ultimately the spatial inhomogeneity will disappear. Hysteresis occurs where the equilibrium pressure for a given composition or reacted fraction is different depending on the history of the reaction, typically observed as the plateau pressure of a pressure-composition-temperature (PCT) isotherm lying at a lower pressure for desorption than for absorption. This means that for a given temperature, a higher pressure is required for the system to absorb than is required for hydrogen release. Hysteresis is a well-known phenomenon in metal hydrides [7,12], although the exact origins are still uncertain.

In the case of a metal hydride that demonstrates hysteresis and is subjected to rapid hydrogenation, the spatial variation of reacted fraction caused by temperature inhomogeneities does not disappear even after thermal equilibrium has been reached. This is because those areas which have a substantial reacted fraction do not release hydrogen because the pressure has not dropped below the equilibrium pressure for desorption. There is then insufficient pressure for further absorption for the unreacted areas even though they have cooled and, therefore, the spatial inhomogeneity is maintained [20].

A consequence of this is that measurements of the pressure-composition isotherm for a common intermetallic such as LaNi₅ can yield very different results depending on the magnitude of the pressure step applied to the sample [21]. Compositional inhomogeneities due to temperature excursions was predicted and observed by Pons and Dantzer [18]. The effect was reviewed by Gray et al. [20] where it was found that the primary cause of this difference, termed the “large aliquot effect”, derives from the temperature gradients in the sample in conjunction with hysteresis. Kisi and Gray [19] observed a difference in the average reacted fraction for a small sample using neutron diffraction by masking out the centre of the neutron beam. This qualitatively indicates the spatial variation of reacted fraction in LaNi₅, but does not give quantitative information that would be suitable for modelling of large scale hydrogen storage tanks. Gray [22] obtained a neutron diffraction pattern for LaNi₅ after a single absorption step which shows substantial peak broadening due to averaging over the mix of phases in the sample. This is reproduced in Fig. 1 and compared to a diffraction pattern for the same uptake, but approached in small steps approximately isobarically. Currently no spatially resolved experimental data on the compositional inhomogeneities in medium scale storage systems exists against which to test the capability of the different models.

The objective of this study was to experimentally map the spatial variation of hydrogen uptake due to the large aliquot effect described above, confirming previous studies and...
verifying the multiphysics model. LaNi₅ alloy in an aluminium sample cylinder cooled at the top and bottom was injected with deuterium gas in a single pressure step to produce an average reacted fraction of the alloy of approximately 0.5. After thermal equilibration the composition of the sample was mapped using spatially resolved neutron diffraction to determine the variation in composition. This is the first time the effect of the large aliquot effect on the spatial variation of hydrogen uptake has been mapped quantitatively. A 3-D multiphysics model for this material and experimental tank design undergoing a single step absorption was solved using COMSOL Multiphysics 4.3 to assess the capability of the commonly-used FEA model by comparison with the experimental data. Multiphysics modelling has not been previously applied to the large aliquot effect and this demonstrates the ability of the model to describe the complex inter-relationship of hysteresis and thermodynamics in the metal-hydrogen reaction.

**Experimental arrangement**

A custom cylindrical aluminium (Al 6061) sample cell, of 1 mm wall thickness, 18 mm ID and 60 mm height with a stainless steel top was used (see Fig. 2). The cell was rated to 55 bar at room temperature, with water from a constant temperature water bath circulating through copper blocks attached to the top and bottom of the cell to actively control the sample temperature. The sample cell contained approximately 45 g of commercial LaNi₅ from The Japan Steel Works, Ltd. A custom manometric gas handling instrument similar to [23] was used to apply D₂ gas pressure to the sample. The sample was first activated by applying approximately 30 bar D₂ pressure with the water bath temperature set to 50 °C, then subsequently desorbed. The sample was then cycled twice more to ensure that all of the sample was activated and that the decrepitation that occurs with the initial hydriding [12] was largely complete. For this cycling, the water bath temperature was set to 23 °C for absorption and 50 °C for desorption for increased kinetics. For the neutron diffraction experiment, with the water bath temperature set to 23 °C, sufficient D₂ gas was prepared in a reference volume so as to result in the sample having a composition of approximately LaNi₅Dₓ (x = 0.5) when applied to the sample in an isochoral step. The single pressure step was applied as fast as possible so as to achieve significant temperature gradients in the sample. The sample was left for approximately 8 h to allow the sample to reach thermal equilibrium and remained in this state for all the diffraction measurements. The low temperature of 23 °C was deliberately chosen to reduce the likelihood of permanent formation of the γ phase [24].

**Neutron diffraction measurements**

Neutron diffraction measurements were taken in-situ on the Engin-X diffractometer at the ISIS spallation neutron source, Rutherford Appleton Laboratories, UK. Through use of the detector collimators and by masking the incident neutron beam, it is possible to observe a small element (gauge volume) in the MH bed while excluding the Bragg reflections from the cell [25]. The hydride composition of the element (reacted fraction) can be determined from the analysed diffraction pattern since the lattice parameters are different for α-phase LaNi₅-D (solid solution) and β-phase (hydride). Translation of the cell allows for a mapping of the composition of the material throughout the MH bed.

The first set of measurements were performed using the 3 mm detector slits and 3 mm horizontal and vertical beam slits, giving a 3 × 3 × 3 mm³ measurement volume. The measurements were taken incrementally in the z-direction for points near the edge of the cell (r = 7.68 mm), starting at z = 2 mm (lowest position) and proceeding in steps of 3 mm up to z = 41 mm. This was the highest measurement position possible for all beam sizes without the neutron beam striking the bolts at the top of the sample cell. This vertical scan of measurement points was repeated at radial values of r = 3.93 mm (approximately halfway along the radius) and r = 0 mm (centre of the cell). To save time, only every second point in the centre of the cell at high z values was measured.

To achieve higher resolution in the z-direction in the lower part of the cell, the vertical beam collimation was reduced to 1.5 mm (3 × 3 × 1.5 mm³ measurement volume) and four
vertical points measured starting at \( z = 0.75 \) mm in steps of 1.5 mm. This was done for both the edge \((r = 7.68 \) mm) and the half radius \((r = 3.93 \) mm).

For higher resolution in the radial direction, the detector collimators were changed to 2 mm. The horizontal beam slits were set to 2 mm and the vertical beam slits set to 8 mm \((2 \times 2 \times 8 \text{ mm}^3 \text{ measurement volume})\). The larger vertical beam size was possible due to the slow change in composition in the z-direction and was made to reduce the time required for each measurement. Five scans were taken for points at \( r = 7.6 \) mm to \( r = 0 \) mm in steps of 1.9 mm, at vertical positions of \( z = 26 \) mm (middle) and \( z = 40.55 \) mm (upper). The vertical beam collimation was reduced to 4 mm \((2 \times 2 \times 4 \text{ mm}^3 \text{ measurement volume})\) and the same radial scan performed at \( z = 5 \) mm (lower). These beam position are shown in Fig. 2. The reason for shortening the vertical beam slits for the scans at the lower was because of the greater change in composition in the z-direction close the bottom of the cell.

The data were analysed with Topas Academic [26] using the Rietveld method to perform quantitative phase analysis (QPA), giving the percentage of the sample in the hydride phase \((\text{LaNi}_5\text{D}_{1-x})\) in the measurement volume of the diffractometer, which is used to calculate the reacted fraction. All parameters were constrained to achieve a stable and realistic refinement.

**Model**

A 3D multiphysics model described and applied to a MH tank system previously [27,28] was used and solved using COMSOL Multiphysics 4.3. In this model, the conservation laws for heat and mass flow are used together with thermodynamic and kinetic equations appropriate to the metal hydride material. Due to the symmetry conditions of the sample cell, the computational domain was chosen as half of the cylinder around the z-axis. This is shown in Fig. 2.

The assumptions listed below are normally employed in metal hydride models and have also been used in this model [27]:

1. The compression work and viscous dissipation are negligible
2. Any injected gas pressure distributes instantly throughout the system
3. The local thermal equilibrium is valid and radiative heat transfer is negligible
4. The tortuosity and dispersion terms can be modelled as diffusive fluxes
5. Both gas and solid have the same temperature (local thermal equilibrium)
6. Thermal and physical properties of the bed are not dependent on bed temperature or concentration in the bed.

**Initial conditions**

Initially, the sample and temperature-regulated cell are in thermal equilibrium, so the temperature of the system is assumed to be equal to the coolant temperature. For ease of computation, we start the model of the absorption process at time \( t = 0 \) s with an initial pressure of 31 bar in the cell and a reacted fraction of zero (no hydride).

**Boundary conditions**

The wall of the cell is impervious and under adiabatic conditions, meaning there is no mass and energy flow from or into the tank from the sides. The symmetry boundary condition around the z-axis is valid and the temperature of the base and top of the cell is taken to be constant at the coolant temperature.

**Results and discussion**

**Time evolution of the average reacted fraction and gas properties**

Based on the manometric uptake measurements, after the reaction had finished the sample had an overall composition of \( \text{LaNi}_5\text{D}_{6.6} \). Since the maximum deuterium uptake of \( \text{LaNi}_5 \) is \( \text{LaNi}_5\text{D}_{6.6} \), this corresponds to approximately 50% of capacity as intended.

An initial test of the model is provided by a comparison of the pressure and average reacted fraction in the bed, as a function of time after the deuterium is admitted to the cell. These are shown in Fig. 3. The experimental determination of the reacted fraction is provided from the recorded pressure and temperature measurements together with knowledge of the volumes and the equation of state for deuterium [29]. Reasonable agreement between the experimental and numerical results can be observed, although the model predicts a slightly quicker response than shown by the experimental measurement.

The temperature in the centre of the bed was measured using a K-type thermocouple and recorded during the experiment. Fig. 4 shows the recorded and the calculated temperature of the centre of the cell during absorption and after reaching thermal equilibrium. It is difficult to estimate both the volume sampled by the internal thermocouple and any time lag that occurred while the temperature was changing,
which makes comparison difficult. Despite this, good agreement is achieved between the time evolution of the experimental temperature in the centre of the sample and the predicted average sample temperature from the model.

Compositional inhomogeneities

The diffraction patterns for each position of the neutron beam in the sample were analysed and the reacted fraction was determined. An example diffraction pattern is shown in Fig. 5. The figure shows a diffraction pattern of a volume element close to the top of the cell which was approximately half reacted (alpha 47%, beta 53%). There is evidence of the gamma phase [24] for this part of the sample and these peaks have been identified in the figure, but these were not fitted. The effect of the gamma phase on the calculation of reaction fraction is estimated to introduce an uncertainty of 5%. This is significantly lower than the observed spatial variation.

As described earlier, three longitudinal (z-direction) scans at different radial positions were made with a $3 \times 3 \times 3$ mm measurement volume over the length of the cell and two more longitudinal scans at $3 \times 3 \times 1.5$ mm close to the lower of the cell. In addition, two radial scans were taken with a measurement volume of $2 \times 2 \times 8$ mm at the middle and top of the cell and another radial scan of $2 \times 2 \times 4$ mm was performed close to the bottom of the cell. The results of the analysed diffraction patterns for the reacted fraction for the longitudinal scans, together with the model results, are shown in Fig. 6.

It can be seen that the material close to the centre of the cell is significantly unreacted ($f < 0.3$), while sample close to the edge of the cell is nearly fully reacted ($f > 0.8$). The radial composition for model and experiment is shown in Fig. 7.

The experimental results shown in Fig. 7 for the radial dependence of the composition, indicate that generally the LaNi$_5$ mostly forms hydride (beta phase) near where it is cooled at the cell wall ($r = 7.6$ mm), while remaining unreacted in the middle of the cell ($r = 0$ mm). As the LaNi$_5$ starts to absorb, heat is released causing the sample temperature to increase. At the wall of the aluminium cell much of this heat is removed, owing to the relatively high thermal conductivity of Al. This results in the sample being hotter in the middle (far from the cell walls) and cooler towards the sides. This is seen clearly in Fig. 8, showing the model results for the calculated temperature variation throughout the cell as a function of time after exposure to deuterium.

The lower temperature regions of the sample then preferentially absorb deuterium due to the lower absorption equilibrium pressure at the lower temperature. Despite the material at the edge therefore releasing more heat, it remains at a lower temperature owing to the active cooling, whereas heat generated from areas that have absorbed in the middle of the cell is not removed and the centre of the cell remains at a higher temperature. This results in material close to the edges forming a greater proportion of the hydride (beta) phase and the material in the centre of the cell remaining unreacted.
(α phase), as is observed in the data and which is consistent with the observations of Kisi and Gray [19]. As described earlier, the presence of hysteresis in LaNi₅ causes the spatial inhomogeneity to be maintained even after the temperature has equilibrated. This is shown in the model calculations presented in Fig. 9 where there is little difference between the last two reacted fraction states at 1000 s and 5000 s.

Fig. 8 shows the temperature distribution in the MH bed and Fig. 9 the variation of reacted fraction throughout the bed at six representative times, 5 s, 25 s, 50 s, 200 s, 1000 s and 5000 s. It can be seen that after 1000 s (16 min) both temperature and the reaction have reached a stable equilibrium and no change is observed after a further 4000 s. As observed in the experimental results (Figs. 6 and 7), the material close to the wall of the cell, which is cooled by the thermal management, contains the majority of the hydride phase. The part of the bed furthest from the active cooling, the centre of the cell, absorbed the least deuterium.

However, all of the experimental results at low z values have a lower reacted fraction than higher parts of the cell, particularly at high r. As can be seen in Fig. 6 for the low z measurements and in Fig. 7 for the set of results along the bottom of the cell, the model estimates a higher reacted fraction along the radius for the lower part of the cell than for higher parts. This is because the aluminium base of the cell is thicker than the wall and actively cooled by a copper block through which the temperature controlled water flows. As a result, the base of the cell is even more effectively cooled than the walls and a higher reacted fraction would be expected.

As the deuterium enters the cell from the top, the top part of the metal alloy is exposed to hydrogen first and absorbs strongly, leaving the material furthest from the inlet starved of deuterium. Entry of gas at the top of the cell was not simulated by the model, as is clear from assumption 2 in the Model section. This depletion of hydrogen due to strong absorption close to the gas entry point has been mapped previously in an in-situ X-ray experiment using LaNi₅ between two Be windows [24]. In that experiment, the large aliquot effect was not observed due to the effective cooling of the thin (<1 mm) sample between the high thermal conductivity windows. So, while the experimentally observed spatial variation in hydride fraction in most of the cell represents an inhomogeneity due to the large aliquot effect, the spatial variation at the bottom of the cell is due to the physical shape of the cell and hydrogen inlet and the preferential absorption of the metal close to the inlet.

For comparison, the model was changed to represent the same sample with no hysteresis. The temperature and reacted fraction profiles for representative times up to 50,000 s are shown in Fig. 10. As expected, it can be seen that the spatial variation of the reacted fraction induced by the temperature gradients does subsequently disappear as the hydrogen in the sample redistributes. The time required for this is quite long due to the lack of hysteresis [30].
Conclusions

An in-situ experiment was carried out using spatially resolved neutron diffraction to measure the compositional inhomogeneities in LaNi5Dx owing to temperature gradients and pressure hysteresis, following a large single dose of hydrogen (the large aliquot effect). It was found that for most of the cell, those parts close to the wall (heat sink) hydrided strongly, while close to the middle of the cell, the sample remained largely unreacted. This quantitative mapping of the spatial variation of hydrogen uptake confirms previous qualitative results in the literature and is consistent with the described mechanism of the large aliquot effect [20]. In addition, for material close to the base of the cell, which was furthest from the deuterium entry point, the experimental results showed low absorption, due to the reduced amount of deuterium reaching those parts.

The quantitative mapping of composition in the current study was used to validate a mathematical model developed and solved using COMSOL Multiphysics. There was a reasonable agreement between the theoretical and experimental results for the upper parts of the sample cell. This demonstrates the ability of the model to successfully predict complex interactions between the metal and hydrogen involving irreversible temperature excursions. Closer to the bottom of the cell, which does not account for the physical location of the gas entry, did not match the experimental results and underestimated the reacted fraction. Further improvements to the model are needed to adequately simulate practical experimental conditions.

The large aliquot effect raises problems for routine characterisation of prospective hydrogen storage materials as well as the use of large scale metal-hydride storage tanks. The characterisation of hydrogen uptake through the measurement of hydrogen absorption isotherms (PCT measurements), as typically performed isochorally in a Sieverts apparatus [22], can be adversely affected by taking large steps in the hydrogen pressure. The resultant measured isotherm then lies between the absorption and desorption isotherms. In addition, the large aliquot effect is a specific example of the more general problem in metal hydrogen reactions which exhibit hysteresis, and this has consequences for operating hydrogen storage systems using hysteretic metal-hydride materials. The relationship between pressure and hydrogen content is only known for operating conditions where the pressure is increased monotonically (for the filling or absorption process) or decreased monotonically (for hydrogen release or desorption). Any pressure or temperature excursion which reverses the current absorption or desorption, such as demand exceeding supply, or the large aliquot effect, renders the state of charge of the tank system impossible to determine from the pressure.

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References


CHAPTER FIVE

Metal–Hydrogen System for Studying Mass and Heat Transfer Flow
during Hydrogenation and Dehydrogenation

5-1 Introduction
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  5-4-4 Thermal fluid system
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References
5-1 Introduction

The small-scale test of the developed model using volume-resolved neutron diffraction demonstrates that the model is able to predict the local phase proportions in the metal hydride bed. The cell containing the metal hydride for the diffraction experiments was too small to allow meaningful measurements of the internal temperature distribution. This requires a much bigger volume of material. Two cylindrical pressure vessels with approximately 30 ℓ internal volume have been designed to allow the internal temperature distribution to be mapped. The strategy is to move hydrogen back and forth between the tanks, so that one desorbs while the other absorbs, at a rate set by a flow controller. This avoids the expense of supplying fresh hydrogen for every experiment and also avoids the continual introduction of impurities in the hydrogen, while providing two sets of data per hydrogen transfer.

A preliminary study was carried out to aid the design of a heat management system. The aim with the choice of heat management system was not to have the best hydrogen storage performance, but to explore the internal temperature distribution under various operating conditions, in order to test the finite-element model to the maximum degree. The fin-and-tube heat exchanger chosen is expected to cause severe temperature gradients and therefore severe inhomogeneity of the phase proportions, which will be reflected in the global pressure–composition curve for the tank. This is to test the strength of the improved model (chapter 3) and a supplementary study for the smaller scale neutron diffraction experiment (chapter 4).

Both the finite-element model and the test tanks have been designed assuming a MH storage medium. There were two reasons for this choice: firstly because of their practicality in real-world applications for which low gravimetric energy density is not a problem and, secondly, because they generally exhibit pressure hysteresis, which via
the resulting compositional inhomogeneities can provide a very severe test of the model.

All the components for the system of tanks with heat management and computer-controlled gas handling have been purchased or built. Time constraints prevented commissioning and using the system as part of this project.

5-2 Choice of metal hydride

Most metal hydrides are based on intermetallic alloys, which are usually in the form of binary phases, often represented as \( A_xB_y \), where “A” is a metal which readily forms a hydride such as La, Ca, Ti, Y, Zr, and “B” is a metal which does not readily hydride such as Ni, Fe, Mn, Co, Cr, V. There are four family groups of intermetallics for hydrogen storage application: \( AB \), \( AB_2 \), \( A_2B \) and \( AB_5 \) [1].

These materials can be modified by substitution of another metal or by changing the relative proportions of elements to produce lighter and cheaper alloys or to change the thermodynamic properties in order to meet the fuel cell requirements (for example, 0-100° C and 1-10 bar).

\( \text{LaNi}_5 \), is the archetypal \( AB_5 \) storage material and has the advantages of fast kinetics, high life cycle and moderately low equilibrium sorption pressure and temperature. This material has been studied extensively, however, it has a relatively low gravimetric capacity (~1.5%) due to the weight of the La element. It has been suggested as suitable for stationary applications of hydrogen storage [1].

Commercial \( AB_5 \) alloys are often composed of mischmetal (Mm) which is a mixture of rare earth elements (Ce,La, Nd and Pr) instead of La, which is cheaper to produce due to the cost of separating the similar large mass elements, and modified by replacing Ni by a mixture includes (Ni,Al,Mn, Co). These modified alloys such \( \text{La}_{1-x} \)
\[ x \text{Mg}_x \text{Ni}_5, \ \text{La}_{1+x} \text{Mg}_{2-x} \text{Ni}_5, \ \text{La}_{1-x} \text{Ce}_x \text{Ni}_5 \] [2-4] and \( \text{LaNi}_{5-x} \text{Al}_x \) [5] can have different absorption/desorption characteristics and sometimes higher hydrogen capacity.

The exothermic hydrogen absorption reaction, and the endothermic desorption reaction requires the removal and addition of heat, in order to sustain the reaction. The enthalpy of formation of most reversible metal hydrides is 20-55 kJ/mol H\(_2\). Thermal management is therefore a necessary requirement of large scale MH tanks systems. Metal hydride beds usually have poor thermal conductivity due to poor contact between the small powder particles. For materials such as LaNi\(_5\), the reaction rate with hydrogen is largely determined by the thermal properties, rather than the intrinsic kinetics.

For this project, LaNi\(_5\) was selected as one test alloy, because it exhibits significant pressure hysteresis and fairly low plateau slope and has been extensively studied. The other alloy chosen is the same as used in the 120 kg H\(_2\) MH storage in the Sir Samuel Griffith Centre at Griffith University [6]. This is a proprietary commercial alloy developed and supplied by Japan Steel Works. It is an AB\(_5\) type with mischmetal in place of La and multiple B-atom substitutions. It is complementary to LaNi\(_5\), with low hysteresis and high plateau slope.

### 5.3 Experimental systems

Different experimental geometries and configurations of tanks and heat exchange systems have been examined to find optimum designs and materials. These can be categorised into two main groups:

1- vertical cylindrical tanks with internal heat exchange systems including coils or fins [7] or a combination of both [8, 9] as well as a combination of external cooling jacket and internal coil system [10].
2- horizontal cylindrical tanks with shell and tube-type exchangers equipped by internal fins and jacket [11]. These designs have been studied in order to reduce hydriding and dehydriding time through investigation of different parameters such as supply pressure, coolant flow rate and heat exchanger type [8, 9].

The goal here was to be able to map the temperature distribution, as a configuration that leads to strong temperature variations was chosen, namely multiple units of MH separated by radial fins attached to the central coolant tube away from the ends of the tank, such that each MH/fin unit should behave in the same way. This made it much easier to incorporate arrays of thermocouples to map the temperature distribution in separate units.

The primary purpose of this dual MH tank system is to test the predictive capability of the MH models such as the Hardy and Anton’s [12, 13] and the improved model [14, 15] described in Chapter 3. Excellent agreement was found with the small scale experiment using in-situ neutron diffraction to investigate the spatial variation of composition after a large aliquot of hydrogen. The comparison with the model results is given in chapter 4. The medium scale experimental arrangement using 100 kg of AB₅ metal hydride in each tank provides a further test of the model.

5-4 Design

5-4-1 System design

Fig. 5-1 shows an overall view of the dual tank system. Each tank contains 100 kg of alloy capable of storing approximately 1.5 kg of H₂.

Two digital pressure transducers measure the inlet pressure of H₂ into the tanks for absorption and out of the tank for desorption. In addition, a flow meter and controller
are located on the inlet/outlet of each tank to determine the amount of hydrogen either stored or discharged. Filters are installed on the gas stream of each tank to prevent powder from escaping.

Fig. 5-1- A schematic of the configuration of the dual tank system

Each tank is equipped with a temperature controlled water bath and circulator which drives temperature regulated water through the tank’s internal thermal management system. A data acquisition and control computer system records the temperatures throughout the hydrogen cycling, as well as controlling the gas and cooling system valves and thermal fluid temperatures. The arrangement of the experimental MH tank system is shown in Figure 5-2.
5-4-2 Tank Design

The AISI 316L pressure vessels were designed by Dr. Clotario Tapia-Bastidas using the AS1210 standard. The working pressure and temperature were chosen to be 30 bar and 370 K, respectively. A 2D drawing of the vessel and its cross section view is shown in Fig. 5-3.

The main components and features of the tanks are given in detail:

- a cylindrical body (I.D.: 204 mm, L: 1000 mm, wall thickness: 8 mm) with welded end cap
- two stainless-steel (AISI 316) flanges; one of them is the lid of the tank. The seal is a metal C-ring coated with PTFE.
- five threaded holes on the top of the tank body for loading metal powder into the tank body are then plugged to close the system.
- the cooling system is internal and consists of two concentric tubes for circulation of the cooling fluid. (external tube ID: 9.525, Internal tube: 6.35)
- eleven radial copper fins (outer diameter 175 mm, thickness 3.0 mm, axial spacing 93 mm centre-to-centre) for heat exchange between the MH powder and
the coolant. The two end fins are 1.5 mm thick and insulated on the outer side with Teflon, creating a boundary that simulates the conditions at the fins that have MH powder on both sides. This is intended to avoid end effects, so that each MH–fin unit (cell) should behave in the same way.

- twenty-four threaded holes for inserting thermocouples (K type, 1.5 mm diameter) sealed with Swagelok fitting with Teflon ferrules: an axial array of 10 in the central cell at a middle radius; a radial array of 9 in near the middle of the adjacent cell; a radial array of 5 near the fin in the other adjacent cell.

Fig. 5-3- 2D drawing from cross section view of the tanks

5-4-3 Gas handling system

The gas handling system is assembled from Swagelok and Hy-Lok fittings, details are shown in Figure 5-4. Hydrogen flows into and out of the tanks from one end of the tank across the top of the bed. In order to avoid metal powder escaping from the tank, a filter (SS-SCF3-VR4-P-225) is used. A pressure transducer with a pressure range of 0–70 bar (Druck DPI104) is placed after the filter to measure the inlet and outlet gas
pressure. A valve is also placed after the filter to make it possible for the pressure gauges to be fixed or changed without exposing the MH to air. A pneumatic valve and flow meter/controller (Bronkhurst F-211CV) control the direction and rate of hydrogen flow.

Figure 5-4- A schematic of the gas handling system

**5-4-4 Thermal fluid system**

Two refrigerated/heating circulators (Julabo-FP 45) with a heating and cooling power of 1 KWh each were chosen to add and remove heat to and from the tanks during desorption and absorption. Each tank is connected to a circulator, the temperature of which can be set by the control computer. This allows for different temperatures to be investigated as well as using different thermal fluid temperatures for absorption and desorption.

An ultrasonic flowmeter (Kobold type DUK) is used in the return stream of the cooling circulation to measure the flow rate.
The two circulators are used to determine the absorption/desorption cycles. When the temperature of the bath is set at the high desorption temperature (353 K) hydrogen is released since the equilibrium pressure at this temperature exceeds the current pressure. The heated water maintains heat flow into the desorbing tank which is cooled by the endothermic reaction. At the same time the other tank is cooled by the cold bath (293 K) and the hydrogen flows into this tank and is absorbed by the metal.

5-5 Fin optimisation

The intention of the overall tank design was to allow for significant temperature gradients in the bed with the quickest possible heat transfer between the adjacent bed material and the fin and tube walls, and poor temperature regulation in the furthest material from the heat sink. The dimensions and material of the fins were optimised to meet this goal. Although fewer fins can also give rise to poor thermal management in the bed, controlling temperature and pressure excursion due to the heat of metal-hydrogen reactions needs to be taken into consideration to avoid slowing the reaction or creating safety issues such as exceeding the working pressure or temperature. 10 fins were considered initially (as mentioned previously), but this was later changed to 11 fins to improve the symmetrical design of the tanks.

5-5-1 Mathematical modelling of the fins

A mathematical model to calculate the temperature profile and heat flux through the fins was built and run. A cross sectional view of the tank with internal cooling system (final design) together with the unit volume selected to apply energy balance in the model, is shown in Figure 5-5 (a). Figure 5-5 (b) shows the internal cooling system attached to the blind flange. Dimensions of the tank and cooling are shown in Table 5-1.
Table 5-1- Dimensions of tanks

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Internal cooling tube ( r_i )</td>
<td>6.35</td>
</tr>
<tr>
<td>External cooling tube radius ( r_o )</td>
<td>9.525</td>
</tr>
<tr>
<td>Internal radius of tank ( R )</td>
<td>102.32</td>
</tr>
<tr>
<td>Tank height ( L )</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Figure 5-5- (a) cross-section view of pressure vessel (b) selected area of fin and surrounding medium to model (c) cooling tube and the fins

In order to simplify the model, the following assumptions were considered:

1- Conduction is the primary heat transfer mechanism within the bed

2- Heat transfer throughout the fin is only in the radial direction and heat transfer is in steady steady state condition
3- Thermal conductivity of the fins is independent of temperature variation

4- Thermal resistance of the tube wall and fin surface with material was neglected

**Energy balance:**

\[ Q_{in} = Q_{out} \quad (5-1) \]

\[ Q_{r+\delta r} + Q_{cond} = Q_r \quad (5-2) \]

After substitution of the Fourier equation into equation (5-2) and solving, a modified Bessel equation with following boundary conditions is obtained:

\[ r = r_o \quad T_{fin} = T_s \quad (5-3) \]

\[ r = r_{fin} \quad -2\pi r_{fin} \delta \lambda_{fin} \frac{dT_{fin}}{dr} = \frac{T_{fin} - T_{bed}}{\ln\left(\frac{R}{r_{fin}}\right)/2\pi(s + \delta)\lambda_{eff}} \quad (5-4) \]

the temperature profile along the fin is given by:

\[ T_{fin} = T_{bed} + (T_{s} - T_{bed}) \left[ \frac{K_1(mr_{fin})I_0(mr) + I_1(mr_{fin})K_0(mr) + \beta[I_1(mr_{fin})K_0(mr) + I_0(mr)K_1(mr_{fin})]}{I_1(mr_{fin})K_0(mr) + I_0(mr)K_1(mr_{fin}) + \beta[I_0(mr_{fin})K_1(mr) - I_1(mr)K_0(mr_{fin})]} \right] \quad (5-5) \]

Where

\[ \beta = \left(2\pi r_{fin} \delta \lambda_{fin} \frac{\ln(R)}{r_{fin}}\right)^{-1} \quad (5-6) \]

\[ m^2 = \frac{4\lambda_{eff}}{\lambda_{fin} s \delta} \quad (5-7) \]

heat flux throughout the fin was obtained by … (or from …):

\[ Q_{fin} = -2\pi r_{s} \lambda_{fin} \delta \left(\frac{dT_{fin}}{dr}\right)_{r=r_{fin}} \quad (5-8) \]

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Since both hydriding and dehydriding are transient process, the temperature profile and heat transfer of the fin will change with time.

**Fin effectiveness and efficiency**

Effectiveness and efficiency are two important factors to evaluate the performance of fins. Effectiveness is the ratio of the amount of heat transferred with fin compared to that without fin. It shows quantitatively how effective the presence of a fin can be for a system [16, 17].

\[
\varepsilon = \frac{Q_{fn}}{Q_{b}} \tag{5-10}
\]

Where

\[
Q_b = 2\pi \delta \frac{(T_f - T_{bed})}{\ln\left(\frac{R}{r_f}\right) + \frac{1}{\lambda_{eff} / r_f h_f}} \tag{5-11}
\]

Efficiency is the proportion of real heat transfer rate of the fin to ideal heat transfer. Ideal heat transfer implies no temperature gradient along the fin [16].

\[
\eta = \frac{Q_{fin}}{Q_{ideal}} \tag{5-12}
\]

Where

\[
Q_{ideal} = 2\pi \lambda_{eff} \left(\frac{\delta + s}{\ln\left(\frac{R}{r_{fin}}\right)} + \frac{r_{fin}^2 - r_s^2}{s} \right) (T_f - T_{bed}) \tag{5-13}
\]
The performance of fins with four different materials, copper, aluminum, brass and stainless steel with the thermal conductivities of 401, 205, 109 and 16 Wm\(^{-1}\)k\(^{-1}\) respectively were compared. The relationship of fin thickness, length \((r_{\text{fin}} - r_0)\) and spacing together with the effectiveness and efficiency were calculated. The number of fins was taken to be 10, the fin thickness 5 mm, length 90 mm and pinch (the centre–centre distance of the fins) 90 mm. The dimensions were estimated based on the design of the tank.

**Fin length**

Although longer fins have greater surface area and therefore a resultant higher heat transfer rate, the temperature gradient in longer fins is much greater and as a result efficiency drops. The effect is worse in fins with lower thermal conductivity. Increasing the length is, therefore, helpful as long as it does not lead to an efficiency below 60% although it may only be acceptable if the benefits outweigh economic issues related to extra costs of the larger fin [17].

The relationship between the effectiveness and efficiency with regard to fin length is shown in Figure 5-6. As expected the effect of increasing in fin length is more dramatic for the materials with lower thermal conductivity.

The graph indicates that the performance of aluminium and copper fins is significantly higher than the other two materials as expected. Copper was chosen for the system because of both easier construction and higher performance. In order to keep the efficiency close to 60% and also to have high effectiveness, the length should not be greater than 90 mm.
Figure 5-6- (a) Effectiveness (b) efficiency versus fin length

**Fin spacing**

The relationship between fin length and effectiveness is shown in Figure 5-7 (a). The impact of the change in the fin length on efficiency can be seen in Figure 5-7 (b).
For efficient thermal management of the MH bed, the distance between fins needs to be as close as possible to achieve the highest effectiveness. However, the intention was to incur severe temperature gradients over the bed via poor thermal management. This optimisation aims to find the most effective fin for quick heat transfer between the thermal fluid and the metal alloys close to the fin, but with a sufficient distance between fins to hinder heat re-distribution over the MH bed.

Changes in the effectiveness and efficiency are relatively small with the fin spacing greater than 50 mm. Although further spacing leads to lower effectiveness and fewer fins, managing the heat of reaction and as a result temperature and pressure...
excursions limits this. On the basis of this study, a spacing of between 80 and 90 mm was chosen for this system implying 10 or 11 fins equally distributed along the tank.

**Thickness**

Figures 5-8 (a) and Figures 5-8 (b) show the effectiveness and efficiency respectively as a function of fin thickness. These Figures indicate that thinner fins are more effective but have lower efficiency. This confirms the existing literature [16]

![Figure 5-8](image)

**Figure 5-8** (a) Effectiveness and (b) efficiency against thickness

However, during hydrogen cycling, AB₅ materials expand and contract by up to 25%, causing stresses on internal elements. There are, therefore, practical limitations for the
very thin fins, which must be of sufficient strength to withstand pressures and stresses during the absorption and desorption processes.

The three-dimensional graphs shows the effectiveness versus fin clearance and spacing (Figure 5-9 (a)) and fin clearance and thickness (Figure 5-9 (b))

![Three-dimensional graphs](image)

**Figure 5-9- Three-dimensional graphs; (a) effectiveness against fin clearance and spacing, (b) efficiency versus fin clearance and thickness**

**5-5-2 Optimisation**

A built-in MATLAB optimiser was used to optimise the fin dimensions. Effectiveness was chosen as the objective function (equation 5-10) to be maximised under three
constraints. Fin clearance, which is the difference between internal tank radius and fin radius, was one of the constraints to avoid hindering hydrogen movement within the bed. In addition, the pitch was also constrained by the specified length of the tank. The third constraint was volume fraction, which is fin volume to reactor volume. The value is between 0 and 1 and is usually chosen less than 0.5 for best efficiency [18].

Equations (5-14) to (5-16) express these constraints respectively.

\[ r_{\text{fin}} < R \]  \hspace{2cm} (5-14)

\[ H = s + \delta \]  \hspace{2cm} (5-15)

\[ \phi = \frac{V_{\text{fin}}}{V} = \frac{(r_{\text{fin}}^2 - r_i^2)\delta}{(R^2 - r_i^2)(\delta + s)} \]  \hspace{2cm} (5-16)

The results are given in Table 5-2. The pitch was fixed at 93 mm and the dimension was optimised for four fixed values of volume fraction.

<table>
<thead>
<tr>
<th></th>
<th>Volume fraction</th>
<th>H</th>
<th>Thickness</th>
<th>Spacing</th>
<th>Fin length</th>
<th>Effectiveness</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>((\phi))</td>
<td>(s + (\delta))</td>
<td>((\delta))</td>
<td>(s)</td>
<td>(l)</td>
<td>((\epsilon))</td>
<td>((\eta))</td>
</tr>
<tr>
<td>F1</td>
<td>0.01</td>
<td>93</td>
<td>3</td>
<td>90</td>
<td>62</td>
<td>154</td>
<td>70%</td>
</tr>
<tr>
<td>F2</td>
<td>0.02</td>
<td>93</td>
<td>3</td>
<td>90</td>
<td>87</td>
<td>230</td>
<td>47%</td>
</tr>
<tr>
<td>F3</td>
<td>0.03</td>
<td>93</td>
<td>4</td>
<td>89</td>
<td>90</td>
<td>204</td>
<td>50%</td>
</tr>
<tr>
<td>F4</td>
<td>0.04</td>
<td>93</td>
<td>6</td>
<td>87</td>
<td>90</td>
<td>175</td>
<td>60%</td>
</tr>
</tbody>
</table>

The second design (F2) has the highest effectiveness and reasonable efficiency and achieves this with less volume fraction (less material).
5-6- Conclusions

A prototype MH tank system has been designed and partly assembled for testing the finite-element model in further work. The heat management system, a fin and tube heat exchanger, has been designed to develop severe internal temperature gradients by including fins with high efficiency to heat/cool adjacent material, while being spaced widely enough to have poor thermal contact with material in the centre of each fin-MH cell. Embedded thermocouple arrays will map the dynamic temperature distribution for comparison with predictions from the finite-element model.

References

CHAPTER SIX

Summary

6-1- Conclusions

6-2- Future works
6-1 Conclusions

Modelling of a metal-hydride tank system is an essential tool for optimisation of the physical parameters and thermal management of the system, as well as the material used and the operating conditions. Modelling can inform the design and implementation of practical systems at considerably lower cost than experimental work and multiple prototypes, however, in order to do this reliably, the model must be accurate and able to specifically model real experimental conditions. Conversely, the accuracy of a model can be tested by comparison with experimental MH systems and improved by modifications arising out of the observed differences. Comparisons between model and experiment are only possible if the model can accommodate the practical aspects of MH tank design and use, such as inflow and outflow of hydrogen, maximum pressure and temperature limits and realities such as incomplete absorption or desorption before the next cycle starts.

Therefore, previous MH models such as the Hardy and Anton model were used as a starting point in this work, require modifications to include more intrinsic features of the MH beds such as hysteresis and volume changes during sorption process. Appropriate experimental data are also required to test the strength of these models to predict different situations of the MH beds.

An improved model, taking into consideration a number of practical features relevant to experimental tanks systems, was presented; two profiles emulating hydrogen flow rate into and out from the tank were introduced into the mass balance equation. The assumption of hydrogen as an ideal gas was investigated through including compressibility factor of hydrogen. Comparison of pressure and equilibrium pressure profiles obtained from the two approaches showed that the approximation of the ideal gas assumption is acceptable. Initial conditions of absorption and desorption processes were defined so as to match hydrogen cycling conditions in a realistic system. This involved setting the initial conditions of each
process to the final state of the previous process and iterating until a consistent result was reached.

Empirical equations for equilibrium pressure were determined for the material used in the system for which the model was applied. Based on those equations, a relationship between temperature and the maximum hydrogen uptake was modelled and used in the kinetic equation. In order to include the dependence of effective thermal conductivity on hydrogen pressure and/or hydrogen uptake, experimental data reported for LaNi₅ was fitted and an empirical equation derived.

The possibility of using one fixed thermal fluid temperature for both desorption and absorption instead of cycling the temperature from low to high during desorption and back to a low temperature during absorption was investigated. The improvement in cycling time for the cycled temperature case was slight and may not be justified economically.

The purpose of the improved model is to make accurate comparisons with experimental systems, to ensure the accuracy of the model and provide feedback from experimental observations to enhance the model. In this project, two experimental systems were planned on different scales: one concerning spatial distribution in a small-scale (a few cc), and a large scale dual tank cycling system with a total of 2 kg of hydrogen to measure the temperature distribution profile over the bed.

The first test of the ability of the improved model was an experiment designed and conducted to generate significant compositional inhomogeneities over the bed. An in-situ neutron diffraction measurement was used to map the hydrogen (deuterium) uptake distribution over a small-scale LaNi₅–D₂ system subjected to a single aliquot of D₂ to approximately 50 % uptake. A significant variation of reacted fraction of the metal hydride through the cell was observed, confirming previous suggestions in the literature. The observed higher uptake at the
edges of the cell compared to almost no uptake in the centre matched the expectations of the large aliquot effect. The improved model was modified to suit the geometry of the sample cell and the operating conditions. Rather than using the hydrogen flow rate profiles created for the model, the initial pressure was chosen to match the amount of deuterium injected to the cell. The model was solved by COMSOL Multiphysics and reasonable agreement between the theoretical and the experimental results was observed, validating the model. The experiment has demonstrated the capability of the model in mapping temperature and compositional gradients and the match with the modelling results shows that the underlying equations for the material and its characteristics must be accurate.

Despite the accurate prediction of the temporal profile of the averaged reacted fraction, temperature and pressure, there is an observed difference between the measured and calculated compositional distribution at the bottom of the cell, the furthest part from the hydrogen entrance. According to the experimental results the top of the sample absorbed more hydrogen than the bottom of the cell despite identical heat transfer conditions. Because of the rapid kinetics of the metal hydride material used, it is believed that the hydrogen is absorbed rapidly near the gas entrance at the top of the cell, depleting the hydrogen before it can reach the bottom of the cell. This indicates the key role of hydrogen inflow in compositional distribution of the bed. The effect can be greater for larger scale systems with slower injection of hydrogen.

In order to provide further checks of the model applied to larger scale systems, a laboratory scale prototype system with two intermetallic-hydride tanks was designed, built and partly assembled to use for validation of the models for MH systems. This allows for testing and enhancement of the model as well as comparison of different materials.
6-2 Future work

The immediate work which continues on from this project is the implementation and testing of the prototype tank system and the subsequent comparison with the enhanced model. Feedback from the experiment can be used to check the accuracy of the model and guide future improvements, for example the measured experimental flow rates through the flow controllers may help improve the modelling of inflow and outflow. The model may also be used to study different scenarios such as partial desorption followed by absorption, as may be experienced if a vehicle tank was filled before being completely empty for example.