

BRUCE THE EFFECT OF AN EXTERNALLY APPLIED MAGNETIC FIELD
ON THE HYDROGEN ABSORPTION PROPERTIES OF LaNi_5 M.A.SC.

**THE EFFECT OF AN EXTERNALLY APPLIED MAGNETIC FIELD ON
THE HYDROGEN ABSORPTION PROPERTIES OF LaNi_5**

By

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A Thesis

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Abstract

Hydrogen fuel cell applications are set to ameliorate the world's energy woes, yet there still exists problems that need to be overcome in terms of their fuelling. While compressed storage, cryogenic storage, chemical storage, and adsorptive storage solutions exist, none meet the requirements that are needed to facilitate a replacement for the gasoline powered automobile.

Metal hydrides have been long studied as an alternative method for storing hydrogen safely and efficiently, with significant developments being made in advanced alloys. While this research is beneficial, it was theorized that an externally applied magnetic field might augment the storage properties of existing magnetically susceptible metal hydrides, without trial and error alloy development.

Constant volume hydrogen absorption experiments were conducted using LaNi_5 in order to test this theory. A known amount of LaNi_5 was exposed to hydrogen, with the absorption equilibrium data collected over a period of 6 hours. An equal sample was then exposed to hydrogen with a 0.7 Tesla applied field applied to the sample. There was a distinct difference between the absorption curves of the two equal samples, with the sample under the influence of the magnetic field achieving an absorption of only 0.60% wt. in comparison with the unmodified sample which absorbed 0.88% wt.

It was concluded that the presence of an externally applied magnetic field has a negative effect on the overall capacity of LaNi_5 through the prevention of a shift in the inner lattice structure of LaNi_5 that would otherwise permit an increased hydrogen capacity. This effect while negative in terms of overall storage capacity could have a possible benefit in terms of the desorption of the stored hydrogen, as the magnetic field could be used in lieu of an increase in temperature in order to drive the hydrogen from the fully filled structure.

Acknowledgments

First and foremost I'd like to express my gratitude towards Professor Gu Xu of McMaster University for his supervision and guidance over the course of this project. His insatiable drive motivated me to achieve my goals and showed me what I can really accomplish if I set my mind to it.

I'd like to thank my research group and friends throughout the department for their support as well as for indispensable technical advice and assistance.

I'd also like to thank the support staff in our departmental office for helping to cut away the red tape and to fluidize my time at McMaster. If 'Departmental Moms' had no negative politically correct connotations, they would be worthy of these honored titles.

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1.0 Introduction

The impact of man has contributed to the decline of diversification, the poisoning of our natural environment and an overall deterioration of the richness of life. If nothing is done to correct this damage, future generations will be left with nothing more than a shell of the planet that our generation has come to know and love. We have been exploiting the earth's natural resources to the extent that in many cases there is no resolve, there is no undoing what we have done, but it is our responsibility to do our best to try to preserve our earth and to realize and rectify our mistakes.

1.1 Portable Energy Conundrum

Since humankind seems so adamant about their choice to continue to burn fuels and forgo a more sensible reduction in energy policy, we need to find a new way of fuelling our high energy lifestyles. The reliance on fossil fuels is realistically going to end within our lifetimes, with supplies dwindling and prices skyrocketing. While there are several alternative approaches currently available, such as electric vehicles, they are all severely limited by their low energy density of batteries. Perhaps the most attractive attribute that fossil fuels have over all of the other available portable fuel sources is its extremely high power density. In order to be a viable fossil fuel replacement that society will accept, the substitute fuel would need to be equal to or greater than the existent one in terms of environmental impact, energy density, safety,

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and cost. Improving on the environmental impact over fossil fuels is the most easily met of the replacement fuel requirements, as even the simplest derivatives of fossil fuels contribute to the pollution of the atmosphere. Safety and cost solutions come through the development of any technology, thus the most limiting factor for an acceptable solution lies with the energy density criteria.

Fortunately there have been recent breakthroughs in a long-standing electrochemical device, the fuel cell, that provide a feasible solution. Fuel cells are based on electrochemical reactions rather than combustion in order to provide a reliable energy source. Work has been done on many different types of fuel cells, which all have niche operations, with the proton exchange membrane (PEM) low-temperature hydrogen fuel cell being touted as the new solution for mobile alternative energy needs.

The PEM hydrogen fuel cell operates as a fuel fed electrochemical cell composed of two parallel channeled plates separated by a semi-permeable membrane. PEM fuel cells use a solid polymer as an electrolyte and porous carbon electrodes containing a platinum catalyst. They need only a hydrogen source, oxygen from the air, and water to operate and do not require corrosive fluids like some fuel cells. A PEM fuel cell consists of a polymer electrolyte membrane sandwiched between an anode (negatively charged electrode) and a cathode (positively charged electrode). Its operation is as follows:

1. Hydrogen fuel is channeled through machined flow field plates to the anode on one

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side of the fuel cell, while oxygen from the air is channeled to the cathode on the other side of the cell.

2. At the anode, a platinum catalyst causes the hydrogen to split into positive hydrogen ions (protons) and negatively charged electrons.
3. The polymer electrolyte membrane (PEM) allows only the positively charged hydrogen ions to pass through it to the cathode. The negatively charged electrons must travel along an external circuit to the cathode, creating an electrical current.
4. At the cathode, the electrons and positively charged hydrogen ions combine with oxygen to form water, which flows out of the cell in the form of water vapor.

This process is illustrated in the following schematic, Figure 1:

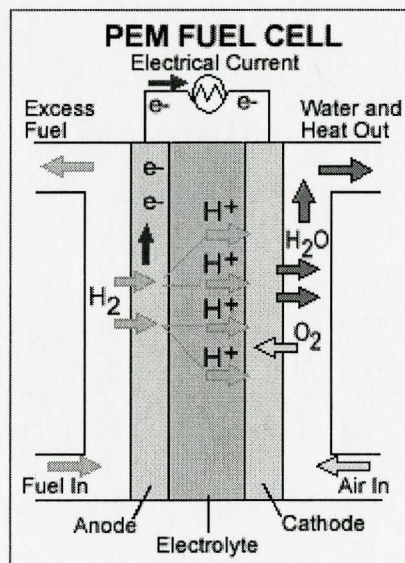


Figure 1: PEM fuel cell operation schematic [Ref. 31]

Fuel cells by design can be operated with a variety of different hydrogenated

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species, with inherent problems associated by fuel type. In terms of potential energy available, and the energy density associated, there exists a ranking of the fuels. This information can be found in Table 1.

Fuel	Hydrogen Weight Fraction	Ambient State	Mass Energy Density (MJ/kg)	Liquid Vol. Energy Density (MJ/L)
Hydrogen	1	Gas	120	8.4-10.4
Methane	0.25	Gas	50	21
Ethane	0.2	Gas	47.5	23.7
Propane	0.18	Gas	46.4	22.8
Gasoline	0.16	Liquid	44.4	31.1
Ethanol	0.13	Liquid	26.8	21.2
Methanol	0.12	Liquid	19.9	15.8

Table 1: Alternative fuel sources for PEM fuel cells

Due to the fact that hydrogen has the greatest mass energy density and produces no carbonated pollutants upon reaction or combustion (CO_x), it naturally seems to be the logical choice for fuel. This data however also shows hydrogen's deficiency: poor volumetric energy storage.

1.2 Hydrogen Storage Technologies

The fuel tank of a typical gas powered automobile has a volume of approximately fifty liters, with a total mass of approximately 48 kg at full capacity. Assuming a reasonable efficiency of 65%, a PEM fuel cell powered vehicle consumes 3.1 kg of hydrogen for a 500 km range. If compressed, a 50 liter volume of hydrogen

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gas at 150 atm (typical laboratory cylinder pressure) would have a mass of only 0.62 kg, providing an inadequate range of approximately 100 km. It is clear that in order for hydrogen to be a competitive fuel, it is necessary to contain it at greater volumetric densities without significantly increasing the overall mass of the storage system. The volumetric densities are typically expressed as the volume of hydrogen at STP per kilogram of storage. A variation of this ratio compares the mass of hydrogen stored to the mass of the overall system then converted to a percentage. This ‘weight percent’ method is very convenient in comparing hydrogen storage solutions, and it can be used as a benchmark across all of the currently available options.

The US Government’s Department of Energy (DOE) has been developing an extensive hydrogen storage research program for over thirty years, and has designated a target for a hydrogen storage solution in automotive applications. This target must meet all related safety and filling designations as needed in re-fuelling and transportation of hydrogen, as well as achieving a level of storage equal to 6.5 wt. % and 62.5 kg/m³. These levels were determined by the typical range of a gasoline powered automobile, as discussed previously. The current technologies can be seen in Figure 2, and will be discussed in the following sections.

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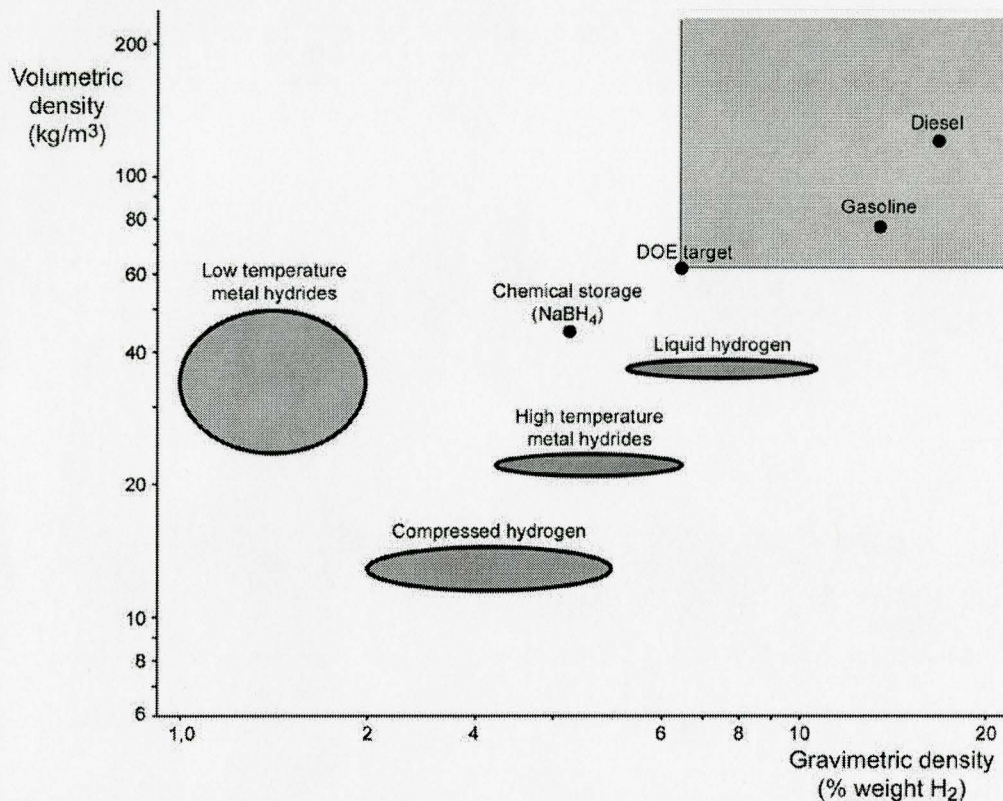


Figure 2: DOE hydrogen storage targets & current technologies [Ref. 5]

1.2.1 Compressed Storage

Compressed storage of hydrogen is the most commonly used storage system in prototype and laboratory work. Hydrogen can be stored at very high pressures, yet due to the cumbersome and heavy design of typical laboratory cylinders, the resultant weight percent stored is less than 1%. Improvements have been made in this field through the work of companies such as Dynetek Industries Ltd. and Quantum Technologies Ltd., and there now exists tanks that can store hydrogen at pressures of 6000 psi with a weight percent of up to and over 10%. The tanks themselves are

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constructed of a multi-layer composite. The innermost layer is composed of proprietary polymeric material that is impermeable to hydrogen and does not break down in the presence of highly acidic species. The second layer is made of carbon fiber composite and provides the tank with its structural integrity. There is a final impact resistant outer layer to protect the vulnerable carbon fiber structural skeleton.

These layers are illustrated in the following diagram, Figure 3:

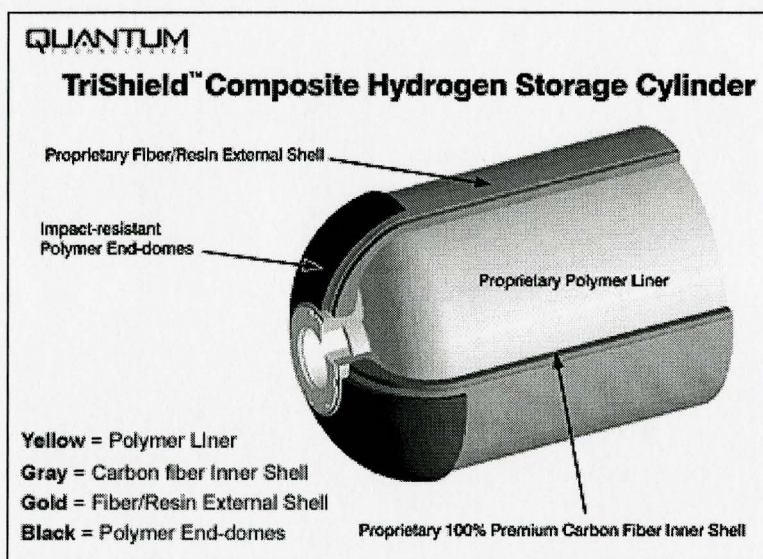


Figure 3: Cutout of compressed hydrogen storage tank [Ref. 28]

Unfortunately, even though these companies have rigorous safety testing procedures and have demonstrated the safety of this technology even to the extent of shooting them at close range with a 12 gauge shotgun, the public will not currently accept them. Considering it will be the public that uses the final product, other options must be considered in order to ease the public's fears.

1.2.2 Cryogenic Storage

Cryogenic storage, hydrogen stored in its liquid state, is one of the highest weight percent storage systems available, with companies such as BMW advancing it through their hydrogen internal combustion engine research. At ambient pressure, liquid hydrogen has a boiling point of 22 Kelvin, and thus the design of such a system is quite difficult and prone to problems. In keeping the hydrogen at such low temperatures to maintain its liquid state, emphasis is placed on the insulating properties of the system rather than designing them to withstand high pressure. This is circumvented through the use of pressure relief valves that bleed hydrogen when the pressure of the system increases. This is detrimental in many ways, as aside from the constant hydrogen losses (insulation is not perfect), if longer term storage were needed energy would need to be constantly supplied to the system in order to keep the temperature down. As an example, the tank system used in General Motor's fuel cell vehicle, as shown in Figure 4, has a rate of hydrogen evaporation of 4% per day after a dormancy of 3 days.

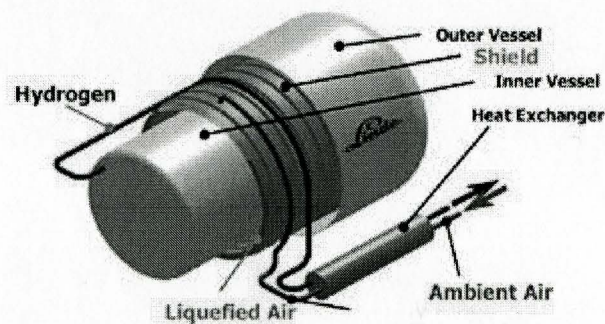


Figure 4: The Linde cryogenic tank [Ref. 30]

In addition, a number of safety and efficiency issues are involved with this technology ranging from the pressure release valves that are prone to freezing, to the simple fact that an energy equivalent to nearly 40% of the specific enthalpy of hydrogen is required to condense it to liquid state.

1.2.3 Chemical Storage

Chemical storage of hydrogen incorporates the storage of hydrogen rich species that are later reformed to draw the hydrogen from their chemical structures. Since the chemicals are not composed entirely of hydrogen, there always will be a waste product generated, despite advanced reforming technology. In the case of the most commonly used chemical storage solutions, ethanol and methanol, the waste generated includes carbon dioxide and monoxide. Aside from being poisonous to humans, carbon monoxide is also highly poisonous to fuel cell catalysts, deactivating them and rendering them inoperative.

Other chemicals that have been investigated recently have included ammonia, diborane, methane, and hydrazine to name a few. All of these chemical storage solutions far surpass the DOE specified 6.5% wt. target, but find faults in the fact that they are either too energetically costly to produce, too toxic for release into the environment, or require too much energy to release the hydrogen bound within them.

Chemical storage still continues to be considered as a viable solution for fuel

cell applications due to the extensive chemical delivery systems already in place globally, combined with strong support from the oil conglomerates that are looking for a continued customer base through chemical fuel production from hydrocarbon sources. Many of the above mentioned chemicals can be synthesized from hydrocarbon sources and the oil companies are all too eager to finance proposals that could benefit their continued success.

1.2.4 Adsorptive Storage

Adsorptive systems have been at the forefront of research of late, as speculative results of amazing feats of hydrogen storage have been reported, despite adsorption reactions being fairly well understood. The concept behind adsorptive storage media is conceptually very simple. The gas species in question is drawn to free surfaces of adsorbant material and is then condensed on the surface. It was hoped that a branch of materials made from microscopic rolled carbon sheets, called carbon nanotubes, would offer a storage solution by tailoring a material that had a huge surface for adsorption at a relatively light weight. A group of single walled nanotubes (SWNT) has been illustrated in Figure 5, with the hydrogen atoms depicted as being adsorbed in the tubes themselves.

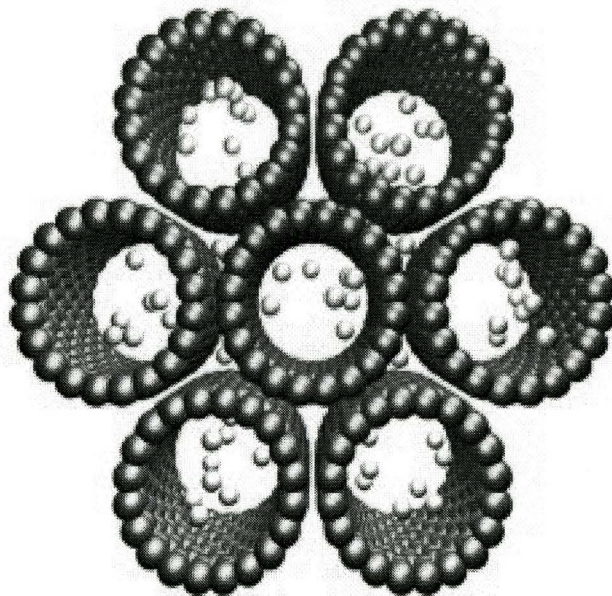


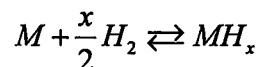
Figure 5: SWNT bundle hydrogen adsorption [Ref. 6]

This concept of substantial internal adsorption was most thoroughly disproved however by the previous work of our group, and is discussed in a journal paper to Applied Physics Letters. It was shown that the monolayer saturation plateau was found on bundled SWNT at room temperature corresponding to an adsorption of only 0.9 wt % [Lawrence & Xu, 2003].

1.3 Hydrogen Storage in Metal Hydrides

Hydrogen storage in metal hydrides relies on the dissolution of hydrogen into a metal, with the individual H atoms becoming bonded to interstitial sites in the metal. This ‘hydrogen sponge’ acts as a reversible hydrogen storage system, controlled through the temperature and pressure of the system, as governed by the exothermic

equilibrium reaction,



where M is a metal or alloy and x is a stoichiometric constant. This equilibrium will be discussed later in detail. As a spontaneous exothermic reaction, these hydrogen sponges can be filled in minutes, and the separation between stored interstitial atoms of hydrogen is smaller than that of intermolecular liquid hydrogen distances. This high volumetric density is unfortunately countered by the fact that the metal lattice is usually composed of heavy elements, resulting in significant system weights. There exist whole ranges of hydrides that are able to overcome this low gravimetric storage, with magnesium-containing hydrides storing as high as 7.5 wt. %, although the kinetics of the reaction are too slow for them to be considered as feasible solutions.

1.3.1 State of Hydride Technology

While at this time there does not exist any current hydride that can meet the DOE specifications, there continues to be a varied and extensive amount of research being done in this area. A number of research groups have been focusing on the addition of small amounts of different additives, such as rare earth alloying elements, in order to improve kinetics and storage capacity [Percheron-Guegan et al. 1985]. Through variation in the metal matrix, hydrides can be tailored and their interstitial pore sizes varied to allow for more hydrogen absorption. Greater catalytic functioning has also been investigated [Rudman & Sandrock, 1982]. Since the

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reaction between hydrogen and these advanced hydrides is not predictable due to the complexity of the models needed, much of this work must be done analytically which makes advances in this direction cumbersome. Another direction that has begun to be investigated is the idea of organo-metallic hydrides [Seayad & Antonelli, 2004]. These hydrides are a combination of metallic centers surrounded by a carbon based scaffolding. The idea behind this research is that if a matrix can be set up where hydrogen can be bonded interstitially at the same volumetric density as that of the metal hydrides, it would be far superior due to the fact that the material would be made up of a much lighter element. This is illustrated in Figure 6:

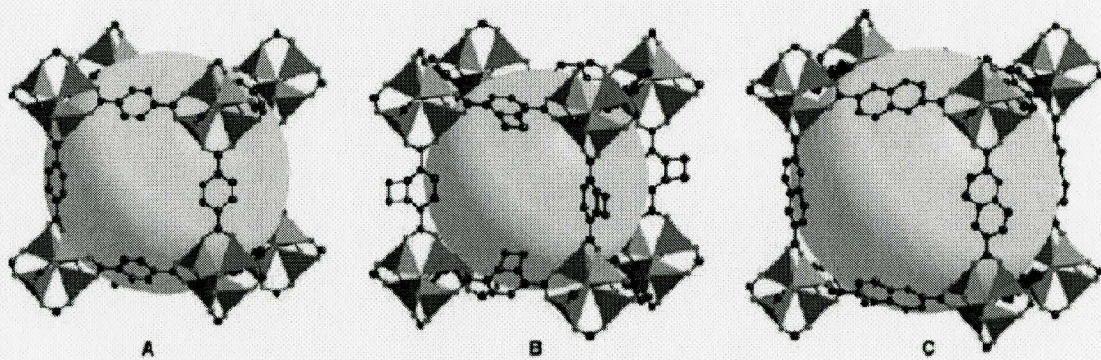


Figure 6: Zn_4 centered carboxylate bridged organic linked advanced hydrides [Ref. 25]

These proposed materials have their merits, but once again will need to be shown in practice.

1.3.2 Manipulation of Existing Materials

With all of the research to find new and better materials for hydrogen storage, it is assumed that the existing properties of the known hydrides have been evaluated

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and catalogued. An abundance of hydrides have been characterized and their properties recorded in a national database maintained by the Sandia National Laboratory in conjunction with the DOE and available for public screening at www.hydpark.ca.sandia.gov. This database, while impressive, maintains only the thermodynamic and physical characteristics of the hydrides. In terms of hydrogen storage, there are several other considerations that could come into play that deal with the intricacies of the reaction between the hydrides themselves and hydrogen gas.

While the thermodynamic properties of hydrides under reaction are always closely measured and tracked, as they dictate the equilibrium behavior of metal-hydrogen system, there are other variables that have not yet been investigated that still merit attention. In the field of wastewater remediation there has been an increased interest in optical catalysis, wherein sunlight or UV light is used in conjunction with chemical species in order to promote a reaction that otherwise would be energetically unstable. One example of this was demonstrated where UV light is used in conjunction with titanium dioxide to facilitate a light driven breakdown of organic compounds [Gulyas, 1994]. With optical energy also expressed as a waveform that can impart directional control in a chemical reaction, why have similar properties not been investigated for hydride reactions? With a hydride system, it would be difficult to control optical electromagnetic waves from the sun, as the system must remain closed to the atmosphere, and the materials

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involved are not permeable to light. As derived from classical wave theory, a simple waveform can be broken down into an oscillating electric field with an associated orthonormal oscillating magnetic field. This waveform is shown in Figure 7.

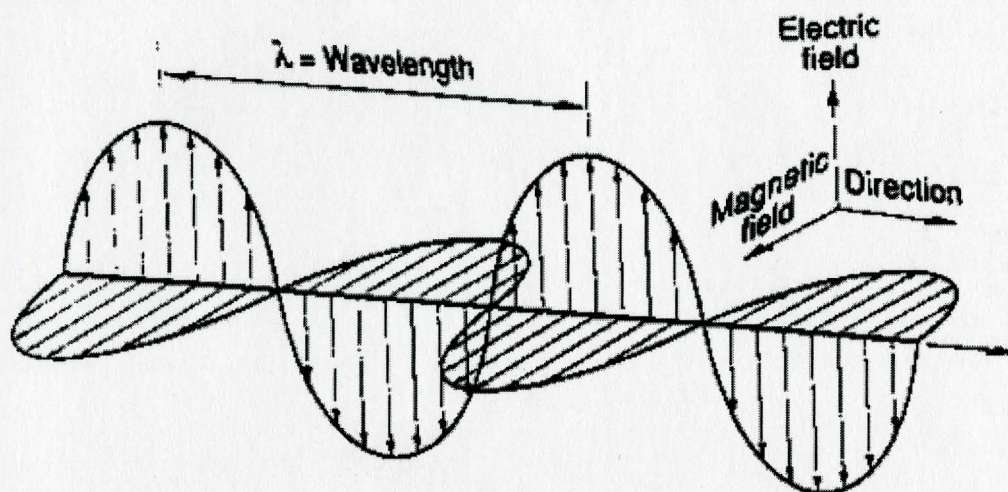


Figure 7: Waveform dissection [Ref. 32]

The effects of such an applied magnetic field on hydride kinetics and capacity are unknown. It is well known that some hydrides undergo a magnetic phase change in the transition to and from their hydrogenated state, yet the influence of an externally applied magnetic field, whether oscillating or static, is not recorded nor reported in literature.

1.4 Research Objectives

The purpose of this work is to investigate the effects of an externally applied magnetic field as it pertains to hydrogen absorption. Given that LaNi_5 could be

argued to be the most studied and also the most commercially available hydride that has been shown to exhibit a magnetic phase transition [Tai et al. 2003], it has been chosen as the subject of this study. LaNi_5 also has the direct benefit of being catalytically active without an elaborate activation procedure needed [Schlapbach 1978], and is not poisoned by standard atmospheric conditions, leading to more accurate results through ease of handling. Furthermore, with nickel being a magnetically active element as well as being a major hydride catalyst, the selection of LaNi_5 would be the most likely candidate to show effects if they do exist.

1.5 Thesis Overview

The remainder of this thesis is broken down into four chapters. Chapter 2.0 provides background information relevant to the thesis including basic hydrogen absorption theory, as well as specific information regarding the material studied, LaNi_5 . Chapter 3.0 details the experimental method, measurement considerations, and data manipulation. Considering the intricacy involved in the measurements of this type, careful instrument construction, and continuous inspection and upkeep comprised a significant portion of the work conducted. Chapter 4.0 details the results generated as well as provides a discussion of those results with a full analysis of the theories generated. Chapter 5.0 gives the conclusions.

2.0 Literature Review

Considering the extensive work already done in the field of hydrogen absorption in metals, a thorough review of the specific properties of the system under investigation is possible. An examination of the process of hydrogen absorption on a theoretical basis shall be reviewed, followed by a close analysis of the direct material properties of the system. Through the complete understanding of the underlying principles of these two concepts (on the theoretical basis for hydrogen storage), a comprehensive grasp of the overall process is achievable.

2.1 Mechanisms of Absorption

Absorption by definition is a process in which one substance permeates another. From a chemical process standpoint, this process can be broken down into various sub-stages in which several basic chemical operations occur. The purpose of this subsection is to understand the mechanics of absorption theory in order to fully understand the underlying process which this system undergoes.

2.1.1 Physisorption

The preliminary stage of absorption is that of physisorption, also known as adsorption. The term adsorption describes the process by which the molecules of gas, liquid, or dissolved solids are adhered to a surface. The surface adsorption is due to

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the presence of an overall short-range attractive force at the surface of the solid caused by the action of electronic dispersion forces, also known as van der Waals forces. These electronic dispersion forces arise from the rapid fluctuation in electron densities within atoms. The fluctuation in one atom induces an electrical moment in a neighboring atom, thereby leading to mutual attraction between the two (Lawrence 2002, Gregg and Sing 1982). This dipole-dipole attraction varies in accordance to the distance between their two atomic centers, r , and is expressed in terms of their potential energy given by:

$$\varepsilon_D(r) = -Br^{-6}$$

Where B is a dispersion constant dependant on the species involved. There exists a more precise evaluation of the attractive force which includes higher order terms representing dipole-quadrupole and quadrupole-quadrupole interactions, but these are generally omitted as the precision of the expression is such that these terms fall within the comparatively large uncertainty of numerical calculation.

There also exists a repulsive force between the adjacent atoms due to the overlap of their electron clouds. This function is represented by:

$$\varepsilon_R(r) = Ar^{-m}$$

Where A and m are empirical constants, the latter typically assigned a value of 12.

This large exponential function decays at a rate much faster than that of the attractive force between the two atoms, leading to a complex relationship known as the Lennard-Jones potential,

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$$\varepsilon(r) = -Br^{-6} + Ar^{-12}$$

and shown in the following diagram, Figure 8,

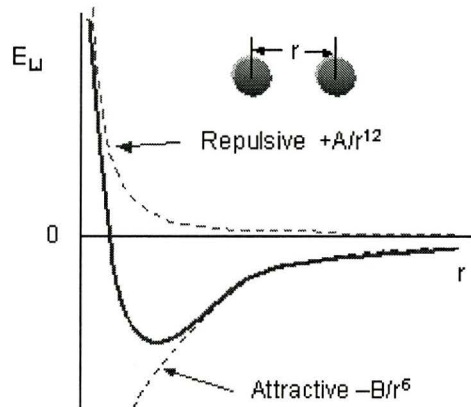


Figure 8: Lennard-Jones Potential between gaseous atoms

This relationship is typical of two atoms in the gas phase, and with slight augmentation can be applied to the attraction between an atom in the gas phase in proximity to a surface. The overall attraction $\phi(z)$ experienced by the gaseous species to the surface is a summation of the pair-wise interactions between them, with r_{ij} being the distance between gaseous atom i and the center of atom j in the solid (Lawrence 2002, Gregg and Sing 1982).

$$\phi(z) = -B_{ij} \sum_j r_{ij}^{-6} + A_{ij} \sum_j r_{ij}^{-12}$$

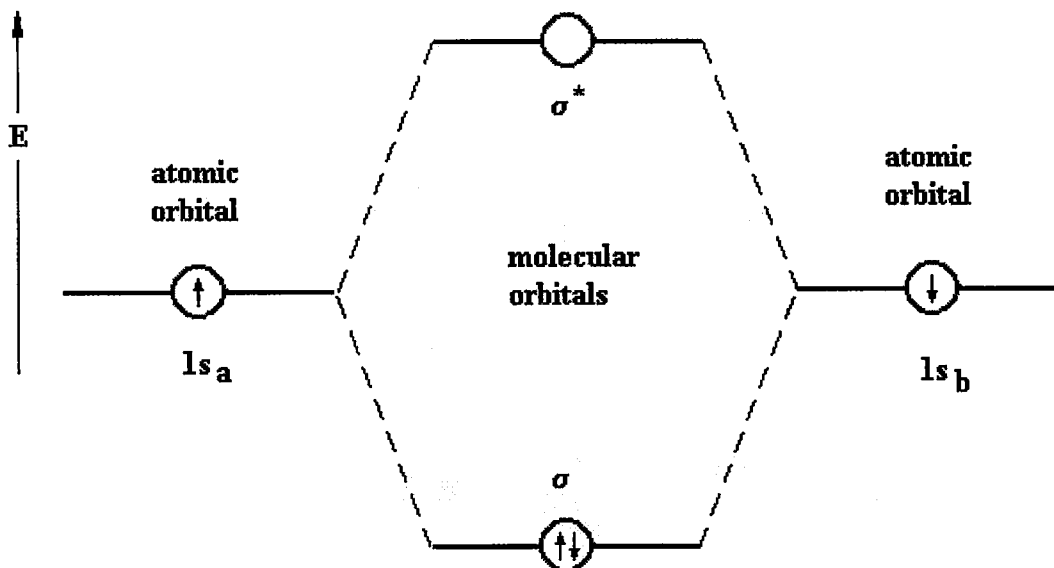
Assuming that the gaseous molecule is influenced by only the central atom j , and there exists a planar solid adsorbant, the distance r_{ij} becomes one value, z . Once again, there exists a more precise evaluation of the attractive & repulsive forces

which include higher order, but are omitted as the precision of the expression is such that these terms fall off rapidly with distance.

In the evaluation of the overall adsorption process both the competing attraction between the gas-gas molecules and gas-solid molecules are considered, with complicated calculations employed using complex statistical techniques.

2.1.2 Chemisorption

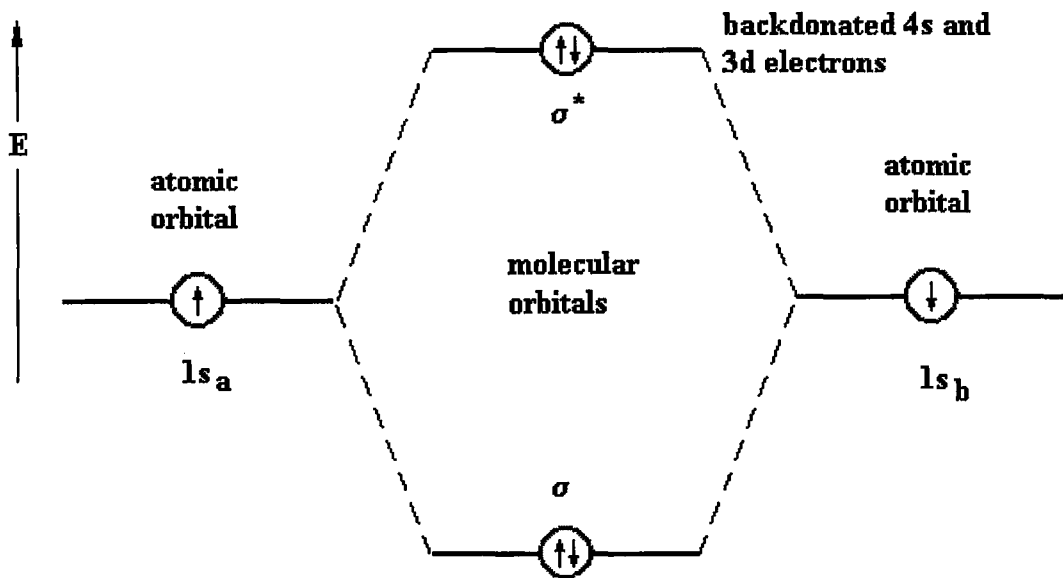
With the hydrogen molecules adsorbed to the surface of the hydride, the next stage of the absorption process is the catalytic decomposition of the hydrogen molecule into lone hydrogen atoms. The active catalyst in most hydrogen systems involves transition metals with an abundance of d-shell electrons. Some good examples with their valence shells reported include Pd: [4d10], Pt: [5d9 6s1] and Ni: [3d8 4s2]. It is the electrons in the d-shell that initiate the hydrogen-hydrogen bond cleavage. The hydrogen present is bonded in the following states (Figure 9):



Energy level diagram for H_2 molecule formed from H_a and H_b atoms.

Figure 9: Molecular energy level diagram for hydrogen molecule

Due to a difference in energy levels between the outer d-shell electron orbital and the antibonding orbital of the hydrogen, a spontaneous jump of electrons occurs from the metal to the physisorbed hydrogen molecule [Kubas 2001]. This occurs due to an overlap of the valence shell electrons of the metal with the closely physically bonded hydrogen molecular orbitals. Electron donation from the d-shell orbital continues, until the antibonding orbital of the hydrogen atom is completely filled, as shown in the following diagram, Figure 10.



Energy level diagram for H_2 molecule formed from H_a and H_b atoms.

Figure 10: Molecular energy level diagram for backdonated hydrogen molecule

By filling the antibonding orbital, the bond order of the hydrogen molecule is effectively zero, and the molecule separates into its atomic elements as the filled antibonding orbital drives the hydrogen atoms apart. This catalytic decomposition is shown below (Figure 11):

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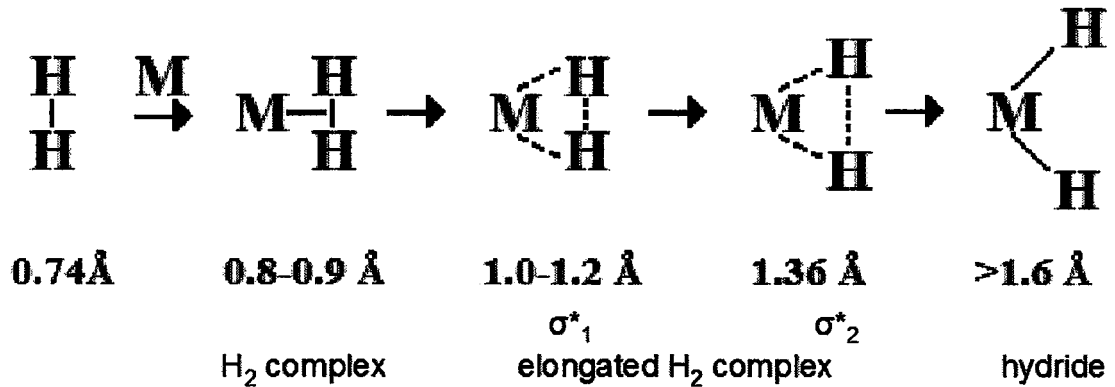


Figure 11: Catalytic decomposition of hydrogen (showing atomic distances)

With the hydrogen now split into single atoms, the absorption process continues through diffusion mechanisms of the atoms through the metal surface and into the bulk metal matrix. For both of these terms, the diffusion depends on the solubilities of the species involved and will be discussed in more detail as it pertains to the LaNi₅ system in the following subsections. In the meantime, it is simply illustrated by the following diagram, Figure 12:

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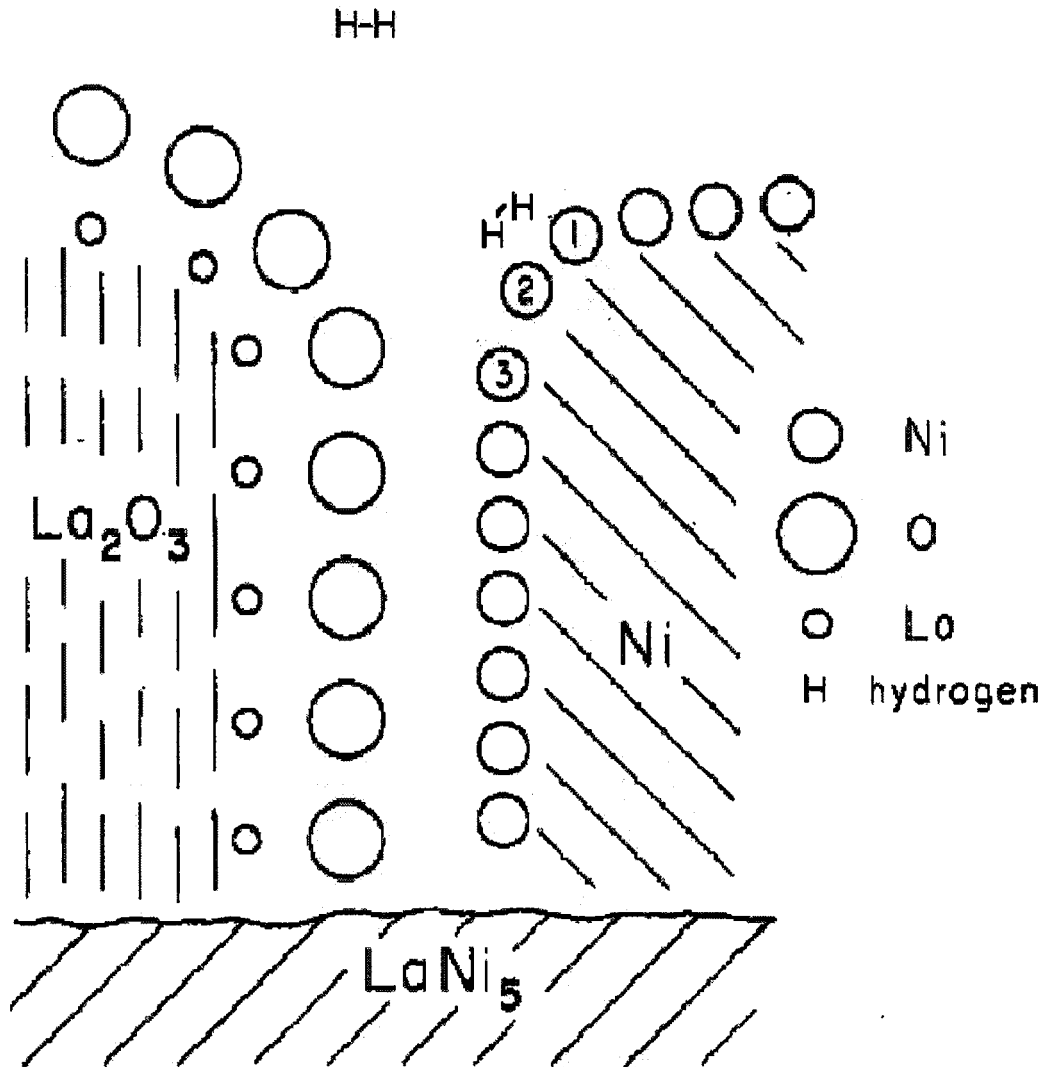


Figure 12: LaNi_5 surface profile showing interfacial diffusion

In every case, diffusion follows typical interstitial and vacancy mechanisms after surface penetration has occurred.

Interstitial diffusion is governed by Fick's Laws of Diffusion [Hines &

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Maddox, 1985]. Consider a particle of LaNi₅ in which the concentration of an interstitial solute (hydrogen) varies with distance, $C_H(x)$. At any point in the material, there will be a flux of solute defined by Fick's First law:

$$J_H = -D_H \frac{\partial C_H}{\partial x}$$

where J is the mass flux measured in $mol \cdot s^{-1} \cdot m^{-2}$, D is the diffusivity measured in $m^2 s^{-1}$, C is the concentration measured in $mol \cdot L^{-1}$, and x is the distance diffused, measured in meters.

At two depths within the particle, the flux of solute will be different, unless the gradient of the concentration profile is the same. The difference in the number of solute atoms entering and leaving the region in a small time interval Δt leads to a small increase in the local concentration:

$$\Delta C_H A \Delta x = (J_1 - J_2) A \Delta t$$

For $\Delta x = x_2 - x_1$ being very small, we have

$$J_2 = J_1 + \frac{\partial J}{\partial x} \Delta x$$

At the limit of Δx and Δt tending towards zero, we obtain the relationship:

$$\frac{\partial C_H}{\partial t} = -\frac{\partial J}{\partial x} = -\frac{\partial}{\partial x} \left(D_H \frac{\partial C_H}{\partial x} \right)$$

With the diffusion of the hydrogen atoms described through Fick's laws, the final stage of absorption is the bonding of the atoms at interstitial sites. Interstitial bonding is akin to the formation of a new phase, and is governed by typical Gibbs free energy considerations.

2.1.3 Modelling

Empirical experimentation of metal hydride systems is typically expressed using the Langmuir model. This model relies on experiments being performed at constant temperature, and the resultant isotherms can be matched to composition versus pressure curves. The Langmuir model is based on the assumption that full compositional absorption occurs with each available interstitial site and there is no interaction between absorbing molecules. Furthermore, the Langmuir model assumes

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that the energies of adsorption and absorption are constant. If θ is the fraction of absorbed species, and at equilibrium the rate of molecules the rate of molecules adsorbing to the surface is equal to the rate of molecules leaving the surface (assuming fully filled interstitial sites), then

$$k_d\theta = k_a P(1-\theta)$$

where k_d is the desorption rate constant, k_a is the adsorption rate constant, and P is an expression of the rate at which molecules are striking the surface – the pressure. The rate constants are dependant on temperature according to

$$k_{a,d} \propto e^{\frac{-E_{a,d}}{RT}}$$

where E is the activation energy of adsorption or desorption, T is the Temperature, and R is the universal gas constant. Rearranging this equation and substituting it into the Langmuir model yields the most common expression of the Langmuir absorption isotherm,

$$\theta = \frac{bP}{1+bP}$$

where

$$b = \frac{k_a}{k_d} \propto e^{\frac{-(E_a-E_d)}{RT}}$$

is the rate constant for absorption, and $E_a - E_d = \Delta H_a$ is the enthalpy of absorption.

The Langmuir isotherm has the profile shown in Figure 13, where the percent

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absorption increases with pressure and eventually saturates at full absorption.

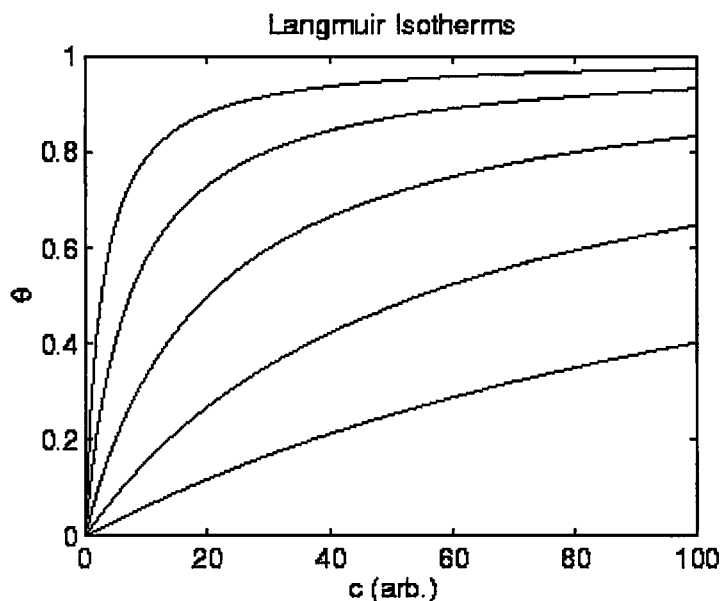
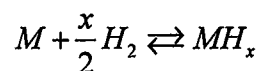


Figure 13: Typical Langmuir isotherms [Ref. 29]

There also exists a more simplistic way of viewing the reaction, when the process is analyzed macroscopically, assuming the reaction proceeds until completion. For the generic exothermic storage reaction there exists a predictable thermodynamic storage reaction,



where M is a metal or alloy and x is a stoichiometric constant. This equilibrium is described by the van't Hoff equation,

$$\ln(P) = -\Delta H / RT$$

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where P is the partial pressure of hydrogen in atm, R is the universal gas constant $0.082057 \text{ atm} \cdot \text{L} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, and T is the temperature in Kelvin. From this correlation it is easy to see that the hydrogen is absorbed when the system pressure is raised, or temperature decreased. This relationship can be seen as linked to the traditional Pressure-Temperature-Composition (PCT) Diagram of hydrogen absorption as follows in Figure 14:

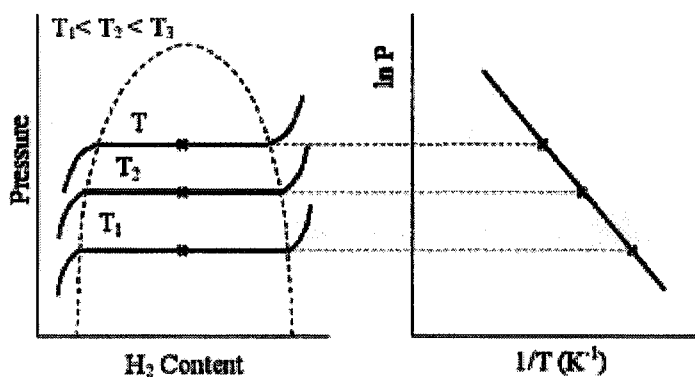


Figure 14: PCT diagram and corresponding van't Hoff plot

2.2 LaNi_5 Materials Properties

The absorptive properties of lanthanum nickel alloys have been studied for the past 35 years, and its structural, magnetic, and thermodynamic properties are well known. Gaseous hydrogen is absorbed in LaNi_5 up to a theoretical capacity of 1.6% by weight of hydride through interstitially bound hydrogen atoms. In order to explain the declarations set forth in the thesis objective, we must first fully understand the

material under investigation in order to have a sound basis to draw further conclusions from the experimental results.

2.2.1 Structural Properties

The empty LaNi_5 lattice has a $P6/mmm$ crystal structure, with the large lanthanum atoms at the unit cell corners, $(0, 0, 0)$ or 1a sites, and the nickel atoms in two nonequivalent sites, $(1/3, 2/3, 0)$ or 2c sites and $(1/2, 0, 1/2)$ or 3g sites [Nakamura et al. 1998] as seen in Figure 15.

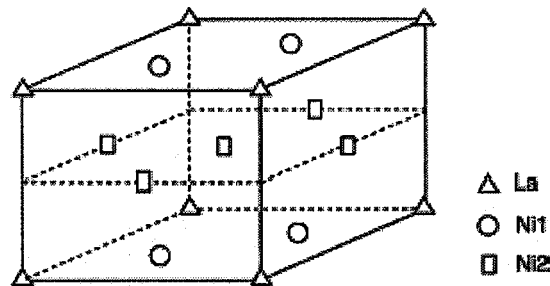


Figure 15: LaNi_5 crystal structure ($P6/mmm$)

The mechanism for this hydrogen sorption and desorption can be characterized into a number of stages; LaNi_5 – pure metal lattice, $\alpha\text{-La}_2\text{Ni}_{10}\text{H}$ – solid solution phase, and $\beta\text{-La}_2\text{Ni}_{10}\text{H}_{14}$ – saturated hydride phase. When hydrogen begins to adsorb into the metal lattice there is no change in the crystal system, but the hydrogen begins to fill interstitial voids in the structure. There are five nonequivalent interstices reported as being available to the hydrogen [Soubeyroux et. al. 1987] as

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follows in Table 2:

Table 2: La₂Ni₁₀H interstices

Site	x	y	z	Coordination	Hole radius (a.u.)
3f	0.5	0	0	La×2, Ni1×2, Ni2×2	0.486
4h	0.333	0.667	0.37	Ni1×1, Ni2×3	0.569
6m	0.137	0.274	0.5	La×2, Ni2×2	1.042
12c	0.204	0.408	0.354	La×1, Ni1×1, Ni2×2	0.733
12e	0.455	0.0	0.117	La×1, Ni1×2, Ni2×1	0.771

In the transition alpha phase of the hydride, the hydrogen have no reported ordered structure, yet there is a preference for which interstitial sites will be filled. This can be seen by comparing the hole radius, or relative sizes of the interstitial sites. The hole radius is defined as “the maximum radius of a sphere which touches the surfaces of the neighboring metal atom spheres without overlapping”. It can be seen that the 6m site has a hole radius much larger than all the other interstitials, so it logically would get filled first. This logical presumption however does not account for any interactions between the molecules, nor the electron densities within the holes. It has been reported that the 6m site indeed does have experimentally determined agreement with this theory and corresponds with the biggest occupancy for hydrogen [Percheron-Guegan et al. 1980], but the theory does not extend to the filling of the other interstitials. The authors concluded that a more careful treatment beyond effective medium theory is required to explain the observed site occupation by hydrogen in the solid solution phase.

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The beta $\text{La}_2\text{Ni}_{10}\text{H}_{14}$ crystal structure was determined by Lartrigue et. al. (1987) by powdered neutron diffraction experiments. It was reported that there were two equivalent structures the hydride can form, the hexagonal $\text{P6}_3\text{mc}$ and P31c structures, which differ by a mirror plane that coordinates the 6c sites in $\text{P6}_3\text{mc}$. Nakamura et. al. (1998) concluded through the use of total energy calculations that the $\text{P6}_3\text{mc}$ symmetry was more probable, and the structure can be seen below in Figure 16:

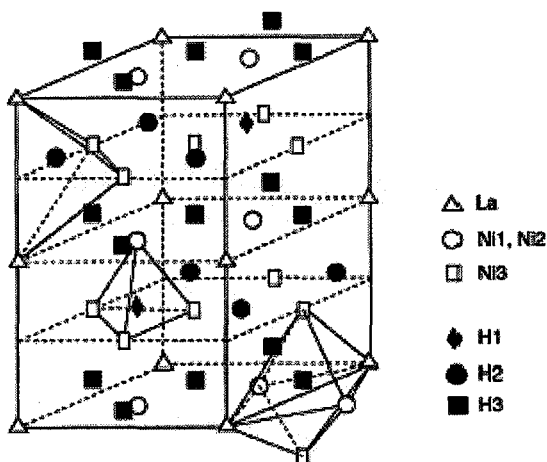


Figure 16: $\text{La}_2\text{Ni}_{10}\text{H}_{14}$ crystal structure ($\text{P6}_3\text{mc}$)

From the diagram it can be seen that the hydrogen are bonded at 3 interstitial nonequivalent sites, two of which are tetrahedrally coordinated and one octahedrally

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coordinated.

The structural data for La₂Ni₁₀H₁₄ can be found in the following table

[Soubeyroux et al. 1987]:

Table 3: Structural coordinates for La₂Ni₁₀H₁₄

La ₂ Ni ₁₀ H ₁₄		a = 10.221 a.u.		c = 16.252 a.u.					
Space group	Pearson symb.	Atom	Wyckoff symb.	Symmetry	x	y	z		
P6 ₃ mc	hP26	La	2a	3m.	0	0	0.9999		
		H1	2b	3m.	1/3	2/3	0.8203		
		Ni1	2b	3m.	1/3	2/3	0.0011		
		Ni2	2b	3m.	1/3	2/3	0.4881		
		H2	6c	m.	0.1593	0.8407	0.2952		
		H3	6c	m.	0.5069	0.4931	0.0577		
		Ni3	6c	m.	0.4999	0.5001	0.2500		
		F31c	hP26	La	2a	3..	0	0	0.0037
				H1	2b	3..	1/3	2/3	0.8297
Ni1	2b			3..	1/3	2/3	0.0061		
Ni2	2b			3..	1/3	2/3	0.4968		
H2	6c			1	0.1680	0.3223	0.2993		
H3	6c			1	0.4895	0.9994	0.0574		
Ni3	6c			1	0.4859	0.0028	0.2500		

The lattice parameters were found for each hydrogenated phase of LaNi₅ and are expressed in atomic unit (a.u.). Nakamura et al. (1998) reported the following experimentally determined lattice parameters for LaNi₅; a=9.481 and c=7.532. Soubeyroux et al. (1987) reported the following lattice parameters for La₂Ni₁₀H; a=9.495 and c=15.082. Lartigue et al. (1987) reported the following lattice parameters for La₂Ni₁₀H₁₄; a=10.221 and c=16.252.

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It would be worthwhile to note the change in unit cell volume from the unloaded to the loaded hydride is 23.4% [Lartigue et al. 1987]. It can be seen from this change in volume and density that there is a relaxation in the lattice strain of the system by a subtle shift in crystal symmetry from 6/mmm to P6₃mc. This shift allows for an inclusion of increased hydrogen, as the original 6/mmm lattice had only five nonequivalent interstitial sites, where the fully hydrogenated phase incorporates seven hydrogen atoms per formula cell unit. The energy required to facilitate this lattice shift comes from the energy released when hydrogen is chemisorbed into the lattice. It is this negative heat of formation which compensates the positive energy contributions required for the volume expansion and internal distortion [Nakamura et al. 1998]. As discussed above, hydrogen occupies interstitial sites in the metal lattice, which can be seen by neutron diffraction techniques. The interstitial bonding of the hydrogen atom also forces the nearest-neighbor metal atoms farther apart from one another, causing an increase of volume of the nearest-neighbor shell of atoms [Oriani 1994]. The free surface of the metal specimen sweeps out to produce a larger volume increase than the volume increase of the inner shell of nearest-neighbor atoms. This volume increase is the physical reason for the increase of the lattice parameters of the loaded hydride.

Another research group headed by Lakner et al. (1980) suggested that the preferential order of filling of these sites is 3f (where the empirical formula for the

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system would be LaNi_5H_3), followed by the subsequent filling of the 6m sites. It was postulated however that there was a blocking effect on the 6m sites, as this configuration would oppose the minimum approach distance of 0.21 nm of two H atoms in a lattice [Hill, 1960]. This blocking effect is due to the 6m sites being too closely spaced to accept more than 0.5H atom per metal atom. The 6m sites form tight hexagons on the $z=1/2$ plane of the lattice. According to Lakner et al. (1980) all six corners of the hexagon can be filled at high pressure, if the planar hexagon is buckled in the shape of the chair conformation of cyclohexane. These new positions are designated 12o in the P6/mmm lattice, and are alternatively situated slightly above and below the $z=1/2$ plane. The shifting to the designated 12o position places the atoms at exactly their 0.21 nm separation distance [Brodowsky, Yasuda & Itagaki, 1993]. This augmented framework for the filled crystal structure of LaNi_5 is shown as follows in Figure 17.

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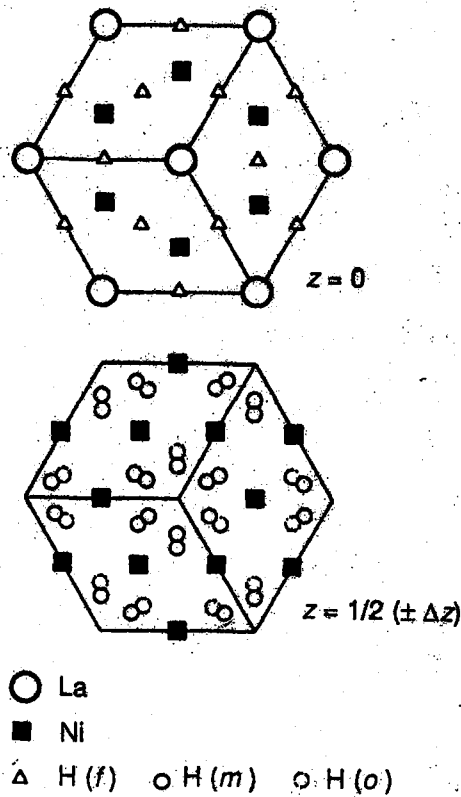


Figure 17: Internally shifted interstitial, fully filled LaNi_5 crystal structure

2.2.2 Magnetic Properties

There have been some conflicting results published when it comes to the magnetic susceptibility of LaNi_5 and its hydride phases. Tai et. al. (2003) reported that LaNi_5 was Pauli paramagnetic, with a susceptibility of 3.8×10^{-6} . It was also reported that the magnetization curves of all hydrogenated phases show ferromagnetic behavior. The authors then continued to explain this phenomenon as being due to the ferromagnetism of pure Ni phases that were decomposed during the hydrogenation process. Blach and Grey (1997) also attribute the increase in magnetic susceptibility

to the precipitation of Ni clusters, with a transition of paramagnetic unloaded LaNi₅ to a ferromagnetic La₂Ni₁₀H₁₄. The authors also proposed several exchange mechanisms for this process, the most likely being that clusters of Ni d-spins internally coupled as in bulk Ni interact via polarization of the conduction electrons in the matrix. A third source, Yang et. al. (2001) concluded that the ferromagnetic behavior was a result of the expansion of the unit cell volume. It was found that the magnetic moments of La and Ni atoms when the unit cell volume is increased, and show an abrupt decrease, reaching nearly zero when the sample is subjected to a volume decrease of ten percent. This third source would be more in accordance with the paramagnetic to ferromagnetic ordering during this reorganization to allow for more hydrogen absorption, as discussed by Brodowsky et al. and Lakner et al. It is most likely that all of these phenomena are present to different extents.

2.2.3 Thermodynamic Properties

In terms of hydride formation, the heat of formation of LaNi₅ has been reported by several authors, (Diaz et al. 1979, Percheron-Guegan 1985) measured by means of calorimetric experimental results and found to be ΔH_f^{298} (kJ mol⁻¹) = -158.9. In a review by Rudman & Sandrock [1982] the full La-Ni phase diagram is shown (Figure 18):

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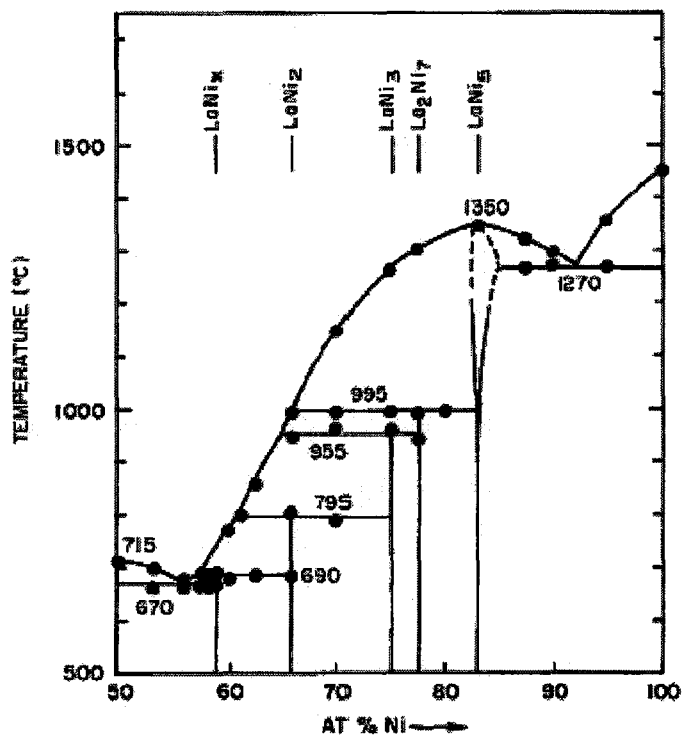


Figure 18: La-Ni phase diagram [Ref. 21]

As useful as the phase diagram is for deducing the hydride properties itself, pressure-composition-temperature (PCT) isotherms are generally used to describe the transformation of hydride species. This was shown earlier in association with van't Hoff plots, and is related to the structural transformation by Figure 19.

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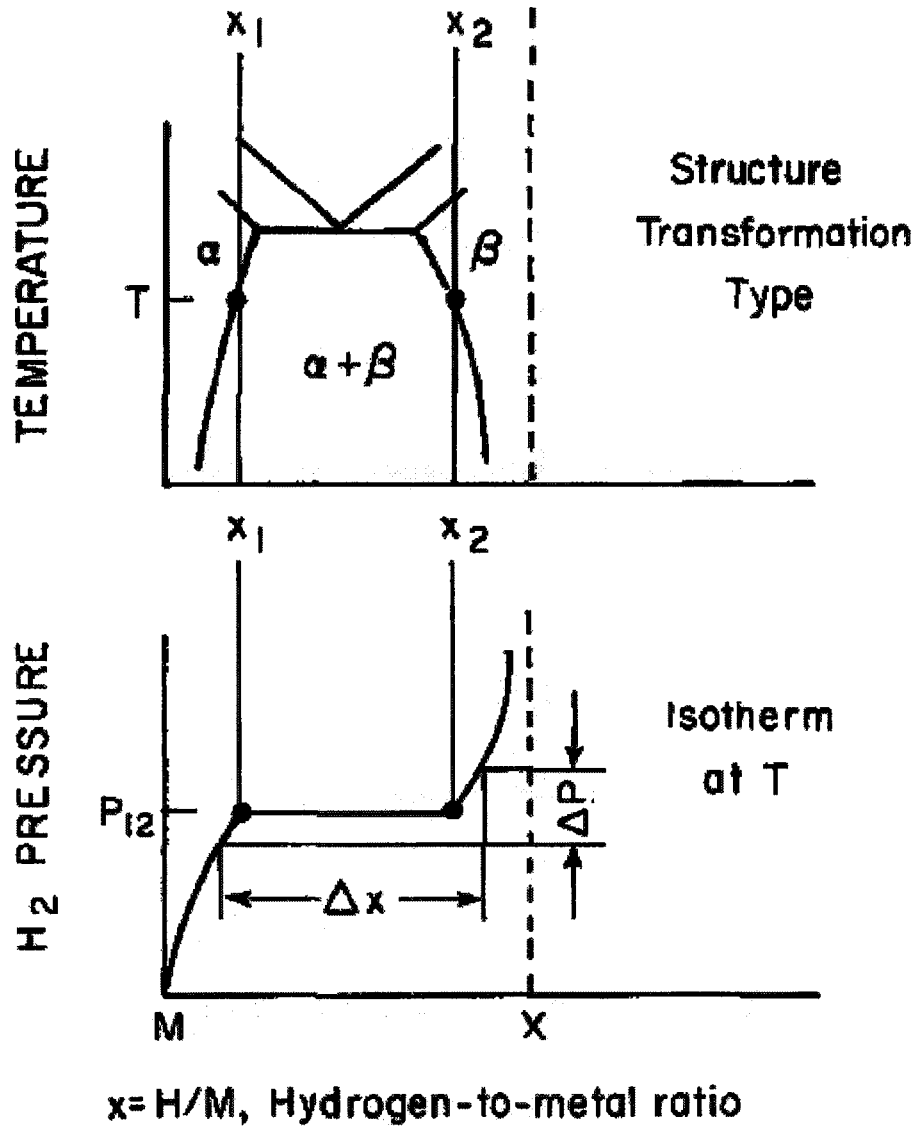


Figure 19: Metal hydride PCT diagram to phase diagram relationship

LaNi_5 only forms one fully concentrated hydride phase, LaNi_5H_7 , thus the isotherm can be broken down into three regions: the α unhydrogenated phase, the β concentrated phase, and the $\alpha + \beta$ transition plateau. These are shown in Figure 20.

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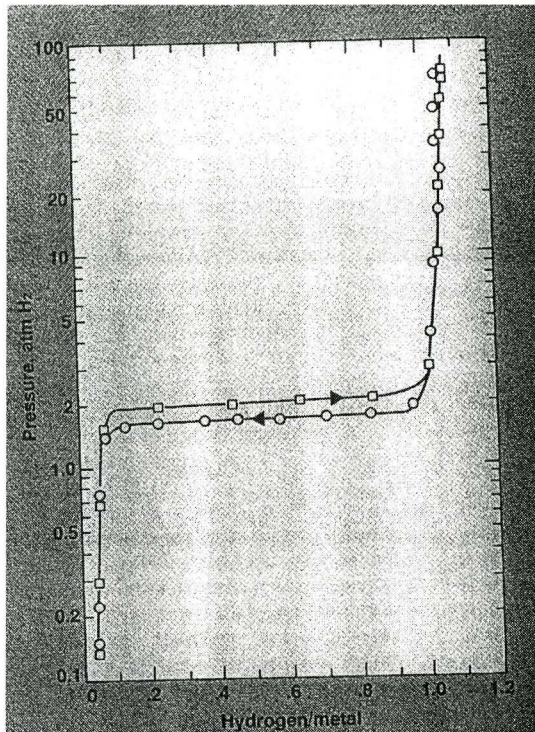


Figure 20: LaNi₅ PCT isotherm

The two-phase region ($\alpha+\beta$) of the P-C-T isotherms, the standard enthalpy and entropy of formation of the hydride phase can be calculated based on the equilibrium pressure – temperature dependence of the system (Percheron-Guegan 1985). This correlation is governed by the equation, and is identical to the van't Hoff model:

$$RT \ln P_{eq} = -T\Delta S + \Delta H$$

Murray et. al. calculated the value of ΔH to be -31.83kJ/molH_2 with ΔS to be -108.7 JK^{-1} .

3.0 Experimental Design

There are numerous experimental designs that have been employed for the study of hydrogen absorption in metal hydrides. Of these methods, some rely on descriptive information gathered during the desorption of the hydride, including temperature programmed desorption (TPD) and temperature desorption spectroscopy (TDS). Both of these techniques generate information from increasing the temperature of the sample under high vacuum from a very low starting temperature. Considering the absorption of hydrogen was the main focus of this study, these techniques were unsuitable, and more comprehensive techniques capable of measuring absorption were investigated.

Gravimetric analysis and volumetric analysis quantify absorption versus pressure and mimic the likely operation of a typical hydrogen storage system. The relative merits of these two systems have been previously reviewed [Robens et al., 1980], and are both comparatively accurate. With gravimetric analysis the absorbent is suspended from a mass balance, and the weight is measured throughout the absorptive process. Considerations are made for the buoyant forces experienced by the apparatus and the sample in these systems to account for the varied high pressure fluid, and commercial solutions are available for such experimentation. Volumetric analysis measures the amount of gas absorbed by recording the pressure decrease as

the sample is subjected to the absorbed species. This is most commonly done through dosing of a sample chamber with a known pressure and temperature of gas, and the resulting absorption calculated using gas laws. There is an advantage of using volumetric analysis over gravimetric, as no buoyancy considerations need to be taken into consideration.

3.1 Experimental Procedure

Volumetric absorption measurement apparatus was constructed as shown in schematic in Figure 21 by a previous student for use in hydrogen adsorption studies on carbon nanotubes:

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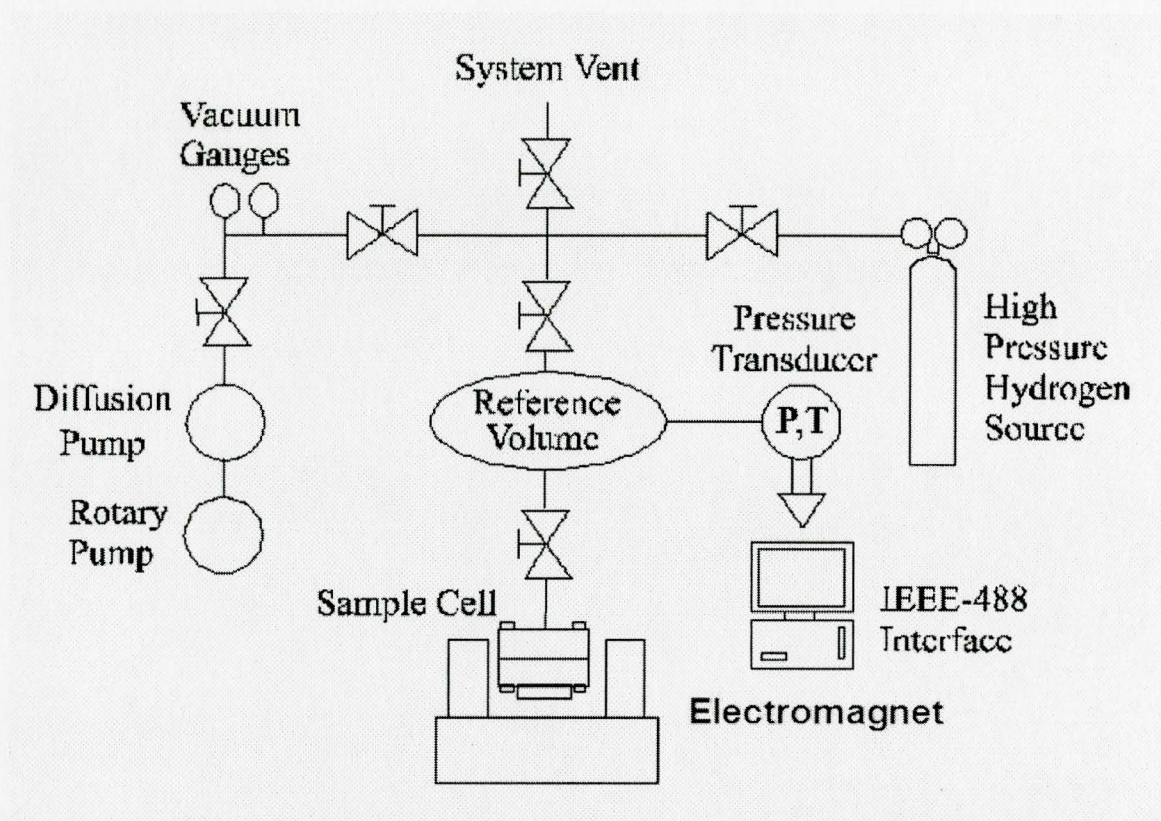


Figure 21: Volumetric absorption apparatus schematic

The current design was chosen due to its cost-effective flexibility in pressure and temperature, and only needed small augmentations to incorporate magnetic field effects on samples. The volumetric apparatus is comprised of two calibrated volumes that are separated by a valve, one of which contains the sample [Lawrence, 2002]. In its most basic operation, the first calibrated volume is pressurized to a known pressure and temperature. This is known as the reference cell, as it contains the referenced sample of gas. The sample cell valve (SCV) which connects the two calibrated volumes is then opened and the sample inside of the volumetrically calibrated sample cell is exposed to the pressurized hydrogen. By recording the initial pressure drop

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and the pressure drop over time, the absorbed moles of gas can be calculated using various gas laws.

The sample cell was designed by the previous student Lawrence (2002) and is composed entirely of 316L stainless steel. The sample is loaded via a resealable Swagelok VCR type fitting, which uses a silver plated stainless steel metal gasket. The deformation of the gasket as it is compressed by tightening the large stainless steel nut provides adequate sealing. Stock stainless steel tubing with an outer diameter of 0.25 inches and a wall thickness of 0.034 inches connect the VCR sealed volume to the SCV. Gas-tight connections were formed through the use of Swagelok's patented double ferrule design. The reference cell is also comprised entirely of 316 stainless tubing and Swagelok fittings, and incorporates the pressure transducer and dial pressure gauge.

The experimental procedure was conducted for raw samples of LaNi₅ acquired directly from Alfa Aesar. The same experimental procedure was also run on an equivalent sample, but under the influence of a 0.70 Tesla electromagnet. The results were then compared and contrasted.

Two alternative methods of evaluating volumetric data are possible. In the first method, pressure versus time data is obtained by the principle that when the known

dose of gas is introduced to the sample chamber, gas laws may be used to convert the pressure drop to absolute absorption. The second method is identical to the first, with the exception that the observed pressure versus time data is compared to that of a calibrated run obtained without any sample present.

In principle, both methods should give the correct isotherm, yet this is not the case. The first method has been shown to provide erroneous results attributed to systematic error, shown by Kiyobayashi et al (2002). These authors proposed to compensate for this error by incorporating the sample cell volume as a function of pressure [Kiyobayashi, 2002]. Although the authors were unable to identify the source of this systematic error, it is speculated by this author that it would be due to surface adsorption of the gas on the internal area of the sample chamber, thus reaffirming the compensation solution proposed by Kiyobayashi et al (2002). As an alternative to the compensation for the systematic error caused by adsorption on the internal surface area of the sample chamber is to use the empty-cell calibration method. By repeating the experiment with an empty sample cell for a given pressure, the systematic error can be separated and eliminated.

3.2 Isothermal Measurement Equipment

The pressure transducer is manufactured by Druck, and has a pressure range of 0-5000 psig with a rated accuracy of 0.08% full scale, including hysteresis. This is

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powered by a BK Precision 1635 DC power supply providing an excitation voltage of 12.0 V with a measured fluctuation of less than 0.04% over a period of 24 hours [Lawrence, 2002]. Pressure data is sampled using a Keithley 177 microvolt digital multi-meter connected to a PC using IEEE-488 interface. The temperature data was recorded through the use of parallel coupled type K thermocouples. One thermocouple was immersed in an insulated, constant temperature ice dewer, with the other attached through a pressure connection to the outside of the sample chamber. Using the ice dewer as a reference, the signal from the thermocouple connection was captured using a HP 3478A Digital Multi-Meter also connected using IEEE-488 interface.

Once the data had been collected from the pressure transducer a series of steps were applied to analyze and convert the signal to system pressure. Pressures in mA are recorded and converted to psi according to the following relationship:

$$\begin{aligned} P(\text{psi}) &= [P(\text{Amps}) - 0.004(\text{Amps})] \cdot \frac{F.S.(\text{psi})}{F.S.(\text{Amps})} + 14.69595 \text{ psia} \\ &= [P(\text{Amps}) - 0.004(\text{Amps})] \cdot \frac{5000 - 0}{0.020 - 0.004} + 14.69595 \text{ psia} \end{aligned}$$

The pressure transducer has a full-scale (F.S.) range of 0-5000 psi, corresponding to an output potential of 0.004 A to 0.020 A. The addition of 14.69595 psia is required to convert the measured gauge pressure to absolute pressure. Atmospheric pressure typically varies by 1%, corresponding to a F.S. fluctuation of 0.0003%, which is

negligible.

The data collected from the K-type thermocouple was calibrated using two fixed references, the normal boiling point of water and melting point of ice. As expected, the thermocouple output followed a linear trend. Since the thermocouple was calibrated by hand, the error associated with it is negligible.

3.3 Calculations & Data Manipulation

The collected data was transferred to spreadsheet form for calculations and data manipulation. The calculations themselves are elegant in their simplicity. The van der Waals gas law was used in calculating the number of moles of gas absorbed associated with the pressure drop when compared against the calibrated empty cell run. The van der Waals gas law is a triatic equation,

$$\left(P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$$

where P is the pressure in atmospheres, V is the volume in litres, R is the universal gas constant = $0.082057 \text{ L} \cdot \text{atm} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, and T is the temperature in Kelvin. The van der Waals gas constants a and b are gas specific constants used as corrective terms to compensate for particle-particle interactions, and the finite volume of molecules in the gas phase, respectively. For hydrogen gas, $a = 0.2461 \left(\frac{\text{litre}^2 \cdot \text{atm}}{\text{mole}^2} \right)$,

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and $b = 0.0267 \left(\frac{\text{litres}}{\text{mole}} \right)$ [Gaskell, 1981]. The Newton Raphson iteration method was

used to solve for the number of moles of hydrogen gas. Starting with an initial estimate using the ideal gas law,

$$n = \frac{PV}{RT}$$

the number of moles was substituted into the Newton-Raphson equation,

$$n_{n+1} = n - \frac{F(n)}{F'(n)}$$

and iterated until the error function,

$$\text{error} = \text{abs} \left(\frac{n_n - n_{n+1}}{n_{n+1}} \right) < 0.000001$$

where

$$F(n) = \frac{n^3 ab}{V^2} - \frac{n^2 a}{V} + n(RT + bP) - PV$$

and

$$F'(n) = \frac{3n^2 ab}{V^2} - \frac{2na}{V} + RT + bP$$

The weight percent absorption was then calculated using the known mass of hydride according to

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$$wt\%absorbed = \frac{n_{H_2} \cdot MM_{H_2}}{(m_{LaNi_5} + n_{H_2} \cdot MM_{H_2})} \cdot 100$$

where m_{LaNi_5} is the mass of the hydride sample in grams, and MM_{H_2} is the molar mass of hydrogen gas in grams per mole.

4.0 Results and Discussion

The general results of this study are broken down into two different subsections in accordance of the samples used. All of the LaNi₅ was acquired through Alfa Aesar, but through much experimentation it was discovered that there had been a switch in their supplier and the material being provided was of an unknown, different crystal structure, although compositionally correct. This was suspected only after all other considerations had been checked and double checked, with a complete inspection and rebuild of the pumping system, valve system leak testing and reconstruction, and total review of theory and recalculation of results. The samples were compared using an optical microscope as well as SEM. Through both of these techniques there was no visible difference between the two sample sets. Examples of the optical microscopy images are shown in Figure 22 and Figure 23. Examples of the SEM images are shown in Figure 24 and Figure 25.

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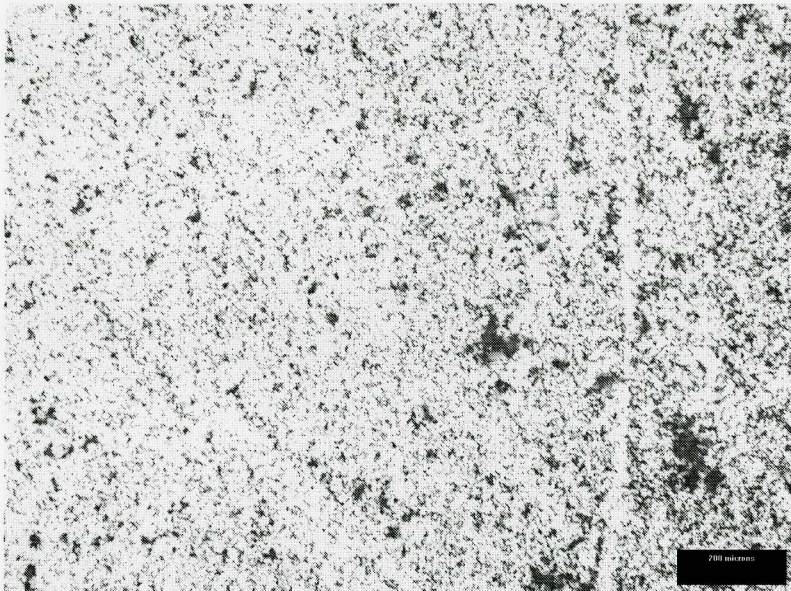


Figure 22: Sample Set 1 optical microscopy image depicting powder distribution

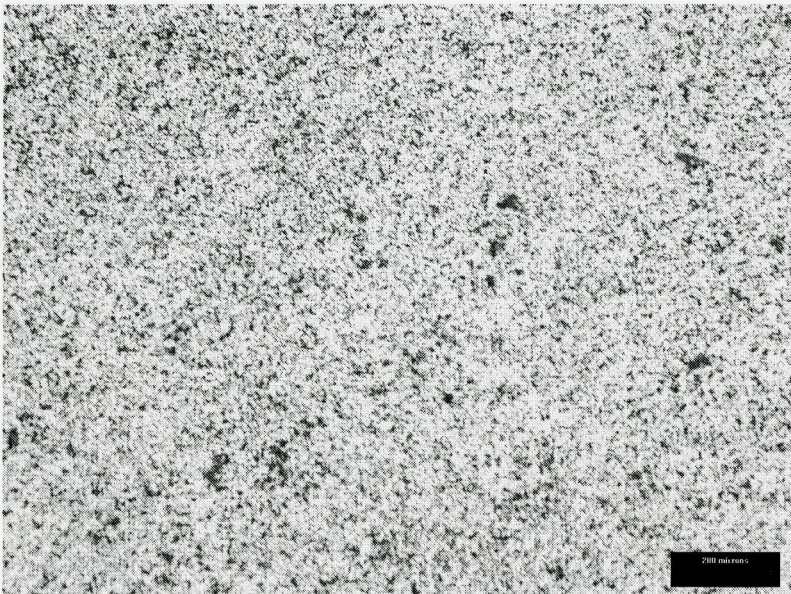


Figure 23: Sample Set 2 optical microscopy image depicting powder distribution

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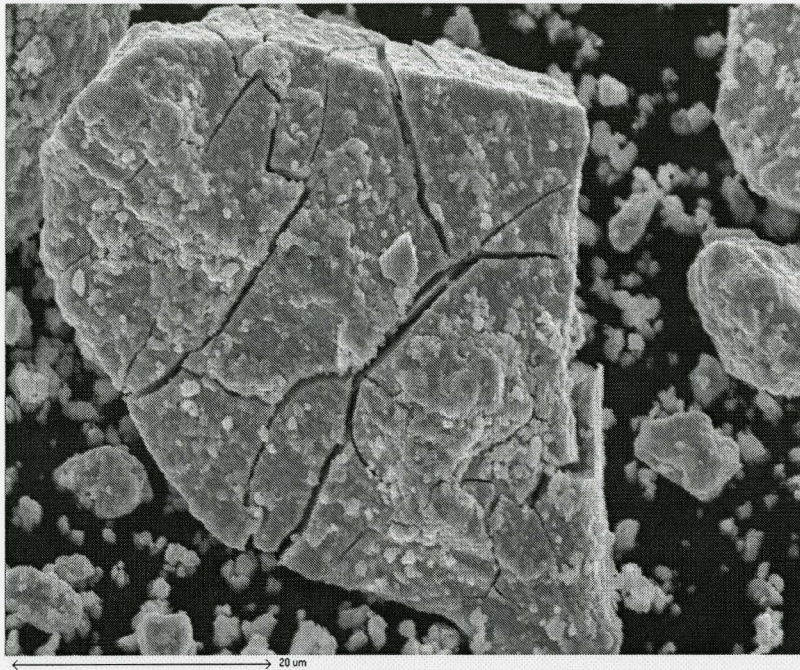


Figure 24: Sample Set 1 SEM image depicting particle morphology

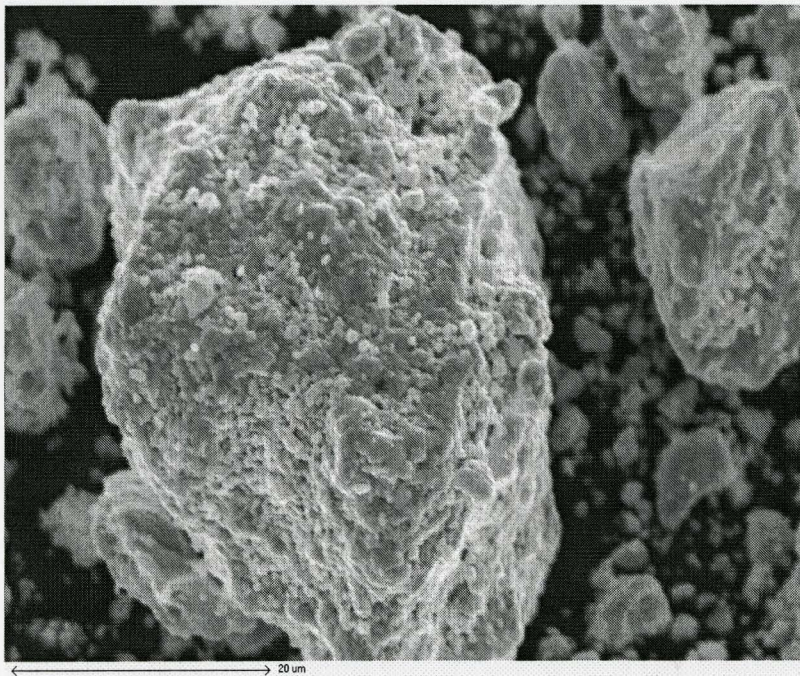


Figure 25: Sample Set 2 SEM image depicting particle morphology

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Although Alfa Aesar reported that the major crystal system for all the samples had remained the same, x-ray diffraction was performed on the different samples and it was determined that they had slightly different crystal systems, as identified by the ranking of their peaks in order of intensity. In x-ray diffraction pattern analysis, the position of the peaks defines the crystal unit cell through their 2θ positions. It is the relative intensities of their peaks that indicate the arrangement of the specific atoms within the unit cell [Cullity & Stock, 2001]. This difference can be seen in the following graphs, in which their x-ray analysis has been plotted and peaks numbered.

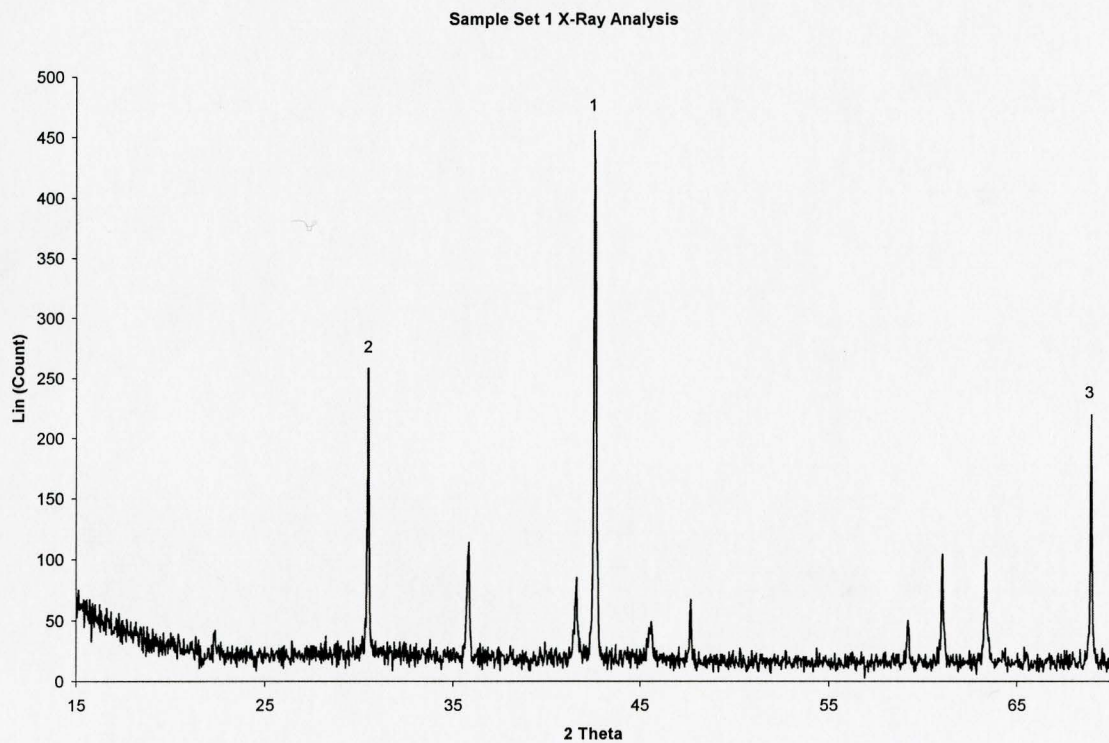


Figure 26: Sample Set 1 - full absorption set x-ray characterization

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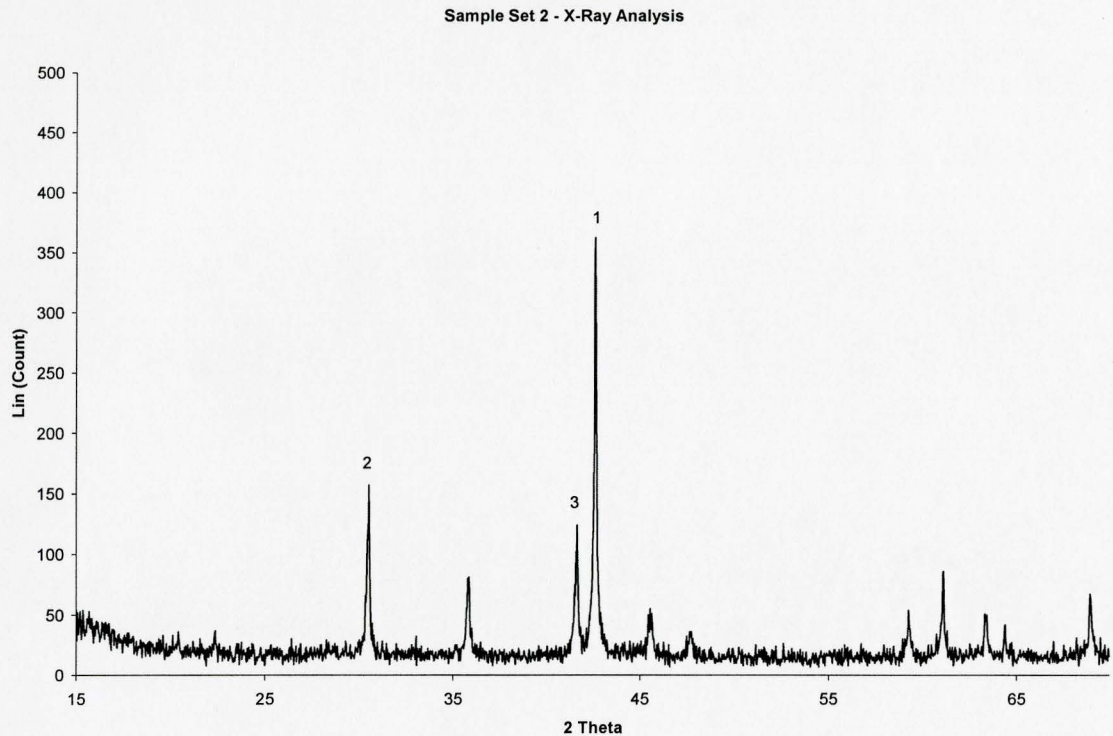


Figure 27: Sample Set 2 - partial absorption set x-ray characterization

Several sets of X-Ray Characterization were performed, and the samples all showed a shift in the ranking of the peaks, confirming the presence of different crystal subsystems. Given that the hydrogen atoms are stored interstitially, even a slight distortion of the crystal structure could lead to deterioration of the hydride's capacity to store hydrogen. In the end, it was found that these subtle differences in their crystal systems produced a substantial difference in results, and thus were broken down accordingly.

4.1 Sample Set 1 – Full Absorption Set

The first series of data to be analyzed belongs to a series of tests dubbed ‘Full Absorption Set’. It was named in this manner as it was typical of several published sources in terms of maximum capacity and kinetics of a typical LaNi₅ sample under standard conditions [Yasuda & Brodowsky 1993, Sandrock & Huston 1981]. It is from this sample set that initial and encouraging results were shown, before the speculated Alfa Aesar supplier switch occurred.

4.1.1 Sample Set 1 – Data Validation

The results were the primary results to be collected for this study, and the results match very well with the theoretical hydrogen storage capacities found in the literature [Yasuda & Brodowsky 1993]. Unfortunately this data is not as clean as the data collected near the end of this study, as there were system problems due to equipment failures and leaking valves which were later replaced. It is due to this variability in the data collected that several different techniques were used to analyze and decipher the true data from the noise. Initially measures were taken to simply eliminate the leaks by modeling out the leak rate linearly, as when the leak rate is small, it would occur at a nearly constant pressure, so the leak would assume a linear

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rate proportional to the pressure of the system in accordance of standard fluid mechanics.

This analysis worked well until the degradation from the repeated opening and closing of the valves caused the leak rate to increase to a point where it was no longer able to be measured linearly. This resulted in the loss of a large portion of the data, as it would be beyond the scope of this project to accurately develop a model to incorporate a variable temperature-pressure leak model into the system.

Another complication that arose was associated with the data collection itself. Due to the capabilities of the computer measurement system, data points could at most be measured once every minute, or else the system would crash due to the large amount of data generated if a higher sampling rate was set. This measurement rate was acceptable during the adsorption process, as the data were seldom under a state of heavy fluctuation, but problems occurred when measuring the initial pressure after immediately opening the sample valve. If the measurement was taken in the brief period of time it took for the system to reach steady state or equilibrium, then an inaccurate measurement was recorded for the initial pressure of the total system. This problem was overcome, and correspondingly the leak modeled data verified, by a quick calculation of the expected system pressure at the reference valve open state. Since the volumes of the reference chamber and sample chamber were known, and

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the initial pressure in the reference volume measured several times for accuracy, the total expected system pressure could be calculated using the ideal gas law. This calculated pressure was compared with the measured pressure, ensuring the hydrogen adsorption calculations were done accurately.

4.1.2 Sample Set 1 – Results

Since it is known that the adsorption curve fits that of the Langmuir isotherm all of the data sets were independently examined thoroughly and if after any leak rate and initial pressure calculations were conducted the typical s curve was not observed, the data was discounted. This refined data can be seen in the plot below of weight percent absorption over time.

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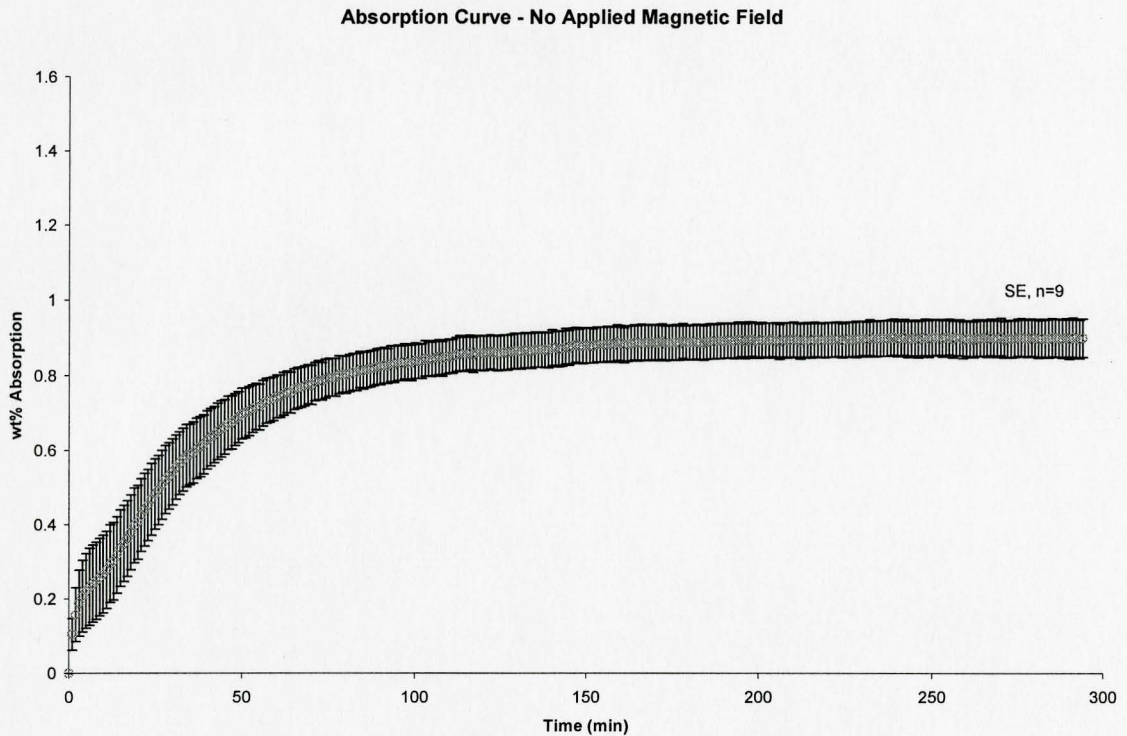


Figure 28: Sample Set 1 no field equilibrium absorption curve

It can be seen that the standard error of the sample is fairly minimal with the sample set of nine runs showing a high degree of accuracy. The standard error is calculated by dividing the standard deviation by the square root of number of measurements that make up the mean [Walpole et al. 1998]. This standard error will be useful in the comparison of the results following the presentation of the magnetically influenced data.

The data for the magnetically influenced adsorption runs was also analyzed

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under the same dissecting conditions, and the results can be seen as follows.

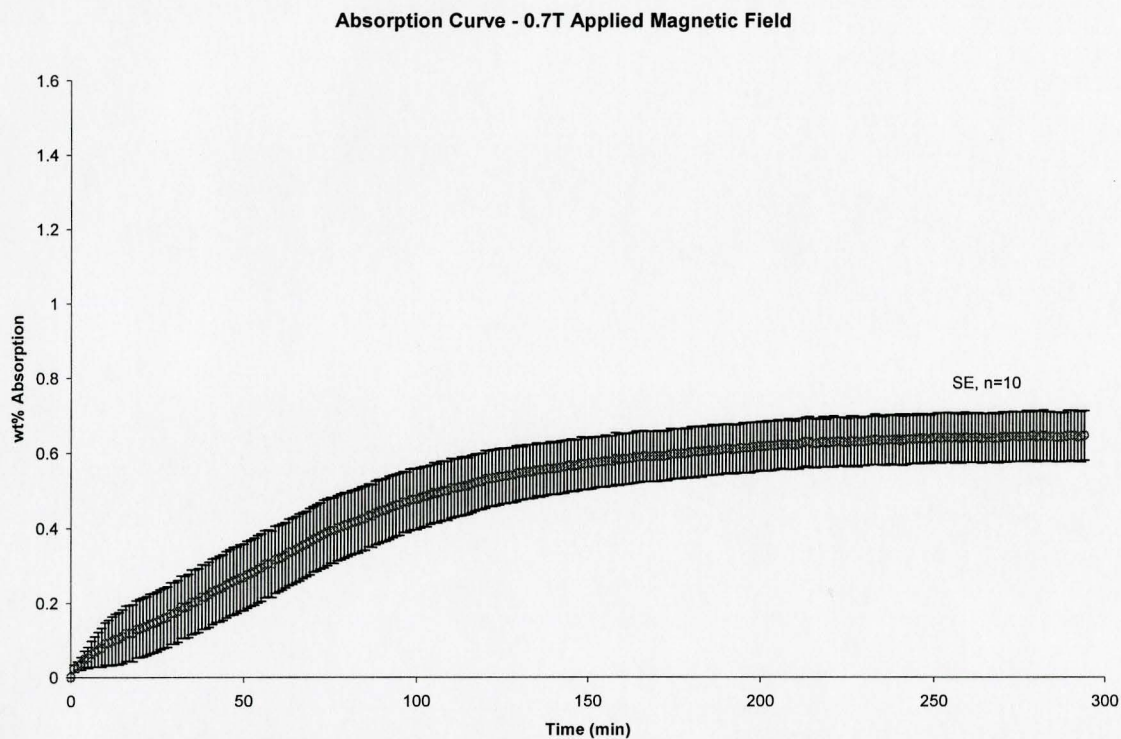


Figure 29: Sample Set 1 0.7T field equilibrium absorption curve

It can be seen that the standard error of the magnetically influenced sample is also small with the sample set of ten runs showing a fairly consistent degree of accuracy.

In direct comparison the two data sets appear to show that there exists a

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distinct difference between the samples with and without the presence of an externally applied magnetic field. This can be seen by the following graph; however, further statistical analysis must be explored before any definite conclusions can be drawn.

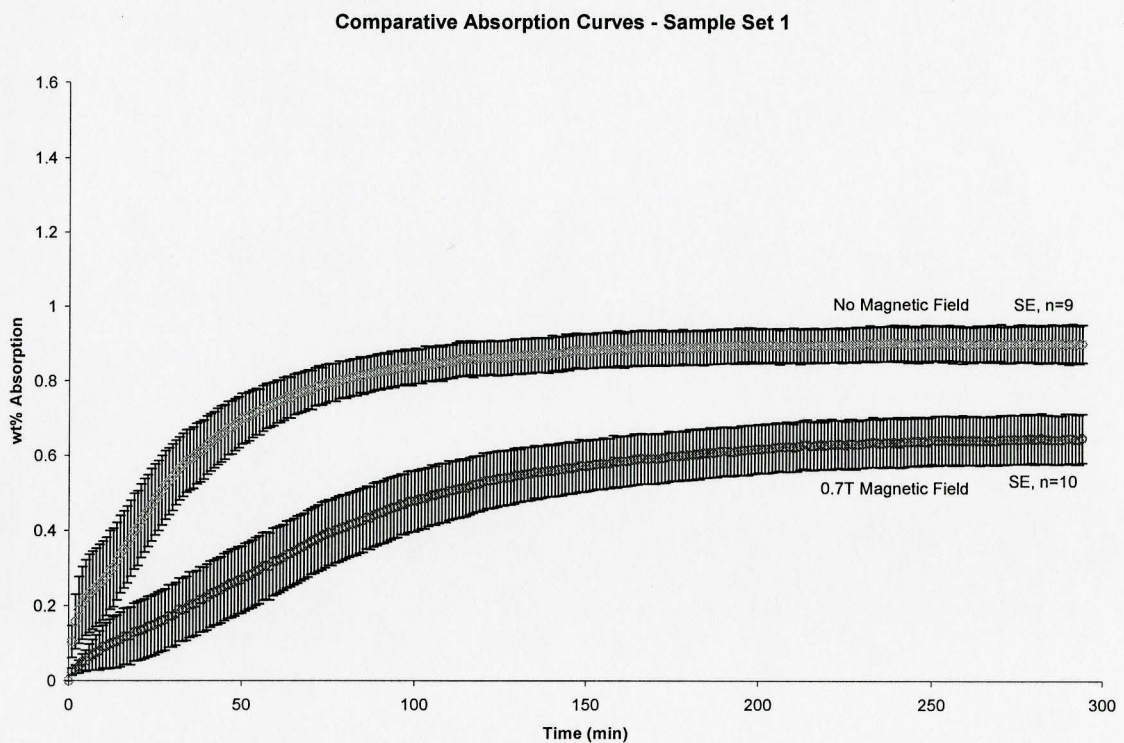


Figure 30: Sample Set 1 equilibrium absorption curve comparison

A Student's t-test was employed for this task. At several places along the two curves, the data was analyzed to check whether their means (and thus their true values) were significantly different with respect to a 95% degree of certainty. Recalling basic

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descriptive statistics, it is seen that a standard error (σ_n) for a mean is calculated from the standard deviation (σ) as follows: $\sigma_n = \sigma / \sqrt{n}$ [Walpole et al. 1998]. This is used in measuring the variance in the difference of the means of the two samples according to the formula:

$$\sigma_d^2 = \frac{\sigma_1^2}{n_1} + \frac{\sigma_2^2}{n_2}$$

With σ_d now known, the t value can be calculated and compared to the critical t value ($p = 0.05$) for 17 degrees of freedom, ($n_1 + n_2 - 2$). If the calculated value exceeds the critical value of 2.11, we are 95% confident that the means differ significantly and there does indeed exhibit a significant effect on hydrogen adsorption capacity of LaNi₅. T is calculated as follows:

$$t = \frac{\bar{x}_1 - \bar{x}_2}{\sigma_d}$$

These results are summarized below for various points on the two curves in the following table:

Table 4: Set 1 Statistical Analysis

Time (min)	\bar{x}_1	$\frac{\sigma_1^2}{n_1}$	\bar{x}_2	$\frac{\sigma_2^2}{n_2}$	σ_d^2	t
30	0.172215	0.006828	0.541243	0.007877	0.121265	3.043139
60	0.319159	0.007931	0.743488	0.003262	0.105797	4.010774
90	0.446385	0.006832	0.823324	0.002332	0.095729	3.937558
120	0.529423	0.005847	0.859119	0.002115	0.089234	3.69474
150	0.570976	0.004612	0.878932	0.002145	0.082198	3.746513
180	0.601789	0.004521	0.887148	0.002047	0.081039	3.521243

As seen from the t-test results, the statistical analysis clearly not only shows a difference between the two sets of data at a 95% confidence, but also at a 99% confidence with the t_{crit} value of 2.90 being surpassed.

4.1.3 Sample Set 1 - Discussion

As shown by the statistical analysis of this set of samples there does exist a significant effect of the magnetic field on the adsorption of hydrogen by LaNi₅. One cause of concern however is the temperature effects of the electromagnet on the sample chamber. While the temperature was kept nearly constant through the use of a heating rope, small fluctuations occurred in both samples. This fluctuation resulted in a variation in the order of 3-5°C, which could have significant effects on the absorption kinetics and equilibrium pressures. This however does not seem to be as dire as thought however, as both the samples were heated to the same temperature with the same heating rope, so they both experienced the same random temperature fluctuations. If this series of tests were to be performed again, a more controlled atmosphere would be designed in order to completely eliminate this variable from the experimental process.

The results of the experiments on this sample set showed that the magnetic field lowers the overall capacity of the hydride. As seen in the 2.2.1 Structural Properties section, the LaNi₅ crystal lattice undergoes a less than subtle shift in order to accommodate a change in unit cell volume from the unloaded to the loaded hydride of a 23.4% volume increase [Lartigue et al. 1987]. Also mentioned was that the degeneracy, or number of arrangements of each type of hexagon, was presented as

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two models; f_k , a disordered ‘paramagnetic’ model in which each of the 12o sites is available, and g_k , a long range ‘ferromagnetic/antiferromagnetic’ ordered model where only a subset of six of the 12o sites is available [Lakner et al 1980]. Under the influence of an externally applied magnetic field it is hypothesized, the degeneracy is limited to g_k , in which the long range ferromagnetic orientation is forced, and only the subset of the six of the 12o sites are used. This would account for the decreased saturation of the LaNi₅, and the magnetic field could be seen to prevent this shift to the disordered model from occurring. This is illustrated in the following figure, Figure 31, which varies subtly from Figure 17.

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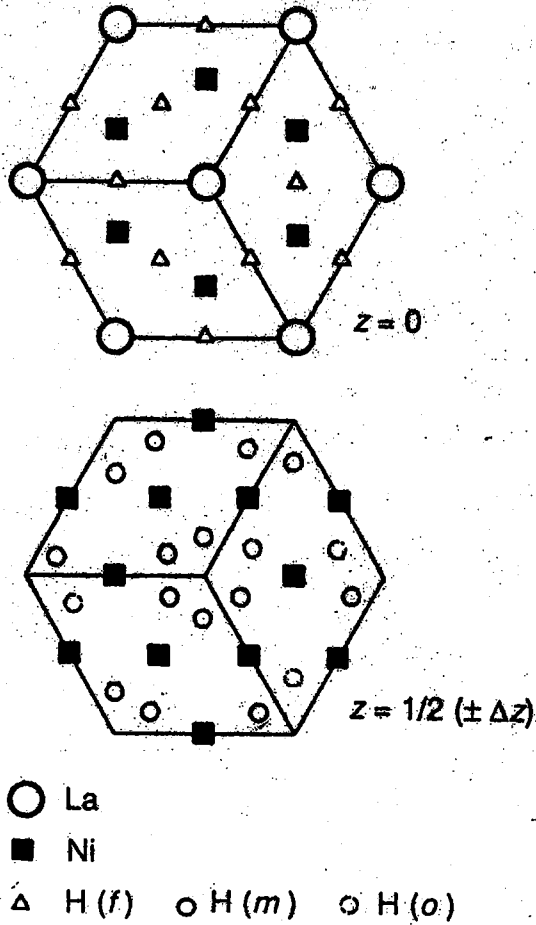


Figure 31: Augmented partially filled LaNi_5 crystal structure [Ref. 12]

Further proof of this effect could be deduced through the variation of the magnetic field when the sample had reached the magnetic pseudo-steady state. If a sample of LaNi_5 were to be subjected to a magnetic field such that the blocking effect takes place, but after the adsorption had fully occurred and equilibrium had been reached the magnetic field removed, then adsorption should then increase to the fully saturated level. This postulated theory is illustrated in the plot below:

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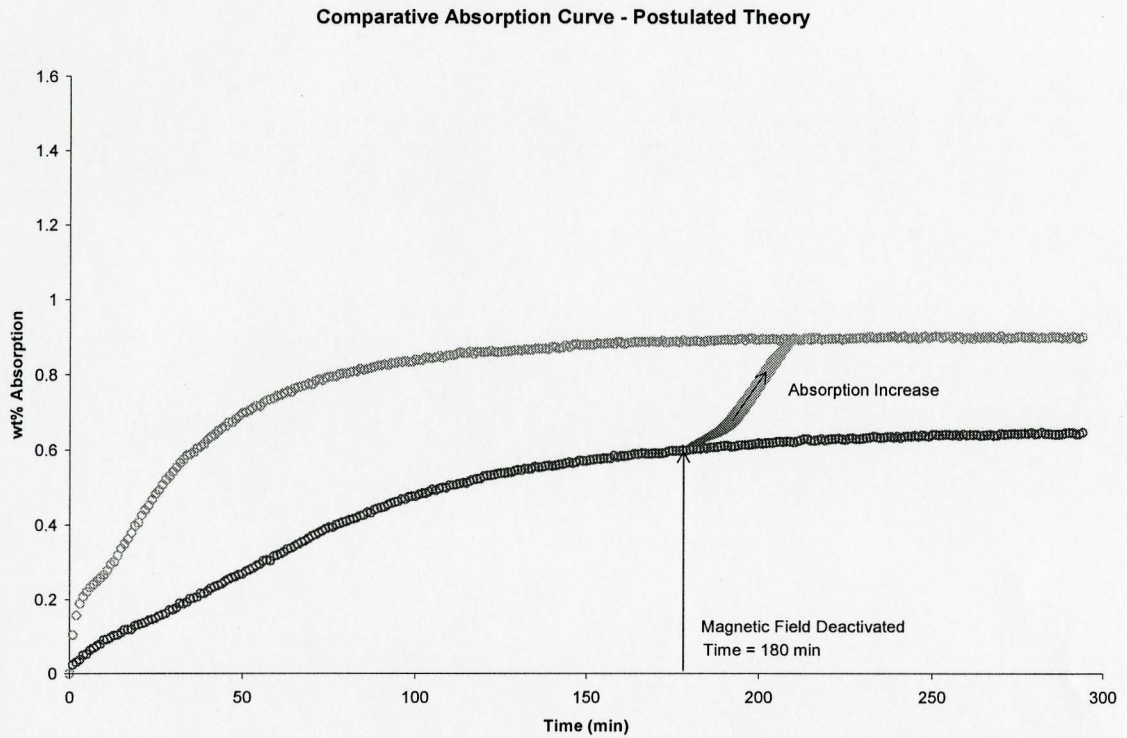


Figure 32: Theoretical transient magnetic effect

Unfortunately, before these new experiments could be carried out, the aforementioned supply switch occurred, and thus this experiment shall remain a conjecture.

4.2 Sample Set 2 – Partial Absorption Set

The second series of data to be analyzed belongs to a series of tests dubbed ‘Partial Absorption Set’. It was named as such as it fell short of the typical published results in terms of typical maximum hydrogen loading capacity under standard conditions [Yasuda & Brodowsky 1993]. It is this sample that represents the current material available through Alfa Aesar.

4.2.1 Sample Set 2 – Data Validation

After it was found that the data being collected was correct, and the material itself was the problem, the experiments were re-run with this new alloy of LaNi₅. The reference chamber valve was replaced, completely eliminating the need to leak model the data, and there was a cooling water line incorporated on the electromagnet in an effort to keep the temperature variation to a minimum. These improvements ensure that the data does not need to be manipulated in any way to draw out the truth. Unfortunately, it was found that this different alloy of LaNi₅ does not store hydrogen, even after activation through standardized methods [Schlapbach et al. 1979]. Another improvement in terms of data collection and validation is an augmentation to the data collection program. As mentioned above, data were collected at a rate of once per

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minute so that the computer would not be overwhelmed by the large amount of information gathered. This obstacle was temporarily alleviated through the use of additional calculations to verify the recorded data, but it was decided that a more rapid collection rate was needed for when the sample was initially exposed to hydrogen in order to increase the resolution of the data during this crucial time. The program was augmented to collect data every second, as opposed to every minute, for the first hour of hydrogen exposure but then revert back to the once per minute sample rate for the following five hours.

One other unfortunate development was the break down of one half of the electromagnet, effectively reducing the magnetic field generated to half that of the previous tests. There were no experiments done with the new material at the maximum field strength that did not have overwhelming leak rates, and thus a direct comparison to the old data is not possible. Even without this direct comparison however, the effects of this less powerful magnetic field were tested and analyzed.

4.2.2 Sample Set 2 – Results

Once again all of the data sets were independently examined and if there was no significant leak rate they were methodically analyzed. The results seen in the plot below of weight percent absorption over time are for the non-magnetically affected

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samples.

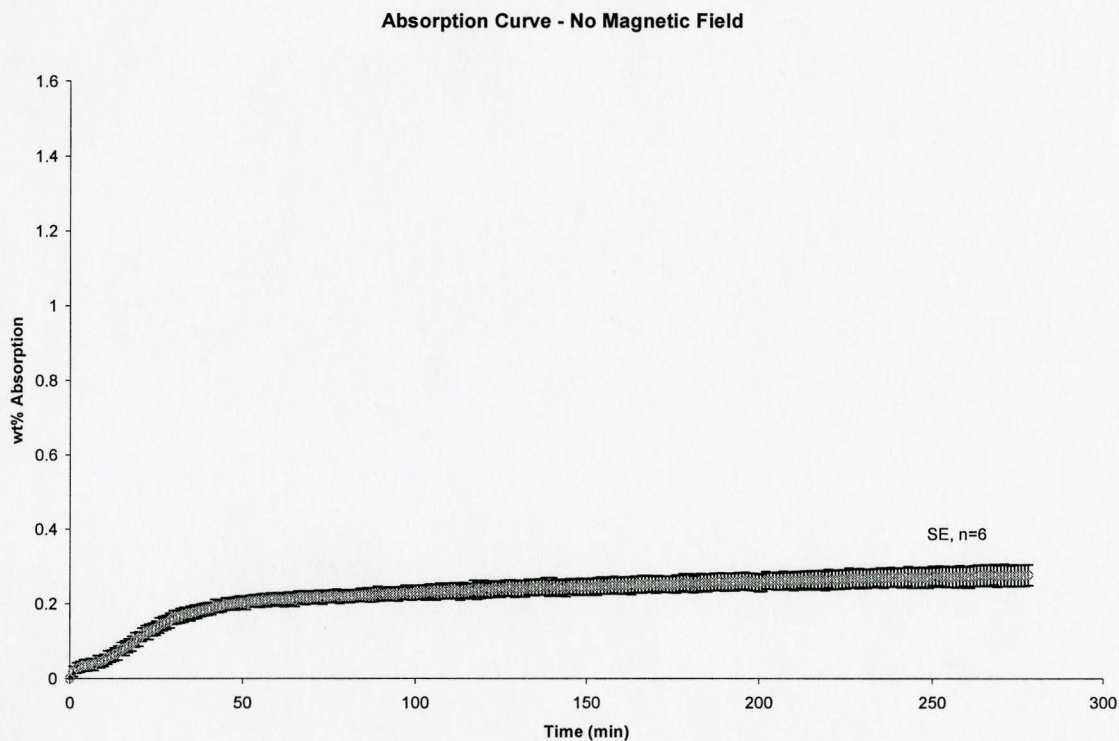


Figure 33: Sample Set 2 no field equilibrium absorption curve

It can be seen that the standard error of the sample is much smaller than sample set 1, with the sample set of six showing an improved degree of accuracy, even though a smaller set was used. This is due to the tighter controls during the experimental procedure, as well as the absence of a significant leak rate.

The data for the magnetically influenced adsorption runs was also analyzed

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under the same dissecting conditions, and the results can be seen as follows in Figure 34.

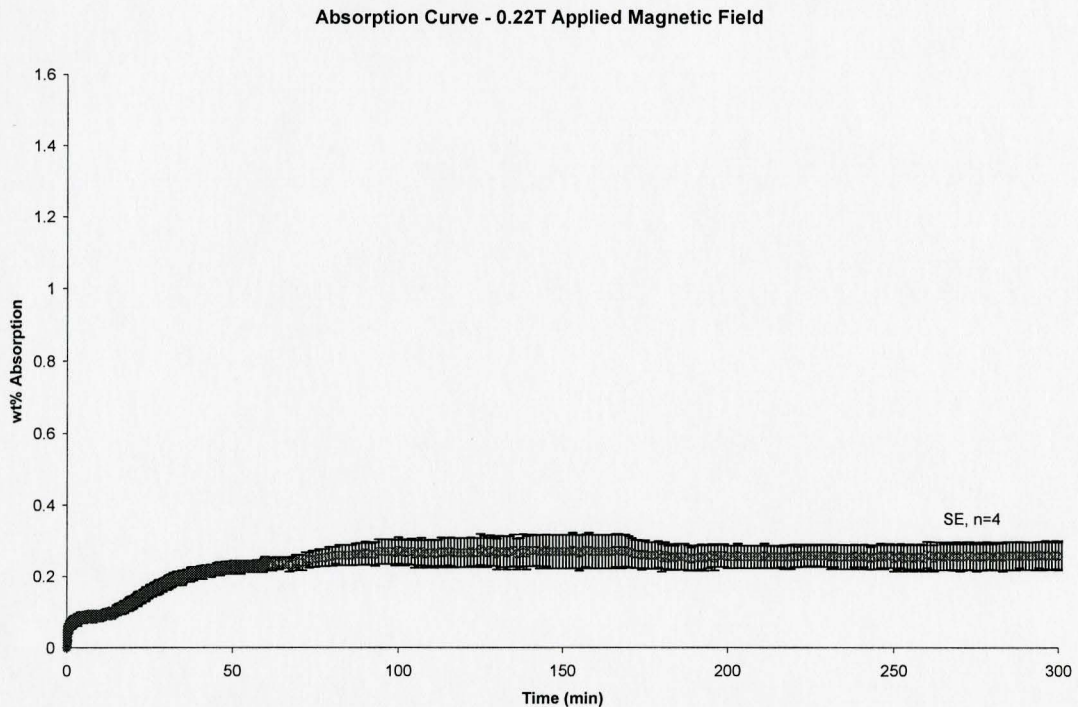


Figure 34: Sample Set 2 0.22T field equilibrium absorption curve

It can be seen that the standard error of the magnetically influenced sample is also comparatively minimal with the sample set of only 4 showing a strong degree of repeatability.

In direct comparison the two data sets do not appear to show that there exists a distinct difference between the samples with and without the presence of an

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externally applied magnetic field, unlike the previous sample set. The comparative results are shown in the graph below. Once again, further statistical analysis must be explored before any definite conclusions can be drawn.

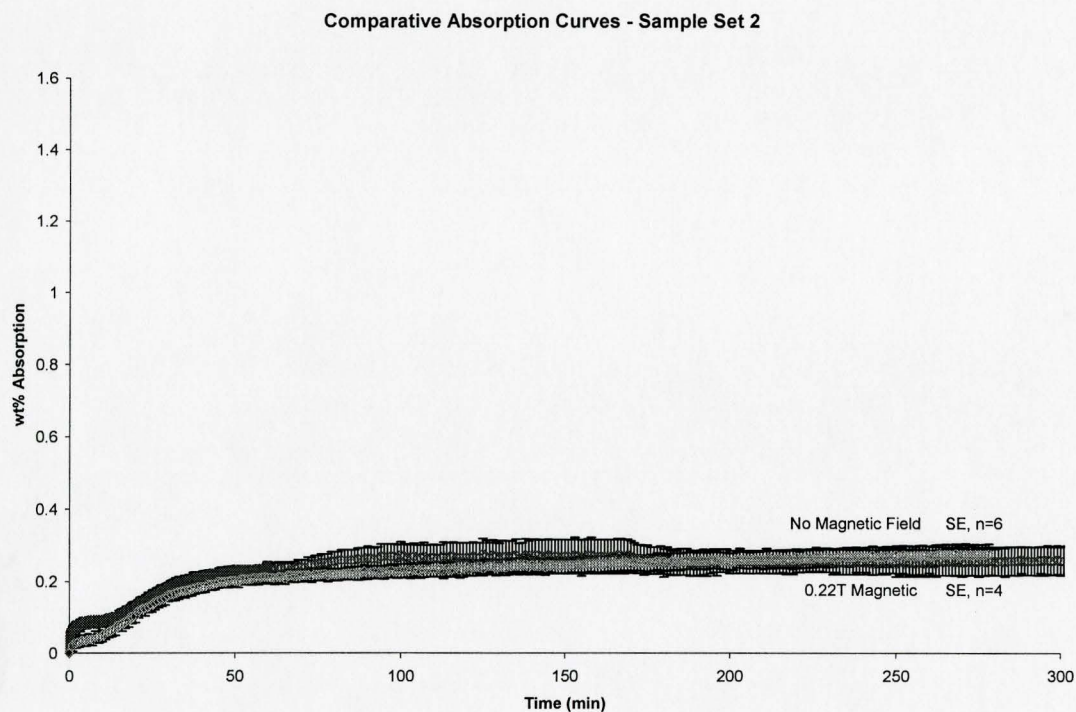


Figure 35: Sample Set 2 equilibrium absorption curve comparison

Descriptive statistical analysis was once again applied to the data, with the results summarized below for various points on the two curves:

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Table 5: Set 2 Statistical Analysis

Time (min)	\bar{x}_1	$\frac{\sigma_1^2}{n_1}$	\bar{x}_2	$\frac{\sigma_2^2}{n_2}$	σ_d^2	t
30	0.179211	0.026679	0.162233	0.045331	0.268347	0.063268
60	0.238151	0.030655	0.210871	0.043815	0.272892	0.099968
90	0.265488	0.06469	0.223082	0.042257	0.327027	0.129671
120	0.265727	0.082152	0.240192	0.052902	0.367498	0.069483
150	0.268804	0.094495	0.243126	0.051403	0.381966	0.067228
180	0.251571	0.077327	0.255266	0.05721	0.366793	0.010073

As expected from the visual inspection of the graph, and since the calculated t value does not exceed the critical value of 2.11, it proves that an externally applied magnetic field does not exhibit a significant effect on hydrogen adsorption capacity of the new samples of LaNi₅.

4.2.3 Sample Set 2 – Discussion

As shown by the statistical analysis of this set of samples there does not exist a significant effect of the magnetic field on the adsorption of hydrogen by LaNi₅. With this sample, the set temperature was more tightly controlled, as the magnet was cooled, so temperature variation was simply due to changing atmospheric conditions. The heat generated from the absorption of the hydrogen also was seen to affect the absorptive properties of this sample, as all of the other variables were sufficiently controlled to show that absorption varies inversely with temperature. While to some this may be seen to be a negative finding in terms of confidence in results, it is in fact the opposite. With this trend we can be certain that the results are completely true, as the slight variation in temperature should affect the adsorption – proving that the precision of our instrumentation and analysis is accurate enough to track this. This increases the confidence in our experiments immeasurably. Also, as both the samples were subjected to the same temperature conditions, and they both experienced the same random temperature fluctuations due to the same heat release through hydrogenation, it is still applicable to do a direct comparison between the magnetized vs. unmagnetized samples.

One final point on the subject of temperature variation is the masses of materials involved. On average, the sample size of LaNi₅ was on the order of 0.4 g. The sample chamber itself weighs approximately 60 g and is composed of 316L

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stainless steel. With this large difference in masses, and thus heat sink capacities it is conceivable that the heat generated by the LaNi₅ is absorbed by the large mass of stainless steel, in effect preventing the temperature differential. This exercise in heat transfer mechanics was not considered further.

Even though there was no witnessed effect from the applied magnetic field, it does not mean that this does not allow for further discussion and comparison with the previous sample set. In fact, this low adsorptive sample set adds to the conclusion drawn in the previous sample set's discussion. It was established by Lakner et al. that the preferential order of filling of the hydrogen interstitial sites is 3f (where the empirical formula for the system would be LaNi₅H₃), followed by the subsequent filling of the 6m sites. It can be clearly seen from the maximum absorption of sample set 2 that the filling of the 6m sites is not accomplished. Since the magnetic field was theorized to limit the degeneracy to g_k, in which only the subset of the six of the 12o sites are used, it would be expected that the decreased saturation of the LaNi₅ would not occur in this sample set, as the magnetic field would not affect the filling of the 3f sites. This was indeed the case for this sample set, as it was observed that hydrogen was not absorbed to a high capacity.

While speculation may arise in the interpretation of this result due to the lowered strength of the magnetic field it must be pointed out that the field strength was only

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decreased by a factor of approximately three. This is noteworthy, yet is not as big of a cause for concern, as the field strength is of the same order of magnitude. If true quantification in terms of energetics were to be done for this phenomenon, an accurate correlation between the variation in field strength (done in a broad spectrum of values) in relation to variation of adsorptive limits would need to be performed. Since the magnetic field was at full strength during the latest round of tests, and no effect was observed, new equipment would be needed to facilitate this.

5.0 Conclusions

Typical hydrogen absorption of LaNi₅ through constant volume equilibrium experiments were shown to achieve an absorption of 0.88% wt. An equal sample when subject to an applied field of 0.7 Tesla achieved an overall absorption of only 0.60% wt. Both samples were subject to the same experimental conditions, with the samples monitored for 5 hours to ensure full absorption at a temperature of 323K and starting pressure of 345 PSI.

The results were repeated with samples that were known to not fully absorb hydrogen. These samples of LaNi₅, also through constant volume equilibrium experiments, were shown to achieve an absorption of 0.26% wt. An equal sample when subject to an applied field of 0.22 Tesla achieved an overall absorption of 0.26% wt. Both samples were subject to the same experimental conditions, with the samples watched for 5 hours to ensure full absorption at a temperature of 293K and starting pressure of 345 PSI.

It was concluded that the presence of an externally applied magnetic field has a negative effect on the overall capacity of LaNi₅ through the prevention of a shift in the inner lattice structure of LaNi₅ that would otherwise permit an increased hydrogen

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capacity.

Overall, it was shown that an investigation into other hydride species is merited, and additional investigation using neutron scattering would be suitable to further verify these results. Another reason to continue this direction of research is the possibility that this result can be used in hydrogen desorption regimes. If a fully saturated hydride were to be subject to an applied magnetic field it would be expected to drive the crystal system into the lower absorption ordered structure, effectively squeezing the hydrogen out of the filled hydride.

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