

2013-04-29

Accurate Measurement of Hydrogen in Steel

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Senadheera, T. D. (2013). Accurate Measurement of Hydrogen in Steel (Doctoral thesis, University of Calgary, Calgary, Canada). Retrieved from <https://prism.ucalgary.ca>. doi:10.11575/PRISM/24654
<http://hdl.handle.net/11023/629>

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THE UNIVERSITY OF CALGARY

Accurate Measurement of Hydrogen in Steel

by

Thushanthi D.A.A.Senadheera

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF MECHANICAL AND MANUFACTURING
ENGINEERING

CALGARY, ALBERTA

April, 2013

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UNIVERSITY OF CALGARY
FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled “Accurate Measurement of Hydrogen in Steel” submitted by Thushanthi D.A.A.Senadheera in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Abstract

Accurate measurement of hydrogen in steels is one of the greatest challenges in the field of applied science. Even though research on hydrogen in steels has been carried out over the last ten decades, very little progress has been made in fundamental areas because of the lack of a reliable method for measuring hydrogen within a steel. The hydrogen atom's small size and its one atomic orbit have caused difficulties in applying readily established measuring techniques to measure the simplest atom. The small size of the hydrogen atom has also made leak proofing the hydrogen measuring systems extremely difficult; thus, most apparatus are vulnerable to leaking. Additionally, the need to measure extremely small quantities and the high degree of statistical variation in the measured quantities have made the measured hydrogen quantities uncertain.

The main task of this research study was to design and construct a new, direct hydrogen measuring device called the Temperature Vacuum Hydrogen System (TVHS) and to explore some higher temperature measurements of hydrogen in steel using this new device.

This thesis provides a study of the direct hydrogen measuring methods available, the improvements implemented on the standard eudiometer method to improve the method's accuracy and the users' safety, a discussion of the problems faced during the construction and operation of the TVHS, and the solutions applied to mitigate them. The hydrogen volumes measured using the TVHS at 50°, 150°, 250°, and 350° C in hydrogen charged AISI 1020 steel samples; and temperature-time relationships for measured hydrogen quantities; an equation to correlate the measured amounts

from the TVHS method with the amounts measured using the standard eudiometer method are also provided in this thesis.

Key findings of the tests carried out using the TVHS were that a significantly higher amount of hydrogen egressed at 350° C compared to the amounts that egressed at lower test temperatures and the time durations took longer than expected for stabilizing the egressed hydrogen amounts. Equations to predict hydrogen amounts egress from steel samples that are charged with low hydrogen concentrations were also derived. In addition, a chemical analysis on a steel sample immersed in mercury at low-elevated temperatures for an extended period showed a possibility for hot mercury to dissolve carbon from the pearlite structure of the steel, leaving the iron in the structure.

Acknowledgements

It is with immense gratitude that I acknowledge my thesis supervisor Professor W.J.D. (Bill) Shaw for teaching me Design & Materials for the last twelve years, supporting me while I explored my research interests, and holding me to the highest academic standard.

It has been a great privilege to spend several years in the Department of Mechanical & Manufacturing Engineering at the University of Calgary and its academic, technical, and administrative staff, and my colleagues will always remain dear to me. The support of the technical staff at the Engineering Workshop, the Engineering Store and the Microscope & Imaging facility at the Health Science Center is etched in my mind. I also grateful to the Teaching Assistantships from the University of Calgary, the Province of Alberta Graduate Scholarship fund and Dr. Shaw's research grants for providing financial assistance for me during the initial years of the thesis.

This thesis would have remained a dream had it not been for the continuous supports of the management and my colleagues at the National Energy Board, Canada; particularly, I am thankful to Sandy Lapointe, Patrick Smyth, Dr. Iain Colquhoun, Dr. Alan Murray (former professional leader) and the team leaders of the Operation Business Unit.

I greatly appreciate my husband Roh (Rohitha) Senadheera for all his support and encouragement, and my children (Lavindu & Chenaya Senadheera) for keeping me oriented and waiting patiently until I completed the thesis, which I have been working on since the days they were born. Their love was my driving force. Last but

not least, I thank my parents (A.A. Alfred & Nanda Dissanayake) and little niece, Sanole Wickramasooriya, for their encouraging words over the phone even being 14,000 kilometers away from me and for my grandmother (Kumarihami Ratnayake) for showing me “*who you are is what you dreamed of.*”

T.D.A.A.S.

*To my first teachers -my parents- and the other dedicated teachers I have met who
have inspired and shaped me.*

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Nomenclature

TVHS: Thermal Vacuum Hydrogen System

$H_{HotExtraction}$: Hydrogen amounts determined using hot extraction method

$H_{Eudiometer}$: Hydrogen amounts determined using mercury eudiometer method

H_{TVHS} : Hydrogen amounts determined using TVHS method

ppm: parts per million

C_v : Coefficient of variation

$C_v\%$: Percent coefficient of variation

STP: Standard pressure and temperature

K: Kelvin

Pm: picometre

P_{STD} : Pressure at standard conditions

T_{STD} : Temperature at standard conditions

V_{STD} : Volume at standard conditions

T_{room} : Room temperature

V_{total} : Total volume of the hydrogen containments at room temperature

T_i : Initial test temperature

T_f : Final test temperature

P_i : Initial test pressure

P_f : Final test pressure

V_{max} : Amount of hydrogen collected at the fifth day of the test using TVHS method

D : Diffusion coefficient

$\dot{C}_H$: Hydrogen egression rate in cm^3 per second

$\dot{C}_{H2880}$: Hydrogen amount egress per 2880 minutes in cm^3 per 2880 minutes

$\dot{C}_{H5760}$: Hydrogen amount egress per 5760 minutes in cm^3 per 5760 minutes

E_A : Activation energy

R : Universal gas constant

Chapter 1

Introduction

1.1 Background

Hydrogen can enter into steels from a number of processes. Some of these processes include casting, welding, acid pickling, electroplating operations, corrosion, and cathodic protection. Once hydrogen enters into steels, being the smallest atom, it can readily migrate through the crystal structure. Hydrogen can reside inside steels in the forms of easily mobile, progressively mobile, or as trapped hydrogen. Table 1.1 provides an example of approximate hydrogen amounts introduced into steel from various operations.

Table 1.1: Hydrogen amounts introduced into steel from various operations [1].

Operation	Source of hydrogen	H amount cm^3 /100g of Fe
Pickling	Acid bath	< 6
Electrochemical plating	Bath	< 2
Enameling	Water in the component	about 2
Welding	Electrode and moisture	< 10

The detrimental effects on metallurgical and mechanical properties of steel resulting from hydrogen are well known. The initial entry of hydrogen makes steels less ductile and can cause brittle cracking. Additional hydrogen can nucleate hydrogen gas, which forms internal voids and surface blisters. In addition, it has been found that hydrogen can react with carbon in steels at elevated temperatures and pressures

to form methane gas; which can also damage steels.

Even though research on hydrogen in steels has been carried out over the last ten decades, very little progress has been made in fundamental areas. Some areas that have been treated as well known are also built on many assumptions; thus, the validity of these areas is also questionable. The types of hydrogen that are most detrimental to steels and the threshold levels of hydrogen in steels are still unknown because of the lack of accurate and reliable methods for measuring hydrogen in steels. The knowledge of the essential fundamental areas will not be available until accurate hydrogen measuring methods are established.

1.2 Challenges in Hydrogen Measurements

Some of the challenges that we face during the measurement of hydrogen are discussed below.

a. Small size of the hydrogen atom

Because of the hydrogen atom's small size and only one atomic orbit, it is difficult to apply readily established measuring techniques for the measurement of hydrogen. The small size of hydrogen atom has also made leak proofing of the hydrogen measuring systems extremely difficult; thus, most systems are vulnerable to leaking. The small size also allows hydrogen to easily migrate through most of the materials, making selection of construction materials for measuring equipment difficult.

b. Smaller quantities

The outcome of some research studies have shown extremely small quantities of hydrogen could have detrimental effects in steels. For example, Fig. 1.1 following

shows how extremely small quantities of hydrogen have resulted in reducing the fracture stress of a type of steel. Thus the hydrogen measuring apparatus must be capable of measuring extremely small quantities of hydrogen accurately to capture the detrimental hydrogen levels. In general, measurement of such small quantities is challenging because of practical problems.

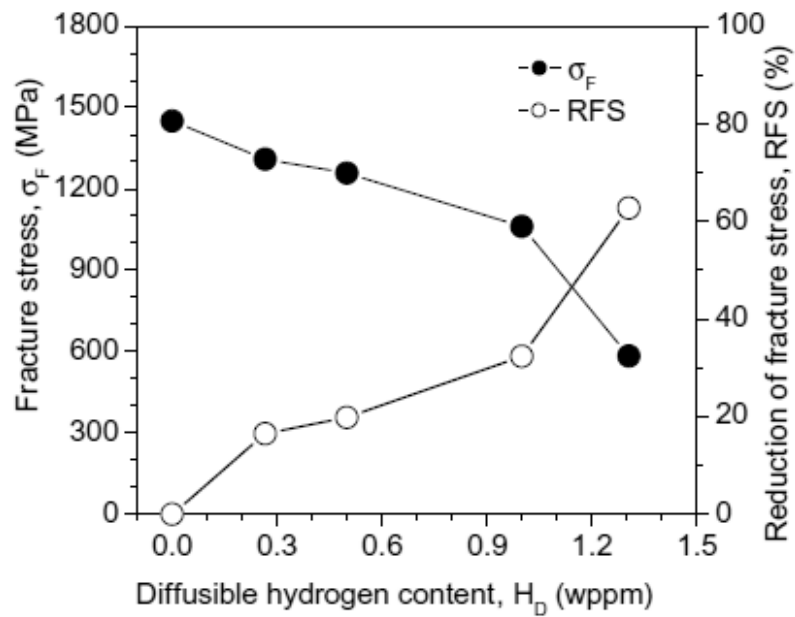


Figure 1.1: Dependence of fracture stress and reduction of fracture stress on diffusible hydrogen content in quenched and tempered AISI 4135 steel [110].

c. High degree of statistical variation in measured amounts

The high degree of statistical variation in the test results has made it extremely difficult to determine the amount of hydrogen measured from a given application. According to previous experience using the standard eudiometer method, which is one of the most reliable diffusible hydrogen measuring techniques currently available,

the results of measured hydrogen amounts indicate that the coefficient of variation of the test results is about 25% [3] This variation is considered very high when compared to the coefficient of variation of 5-10%, which is normally the accepted range for most mechanical tests.

d. Possible methane (CH_4) formation and decomposition

Hydrogen attack is a phenomenon that occurs when carbon steel is used in circumstances over $200^\circ C$ of temperature and over 7 kg/cm^2 (about 7 atm) of hydrogen pressure, hydrogen reacts with iron carbide (Fe_3C) in carbon steel to generate methane (CH_4) [4]. The methane gas created cannot diffuse outside because of its size, so it creates cracks in steel and causes failure. It has been also reported that at a temperature around $900^\circ C$, the methane can decompose into hydrogen and carbon. The methane formation and decomposition temperature varies with the system parameters such as temperature, hydrogen partial pressure, stress level, exposure time, steel composition, and structure and catalysts present in the system [5],[6],[7].

The above phenomenon could cause two challenges during hydrogen measurements.

- If some (or all) of the hydrogen enters in to steel it could convert to methane in a given situation, and the amount of hydrogen measured would not provide accurate level of hydrogen in the steel.
- It is not known whether elevation of temperature of a previously-hydrogen charged test sample could also result in the above phenomenon: that is, whether the charged hydrogen in a steel test sample could cause the formation of methane at elevated temperatures. Examples in the literature always point

to the test samples in high pressure hydrogen environment but not to the test samples previously charged with hydrogen.

The effects of methane formation and decomposition on the hydrogen measurement have not yet been systematically studied. This would require accurate measurement of both methane and hydrogen and further research in establishing the phenomenon as well as measuring techniques of methane. Therefore this was not included in the objective of this research study. Measurement of methane is complex because techniques such as hot extraction, which are used for measuring hydrogen, cannot be used for measuring methane. Elevating the temperature will not allow methane to diffuse out of steel due to its larger molecule size. (*See Table 4.3*). Therefore, a technique that is based on dissolving the test sample to release methane followed by a quantification technique would be required. This requires development of separate equipment to measure methane amounts.

When the above mentioned challenges are considered, some of them cannot be fully overcome ; however, better design and construction of an apparatus could reduce the discrepancy in the measured hydrogen amounts. More details on this matter are discussed below.

1.3 State of Present Hydrogen Measuring Systems

Even though the concepts behind the hydrogen measuring techniques are appreciable, it is difficult to rely on the design and construction of most of the present measuring systems. Following are some of the common deficiencies that were observed in these measuring systems:

- Too complex systems that make it hard to locate leaks when they occur.
- Improper sealing techniques that lead to leaks.
- Improper selection of construction materials.
- Inadequate safety features.
- Restrictions in test sample (specimen) size and shape

Also, most of the laboratory types of measuring systems are not adaptable for commercial use because of their complexity and inflexible design. Even though such adaptability for commercial use is not essential, when the global picture of hydrogen problems is considered, it would be useful to develop such a versatile system.

In addition to the above-mentioned system deficiencies, the following deficiencies that are related to the measuring procedures also exist:

- Lack of a leak detection system or a procedure to detect leakages in the measuring systems.
- Use of uncertain hydrogen charging techniques to introduce a control amount of hydrogen into test samples, which could lead to questionable end results. For example, it has been found that it is not advisable to use cathodic charging for hydrogen charging because of the unacceptable level of statistical variation in the charged amounts [8].

Further, lack of a reliable standard test procedure for measuring progressively mobile hydrogen at elevated temperatures and total hydrogen contents has made comparison of inter-laboratory results of the total hydrogen quantities difficult and

impracticable. At present, the internationally recognized standard methods address only the methods of measuring the diffusible hydrogen contents. In addition, it has become exigent to use most of the previous research work conducted by others for comparisons because of uncertainties and obvious flaws in the measuring procedures.

1.4 Research Objective

The main objective of this research study is to develop equipment and a related procedure to accurately measure hydrogen amounts in steels and measurement of hydrogen at elevated temperatures using the equipment.

1.5 Thesis Structure

This thesis consists of thirteen chapters. This chapter - Chapter 1 provides the introduction. Chapter 2 and Chapter 3 provide findings of the literature review. Information related to the newly developed hydrogen measuring system (TVHS) is included in Chapter 4 to Chapter 8. Chapter 9 describes the improvements implemented on a standard hydrogen measuring method called the mercury eudiometer method and an analysis which was carried out on interaction of steel with mercury..

Chapter 10 and Chapter 11 provide test methods and results of the test carried out using the TVHS and the improved eudiometer, respectively. The last two chapters are devoted to discussion and conclusions.

Chapter 2

Literature Review (Part 1): Hydrogen in Steels

2.1 Entry of Hydrogen into BCC Steels

Hydrogen can enter into BCC (Body Center Cubic) steels naturally or artificially. The natural methods include fabrication processes and subsequent services. The fabrication processes that lead to picking up hydrogen described in this chapter include steel making, pickling, welding, and electroplating. The subsequent services include the service environment, corrosion, and cathodic protection.

The methods used to charge hydrogen into test samples (specimens) in the laboratory can be identified as artificial methods of entering hydrogen. Such charging methods include electrochemical cathodic charging, charging using acids, and the presence of hydrogen sulfide (H_2S) in an aqueous solution.

2.1.1 Natural Methods

During Steel Making Process

Hydrogen related problems in steels first appeared in the beginning of the twentieth century in machinery, railroad products, guns, and armor. The major problem in that period was thermal flaking or fisheyes in the products. The first association of hydrogen with flaking came in the 1920s [9].

Moisture is the main reason for hydrogen pick up during the steel making process. Moisture can be introduced by raw materials, slag, alloys, and also by the refractory

material used in pouring and casting areas. As a result of the high temperatures in the steel making processes, the moisture decomposes to hydrogen and is absorbed into molten metal.

The advent of the vacuum degassing method in 1952 in Europe helped to reduce the hydrogen content to a manageable amount [9]. A paper [10] describes some practical measures that resulted in reducing the hydrogen level in a steel making plant to 1.2-1.8 *ppm*.

Pickling

Pickling is a process that removes oxide and mill scale of metal components by immersing the component in a solution. Pickling is one of the oldest known methods for the entry of hydrogen into steels. The diffusion of hydrogen through a wall of a hollow cylinder, which was immersed in sulphuric acid was first observed in 1863 [11].

During the pickling process, hydrogen gas evolves from the dissolution of steel in strong acids at elevated temperatures. Hydrochloric acid (*HCl*) is one of the most commonly used acids for pickling. The reactions can be written as follows:



It is believed the atomic hydrogen (*H*) and molecular hydrogen (*H₂*) enter into steel during pickling. It has also found that the amount of hydrogen that enters into steel varies with the types of inclusions in steels and the heat treated process that the steel has undergone (i.e. hot rolled or cold rolled) [12],[13].

Welding

During the welding process, high temperatures are used to melt the adjoining zones of metal parts to bond them together. The high temperatures decompose the moisture in the atmosphere to hydrogen. This hydrogen is absorbed into weldments. The absorption becomes worst if the welding takes place under water or in humid weather.

In addition, moisture in flux coated electrodes turns to hydrogen during welding and the hydrogen travels into weldments. The flux coated electrodes, also called stick electrodes, are used in manual or semi-automatic electric welding. At present, these electrodes are pre-heated before use to reduce the amounts of moisture and thereby reduce the hydrogen. It has been also found that post-heating the welded components helps in removing some of hydrogen that enter during welding. In addition, research and development are continuously being carried out to manufacture better low hydrogen electrodes [14]. It has been also found that the some constituents in the flux coating affect the amounts of hydrogen. Details on the role of flux constituents (e. g. fluorides, oxides, calcium, silicon) on the hydrogen content can be found in [15],[24].

Electroplating

It is believed that during the electroplating process, the hydrogen gas that evolved from the metal surface is partially absorbed by the metal. Furthermore, some types of plated layers, such as cadmium coatings, can prevent the diffusion of hydrogen out of the component into the environment, giving delayed failure phenomena [16] [17].

Exposing to Gaseous Hydrogen

When steels are used as hydrogen storage media, they are exposed to a high pressure gaseous hydrogen environment because the gas pressure at which hydrogen is commonly stored ranges from 10 to 100 MPa (100 to 1000 atm). Steel pressure vessels that have been used as storage media at room temperature and at elevated pressures for many years have not shown any failure or detectable evidence of damage [18]. This indicates the charging rate in gaseous hydrogen is very slow at room temperature even though the gaseous hydrogen is at elevated pressures.

According to researchers, the surface behavior of steels governs their properties in gaseous hydrogen environments at both elevated pressures and atmospheric pressure. This suggests that the hydrogen pick up involves a process other than diffusion. In fact, the acceleration crack growth of pre-cracked tension and fatigue specimens has found to be inhibited or completely eliminated by the addition of a small amount of oxygen to the hydrogen gas. This inhibiting capacity of oxygen is believed to be related to its ability to contaminate the surface of steel and to limit or prevent the adsorption of hydrogen on the exposed surfaces [18].

Hydrogen Sulfide Environments

Hydrogen sulfide (H_2S) is encountered in a number of environments and is known to accelerate not only general corrosion but also embrittlement of steels [25]. In spite of several investigations, the influence of H_2S on the mechanism of entry of hydrogen into steels is not yet well established [19]. In addition, it has been found that the effect of H_2S on the entry of hydrogen into steels varies with the pH, concentration, temperature, and surface conditions of the H_2S environment [19], [20], [21].

Corrosion

The hydrogen charging from the corrosion process is significant to steel fabricators and users. During the corrosion process, at a deareated condition, hydrogen atoms are liberated on the cathodic surface. Depending upon the electrolyte, this liberation process of hydrogen atoms can be written as follows [22],[23]:

in acid solutions:



in neutral/alkaline solutions:



This atomic hydrogen (H) either can be adsorbed by the steel or may recombine to form molecular hydrogen:

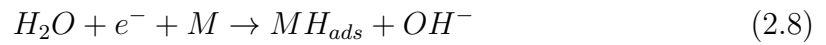


The adsorption process of atomic hydrogen by steel (M) can be written as follows:

in acid solutions:



in neutral/alkaline solutions:



The hydrogen atoms will dissolve and diffuse into the steel according to the solubility and diffusivity behavior.

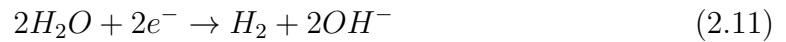
Cathodic Protection

Cathodic protection reduces the corrosion rate by cathodic polarization of the corroding metal surface. When steel corroding in a deareated neutral or alkaline electrolyte

solution is considered, the respective anode and cathode reactions are



Cathodic polarization reduces the rate of the anodic reaction with an excess of electrons, which also increases the production of H in the cathodic reaction. As explained before, such produced atomic H can enter to the steel. If cathodic polarization becomes excessive, the direct reduction of water becomes thermodynamically possible [22]:



2.1.2 Artificial Methods

Three methods that can be used to artificially charge hydrogen into steels are described below. Usually, these are the widely used methods to charge hydrogen into test samples (specimens) in the laboratory for experimental work. A closer look at the artificially charging methods clearly shows that they are similar to the natural methods that were previously described.

Acid Pickling

The acid pickling charging method is suitable where low charging conditions (low amount of hydrogen) are needed. This method used to be known as a method that produces charging amounts with much scatter. However, according to Shaw et al. [8], letting the charged sample sit for at least 15 minutes after charging provides

less scatter in measured hydrogen amounts. This waiting time helps to diffuse the hydrogen evenly in the sample.

Using Hydrogen Sulfide

This method is suitable where heavy hydrogen charging is needed. The basis of this method is saturating of a suitable solution by bubbling of H_2S through reaction kettles where the samples to be charged are immersed. Normally, the time duration is 24 hours.

Potentiostatic Charging

In this method, hydrogen is charged by making the sample to be charged into a cathode in an artificial corrosion environment. Even though this method is popular as a hydrogen charging method, some researchers do not recommend this method because it creates too much scattering in the measured amounts of hydrogen [8].

2.2 Egress of Hydrogen from BCC Steels

Two methods which are used commonly to egress (remove/degass) hydrogen from steels are the application of temperature and the vacuum. Hydrogen can be removed by keeping a component at room temperature or by increasing its temperature. The latter is commonly known as “baking.”

The amount of hydrogen that is removed by any of these methods depends on several parameters, such as

- time
- geometry and size of the component

- hydrogen concentration inside and outside the component
- alloy composition of the component
- surface treatments (i.e. plating, shot peening) that have been applied

2.2.1 Natural Room Temperature

The easiest but most time consuming method that is used to remove hydrogen from a component is leaving it at room temperature for an extended time period. The time period could be from days to months. The required time period to egress out hydrogen depends on the thickness of the component; thicker components need more time.

2.2.2 High Temperatures

Hydrogen can be removed from a component in a shorter time by elevating the temperature (i.e. baking). The commonly used temperature range for steel components is 150°C to 160°C , and the time duration is about 15 – 16 hours [27].

Effect of baking time

Troiano [28] has shown that not only the baking temperatures but also the baking time have a great effect on the egress of hydrogen. Fig. 2.1 shows the failure time for cathodically charged AISI 4340 steel that had been baked for various time intervals at 150°C . Accordingly, lower baking durations caused failing of the samples quicker with lesser applied stresses.

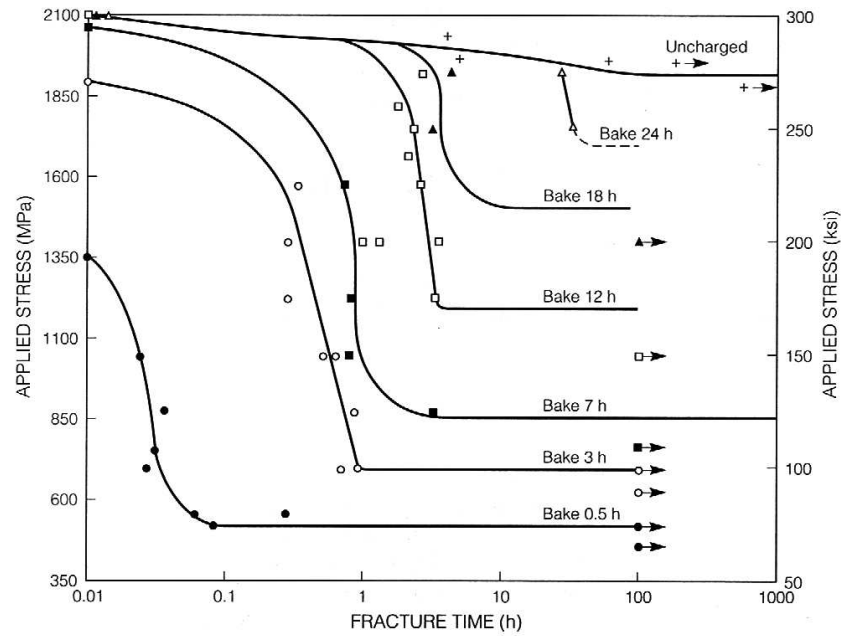


Figure 2.1: Effect of baking time on fracture of AISI 4340 steel. [28].

2.2.3 Vacuum

The vacuum has been used for providing suction of hydrogen from steels. Only a few studies are available on the application of the vacuum without thermal energy to remove hydrogen from steel. Some work describes the application of a vacuum in the range of 20-30 *Hgmm* to remove hydrogen [27]. The time duration of the application of a vacuum would depend on the size (thickness) of the sample.

2.3 Classification of Hydrogen in steels

This section provides a brief description on the basis of classifications used to describe the types of hydrogen that reside in steels.

No literature gives a clear, common classification on the types of hydrogen that reside in steels. However, diffusible hydrogen, residual hydrogen, trapped hydrogen, and total hydrogen are some of the terms that have been used in the literature to describe different types of hydrogen. The following explains a few different ways for classifying hydrogen, including the method that is used in this thesis study.

2.3.1 Based on Moving Ability

Easily mobile, progressively mobile, and totally trapped hydrogen

The types of hydrogen residing in steels can be classified as easily mobile, progressively mobile, and totally trapped hydrogen based on the ability of hydrogen to move in or out from its trapping sites. In other words, this classification is based on the tendency for hydrogen to be trapped in a trapping site. Thus, easily mobile hydrogen is a type of hydrogen that can easily move through the material. The progressively mobile hydrogen cannot move easily unless some external energy is provided. As implied in the name, totally trapped hydrogen is the type that is totally trapped in the trapping sites, which cannot move at all. It is believed the tendency of hydrogen to be trapped is governed by the energy of motion of the hydrogen and the nature of the trapping site. The nature of the trapping sites determines the jump probabilities for the hydrogen.

This is the classification method that is used in this research study. Because this classification is based on the moving ability of hydrogen which is a relative property, distinct temperature values were used to define the types of hydrogen. Further details on this is given in Chapter 4.

2.3.2 Based on Types of the Traps

When hydrogen is classified based on types of traps, the total amount of hydrogen in steels can be considered as a summation of the several terms, as follows [30]. Thus the total amount of hydrogen in steels can be considered as a summation of the several terms, as follows.

$$H_{Fe} = H_s + H_v + H_d + H_m + H'_a + H_{ch} \quad (2.12)$$

Where

H_s : hydrogen in solid solutions

H_v : hydrogen bound to vacancies

H_d : hydrogen fixed on dislocations

H_m : molecular hydrogen in the pores

H'_a : hydrogen adsorbed on the surface

H_{ch} : hydrogen bound in chemical compounds (hydrides) or dissolved in chemical compounds (carbides, nonmetallic inclusions ect..)

Reversible and irreversible hydrogen

The most common classification that has been used to describe the types of traps that hydrogen could reside in steels is reversible and irreversible traps. Thus, the hydrogen that is trapped in reversible traps can be identified as reversible hydrogen,

and the hydrogen that is trapped in irreversible traps can be defined as irreversible hydrogen.

According to Pressouyre [29], reversible traps could exchange hydrogen with stronger traps, thereby acting as hydrogen sources and sinks. The irreversible traps are strong and will not release hydrogen at all. Therefore, they act as hydrogen sinks. Thus, the irreversible hydrogen could be analogous to totally trapped hydrogen and the reversible hydrogen could be analogous to mobile and progressively mobile hydrogen.

According to [30], the escape probability of a hydrogen atom from a physical discontinuity in a lattice (eg.: voids, grain boundaries, dislocations ect) can be given by

$$P_e = k_o \exp(-E_T/k_B T) \quad (2.13)$$

where

P_e : escape probability of hydrogen atom

k_o : frequency factor

E_T : trap energy depth

k_B : Boltzmann constant

T : absolute temperature

Saturable and unsaturable hydrogen

Some researchers have classified traps as saturable and unsaturable. Accordingly, if the number of trapping sites is permanent (fixed), for example as for a grain boundary, they are called saturable. Thus, the hydrogen that resides in these traps can be defined as saturable hydrogen. Conversely, if the number of the trapping sites is not permanent (not fixed), for example as for a void, it is unsaturable [30]. Thus, the hydrogen that resides in these traps can be defined as unsaturable hydrogen.

According to [29], reversible traps can become saturate traps because they act as both sinks and sources of hydrogen; however, irreversible traps cannot become saturable because they act only as sinks.

2.4 Hydrogen Measuring Techniques

This section describes various hydrogen measuring techniques that are available to quantify hydrogen amounts in steels.

2.4.1 Overview

There are several techniques for measuring hydrogen amounts in steels. Fig. 2.2 provides a summary of the available hydrogen measuring techniques. As shown from the figure, the measuring techniques can be divided into two main categories: direct hydrogen measuring methods and indirect methods. In direct techniques, hydrogen that egressed out of a test sample is collected and measured. The currently available indirect measuring techniques are capable of quantifying only easily mobile hydrogen contents. Examples of indirect techniques include the barnacle cell method and the Devanathan cell method. In indirect techniques, an certain amount of electric current is applied to a test sample to oxidize the hydrogen that escapes from the

surface of the test sample. The amount of current required is measured to estimate the amount of mobile hydrogen in the sample. The estimated amount of hydrogen is usually given as a measure of current density in micro amperes per square centimeter ($\mu A/cm^2$). A reliable correlation between the measured current density and actual hydrogen volume that has escaped from the surface has not yet been found. Because of that, the direct hydrogen measuring techniques are more accurate than indirect techniques.

The literature on direct hydrogen measuring techniques is reviewed in detail below because this thesis work is focused on them.

2.5 Direct Hydrogen Measuring Techniques

2.5.1 Overview

Direct hydrogen measuring techniques can be used to quantify directly the amount of the three types of hydrogen (i.e. easily mobile hydrogen, progressively mobile hydrogen, and total hydrogen) in steels. Descriptions of techniques that can be used to measure the three types of hydrogen are given in the following sections.

When the hydrogen measuring techniques are reviewed, it is clear that they all have a common base. That is, all the techniques need the following three activities to measure hydrogen amounts:

- Extraction of hydrogen from the sample
- Collection of the extracted hydrogen
- Measurement of the collected hydrogen

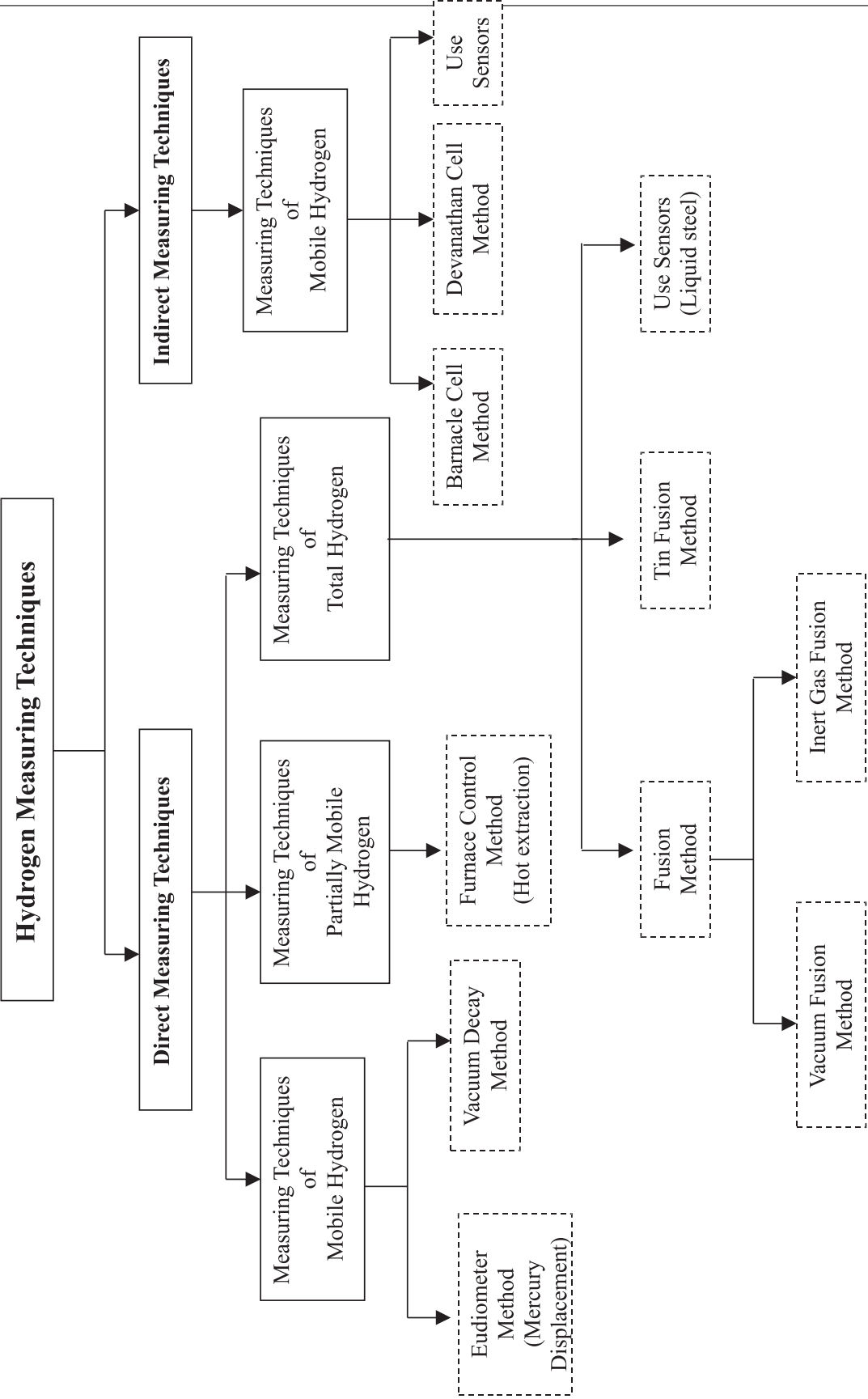


Figure 2.2: Overview on the hydrogen measuring techniques.

These activities are shown on a flow diagram in Fig. 2.3. Thus the capability of measuring different types of hydrogen (easily mobile, progressively mobile, total) depends on the amount of the energy that is needed to extract different types of hydrogen from the sample. It is also important to note that, at present, all the direct measurement techniques mainly use elevated temperatures to extract hydrogen from a sample.

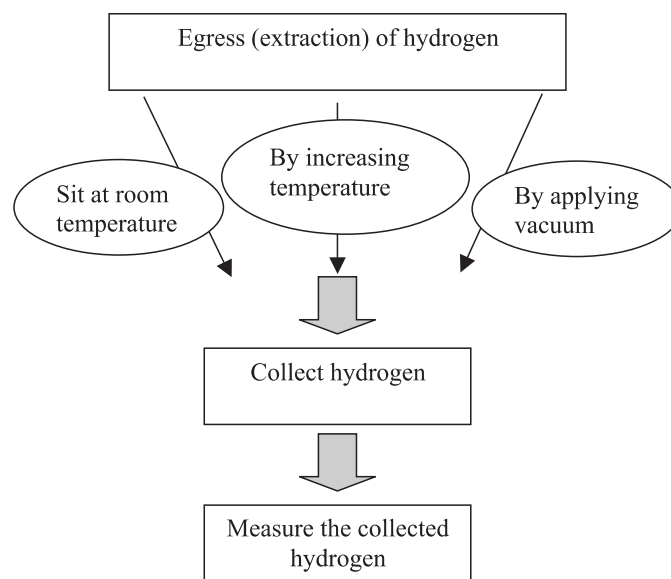


Figure 2.3: Base of the direct measurement techniques.

2.6 Methods of Measuring Easily Mobile Hydrogen

2.6.1 Overview

The methods that are commonly used to measure easily mobile hydrogen include the eudiometer method and the vacuum foil method. The eudiometer method uses low-elevated temperature to promote hydrogen to egress out from a sample while

the vacuum foil method uses a vacuum. In the early days, the hole and pressure method had also been used as the easily mobile hydrogen measuring technique. In this method, a blind hole was drilled in the sample and pressure build-up from the collection of hydrogen in the hole was measured using a pressure gauge. This method provided a direct indication of hydrogen amount in the sample.

2.6.2 Eudiometer Method

The eudiometer method is commonly known as the mercury displacement technique. This is a standard method that has been adopted by the following standards:

1. AWS A 4.3:1993: Standard methods for determination of the diffusible hydrogen content of martensitic, bainitic and ferritic weld metals produced by arc welding (a standard of the American Welding Society)
2. ISO 3690:2000(E): Welding and allied processes - Determination of hydrogen content in ferritic steel arc weld metal (a standard of International Standard Organization)
3. AS/NZS 3752:1996: Methods of determination of the diffusible hydrogen content of ferritic weld metal produced by arc welding (a standard of Australian and New Zealand Standard institute)
4. BS 639:1976: Covered electrodes for the manual metal-arc welding of carbon and carbon-manganese steels, Appendix C: Method for the determination of diffusible hydrogen content (a standard of British Standard Institute)
5. IIW 959-1981: The determination of the hydrogen content of ferritic arc weld metal (a standard of International Institute of Welding)

A description of the eudiometer method and the modifications that were implemented on the method to improve the accuracy and reliability of measured hydrogen amounts is provided in Chapter 9.

2.6.3 Vacuum Foil Method

Method

The experimental setup for the vacuum foil method is shown in Fig. 2.4. In this method, a thin austenitic stainless steel foil is glued on to the sample. Austenitic stainless steel was selected because it is not expected to absorb hydrogen under a vacuum. Once the foil adhered properly onto the sample surface, a vacuum was introduced through the attached capillary tube to the foil. With time, the hydrogen in the sample started coming out from the sample and it resulted in decay in the vacuum. This decay in the vacuum was a direct indication of the amount of hydrogen that existed in the sample.

The vacuum foil method was also established by industry as a technique of measuring corrosion in the 1990s. The amount of hydrogen generation on a corroding surface is taken as a direct indication of the corrosion rate based upon the cathodic reduction reaction. Thus the amount of diffusible hydrogen is taken as a reflection of the amount of corrosion occurring [31][32].

2.6.4 Discussion

When the vacuum foil method is compared with the eudiometer method, the vacuum foil method has the following advantages.

- The foil can be glued on to industrial components such as pipes and pressure

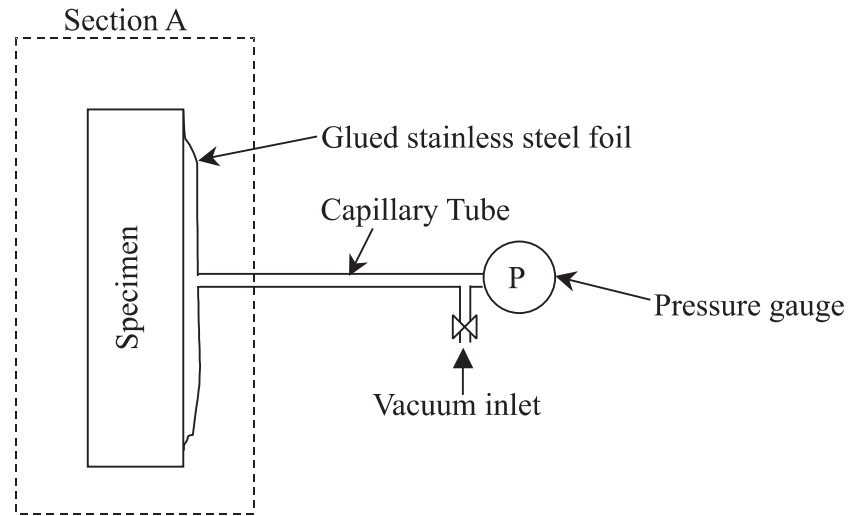


Figure 2.4: Experimental setup for the vacuum decay method.

vessels to measure the mobile hydrogen quantities in them. Thus, this method can be used even in the field as a non-destructive method of measuring mobile hydrogen contents. Conversely, the eudiometer method requires specially made test samples to carry out the tests and the tests are considered as destructive tests.

- The foil can be glued on to a sample of any shape.
- Unlike the eudiometer method, the foil method could be automated.
- This method is safer because it does not use mercury.

The accuracy of the vacuum foil depends on accurate measurement of volumes of parts of the apparatus and the volume between the sample and the foil. Among all the volumes, the latter is the most difficult to measure because the shape of the foil always tends to change from pressure. As a solution, the thin foil can be replaced

by a thin plate of austenitic stainless steel that could form into a permanent shape. Thus, the volume created by the permanent shape would be easier to measure due to the stability of the shape. However, problems could still occur while attaching a permanent shape on to a sample because its lack of flexibility. The accuracy of the method could also be affected from the atmospheric pressure, which could exert a force on the thin foil. In addition The vacuum foil method is time consuming because before starting each test, it is required to verify there are no leaks in the system.

2.7 Methods of Measuring Progressively Mobile Hydrogen

2.7.1 Overview

Compared to the methods that are used to measure easily mobile hydrogen, the progressively mobile measuring methods need to supply a higher amount of energy to a sample. The energy is mainly supplied as heat (thermal energy) using a furnace to elevate the temperature of the test sample. Thus, the method is called the furnace control method or hot extraction method. It is also common to use a vacuum in combination with elevated temperatures. Then the method is called the thermal-vacuum method or hot-vacuum extraction method.

2.7.2 Furnace Control Method

The following section summarizes a few, selected progressively-mobile hydrogen measuring apparatuses that have been used by researchers, highlighting their main features. Some of the apparatuses described in Section 2.8 also have been used as progressive-mobile hydrogen measuring techniques by elevating the sample temperature below its fusion temperature.

Apparatus used by Addach

Addach et al. [33] used the furnace control method to determine hydrogen in zinc and chromium plated low-alloy steel samples. Fig. 2.5 provides a schematic of the system. The external cell, which was inside a furnace was used to heat up the sample to the required temperatures. The cell was made of silica and was considered to have less permeability to hydrogen and resistance to high temperatures than other considered materials, despite its brittleness. The cell size with a volume 175 ml was selected to accommodate larger sized industrial parts without a problem.

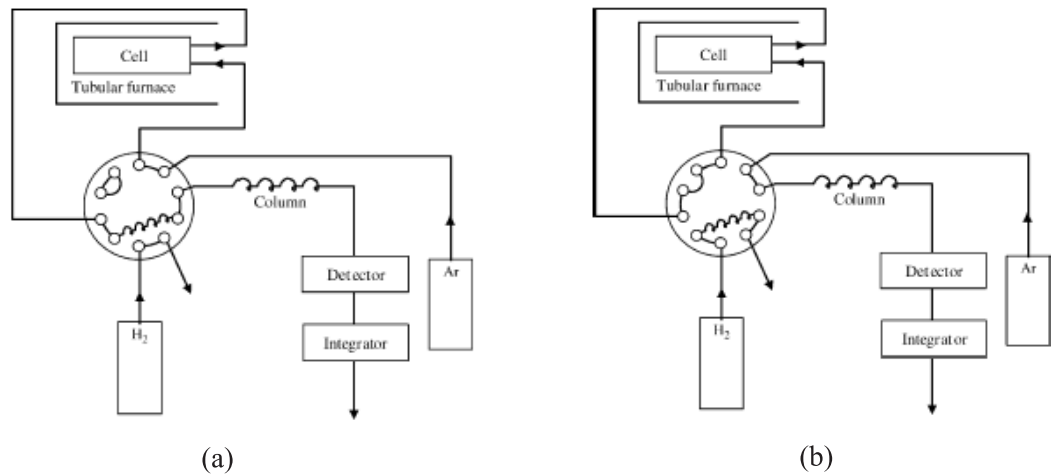


Figure 2.5: Furnace control system used by Addach, H. et al. (a)Injection position (b)Standby position [33].

During measurement, the sample was placed inside the cell in which the air was displaced by argon gas (injection position). Then, the sample was heated to an elevated constant temperature (standby position). After a predetermined period, the released hydrogen was injected with the argon gas to the section where it was analyzed (injection position). The analysis section consisted of a gas chromatograph.

According to the authors, this method was used successfully between 50 and 1000° C.

Apparatus used by Quantan

Quantan et al. [34] used a similar system to the one above. They fabricated the sample holding chamber (cell) in a 304 stainless steel round bar, because of the relatively low diffusivity of hydrogen in austenitic stainless steels. The connectors in the chamber were made of 316 stainless for the same reason and for durability. An O-ring type gasket made of butyl rubber was used in the lid of the chamber to provide better sealing between the lid and the chamber. Butyl rubber was selected, considering its minimal hydrogen permeation. However, the rubber part limited the maximum operating temperature to 150° C.

Apparatus used by Das

The apparatus that was used in [35] is shown in Fig. 2.6. This system consisted of three methods for extracting hydrogen.

In this apparatus, the hydrogen that was liberated from the sample was directed towards the activated Pd-Ag membrane by the flowing of a carrier gas. The membrane lets only hydrogen permeate through it. The membrane was attached to a vacuum chamber and the latter was attached to an ion pump. Thus, when hydrogen permeated through the membrane to the vacuum chamber, the ion pump indicated an increase in ion current, which was taken as a direct indication of the amount of hydrogen in the sample.

Apparatus used in Sohrman

The method used in [36] is shown in Fig. 2.7. An infra-red (IR) furnace was used to provide thermal energy to extract hydrogen. IR was used because of its capability

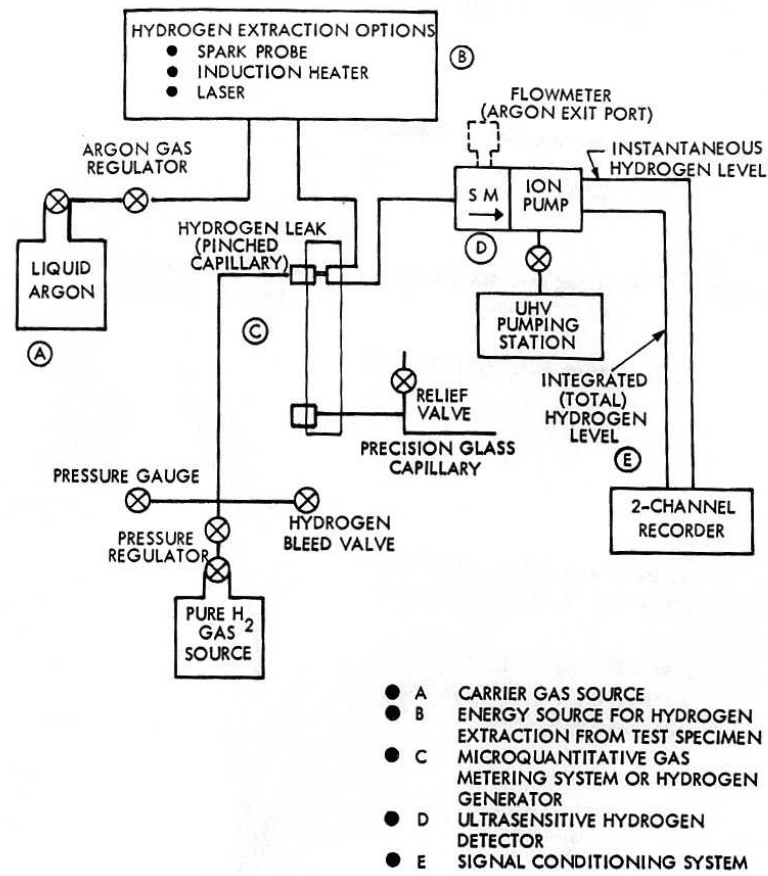


Figure 2.6: Furnace control system used by Das et al. [35].

to make rapid changes in the temperature. Thus the procedure required only about ten minutes from start to finish. A Thermal Conductivity Detector (TCD) was used in quantifying the hydrogen amounts. According to the test results, the hydrogen content was shown as two separated peaks at 400° C and at 650° C. However, the first peak was not observed if the sample was first placed in the mercury eudiometer at 25° C and then placed in the system. The authors believed the extraction of most of the hydrogen from the eudiometer method eliminated the peak at 400° C.

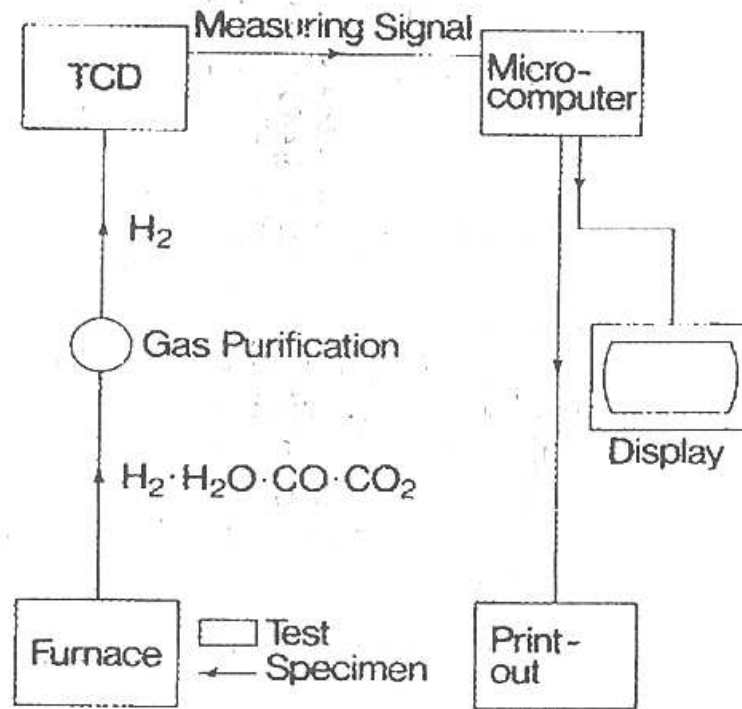


Figure 2.7: Furnace control system used by Sohrman [36].

Apparatus described in US patent 4142399

An automated apparatus, patented in the United States, assigned to the inventors by Nippon Steel Cooperation, Japan, for measuring hydrogen quantities in steel is described in [37]. In this method, the hydrogen that egressed from a heated sample was collected in a hydrogen collecting container, which was then measured using a gas chromatograph. The method was capable of measuring progressively mobile hydrogen up to 1000° C. The method was calibrated using the mercury eudiometer method. The results of the calibration tests can be found in Table 2.5.

Similar patented apparatus are described in [38],[39].

Apparatus used by Padhy

Padhy et al. [40] describes a method that used a hydrogen sensor to measure hydrogen that was collected using the hot extraction method. A cylindrical hot extraction chamber was designed for collecting hydrogen at 400° C from welded samples. The chamber was made out of austenitic stainless steel and closed on both ends by a flange with a copper-viton gasket. The chamber was helium leak tested before being used for the measurement. Once hydrogen was collected, it was measured using a Proton Exchange Membrane Hydrogen Sensor (PEMHS). More details on the sensor can be found in [40]. The method has been calibrated using the standard mercury eudiometer method. Accordingly, the relationship between the mercury eudiometer method and the hot extraction-sensor method was given by

$$H_{HotExtraction} = 0.998H_{Eudiometer} + 0.03 \quad (2.14)$$

where,

$H_{HotExtraction}$ = Diffusible Hydrogen obtained by hot extraction-sensor method at 400° C

$H_{Eudiometer}$ = Diffusible Hydrogen obtained by eudiometer Method

However it is not clear how or whether the eudiometer method was used at 400° C for calibration.

2.7.3 Hot-Vacuum Extraction Method

The hot-vacuum extraction method, also known as thermal-vacuum extraction, was first proposed by Ransely [41] in 1955 for determining hydrogen contents in aluminum and its alloys. A few examples of apparatus that are based on this method are given below.

Apparatus used by Ransley

In this method [41], the extraction system in the apparatus heated the sample to extract gas and the analytical system collected and analysed the gases. The evolved gases were removed continuously from the extraction system by means of a mercury-diffusion pump and then analysed by physical methods. The physical method involved measuring the pressure of the gas, which was in a constant volume container, using a McLeod gauge. A heated palladium foil was used to diffuse hydrogen from the gas mixture. The difference of the pressure before and after diffusing hydrogen was used to calculate the hydrogen amounts. The small amounts of gases remaining in the system were the residual gases that egressed from the sample, which is common to Aluminum.

Apparatus used by Degreve

Fig. 2.8 shows a schematic of the apparatus and the furnace section of the apparatus used in [42]. During measurements, a solid cylindrical metal sample (E) was heated under high vacuum (10^{-6} torr) in a quartz tube that was previously baked at 800°C for 3 hours to eliminate adsorbed water. Evolved hydrogen from the sample was extracted through a diffusion pump (DP) and stored in a collection chamber (CC) with a collection pump (CP). Then the hydrogen amounts were measured using a mass spectrometer, which was previously calibrated using volumes of hydrogen collected in to CC under standard pressure and temperature conditions.

Apparatus manufactured by LECO Corporation.

LECO Corporation in the United States has developed one of the most recent hydrogen measuring device named *DH603*, which can be used to measure progressively-mobile and total hydrogen in steel samples [43]. The system is a fully automated

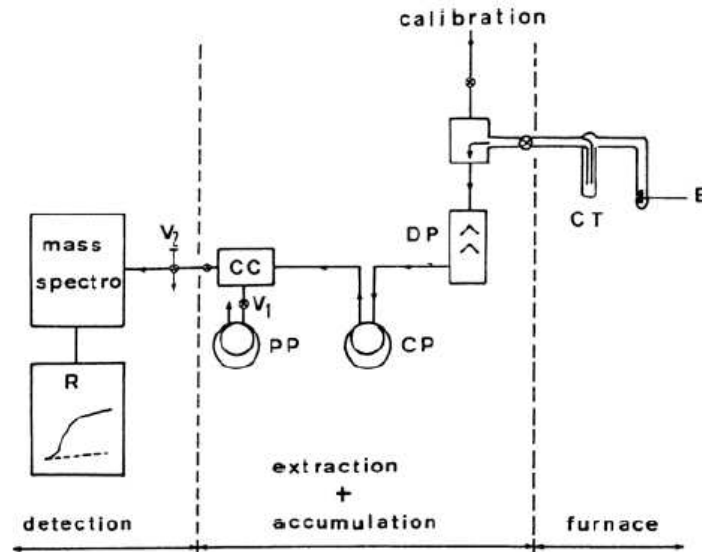


Figure 2.8: Apparatus used by Degreve [42].

system, commercially available; however, the sample size is limited to approximately 6 g.

Apparatus used by BAM

One of the most recent advancements for measuring hydrogen in solid materials including steels, has been developed by the federal materials research institute (BAM) in Germany is provided in [44]. Fig. 2.9 shows a schematic of the system. The furnace has a capability of reaching up to $1500^{\circ}C$ during the measurements and the measurements, are carried out using a mass spectrometer.

2.7.4 Discussion

Both the furnace control (hot extraction) method and hot-vacuum extraction methods have been used widely to measure hydrogen amounts in steels and other metals.

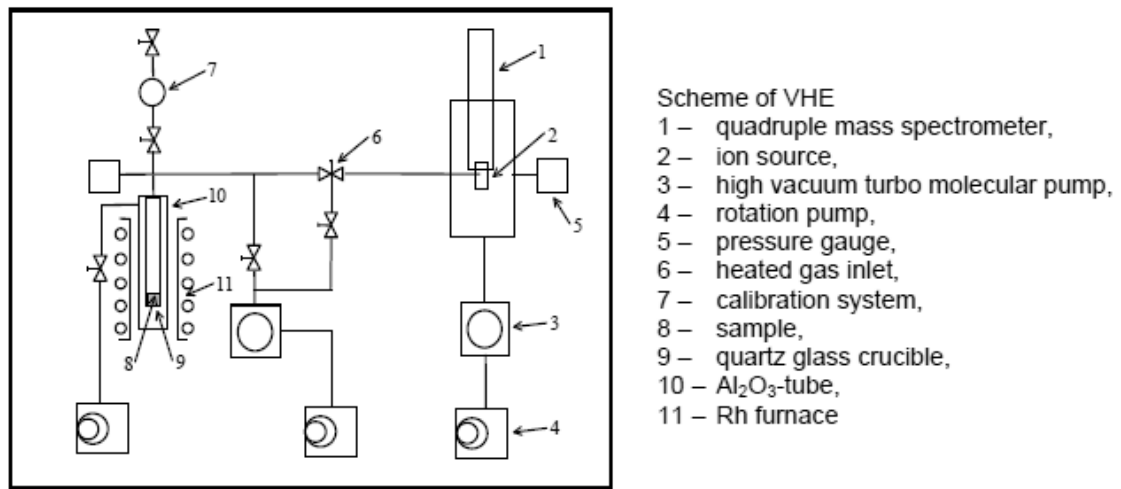


Figure 2.9: Hot vacuum extraction apparatus used by BAM [44].

The latter has been used as the base technique of the recent commercially available apparatus. In each apparatus, separate containers were used to hold the sample that was placed in the furnace. Austenitic stainless steels were used as the container material in the recent apparatus. After hydrogen was collected into the container, it was measured using various methods. The gas chromatograph or mass spectrometer has been used widely for this purpose.

As given in the literature, one of the challenges in both the hot extraction method and the hot-vacuum extraction is finding suitable materials that withstand higher temperatures without absorbing hydrogen. Even though materials that could withstand high temperatures are available, their interaction with hydrogen is not known. From the two methods, the hot-vacuum extraction method has become more challenging as it requires retaining a vacuum at elevated temperatures. In addition, most of the past and current apparatus are capable only of using smaller size test samples;

this will have an effect on the accuracy of the measured hydrogen amounts.

2.8 Methods of Measuring Total Hydrogen

2.8.1 Overview

It is believed that the total hydrogen contained in a sample would evolve when it is fused. Three types of fusion methods are being widely used: vacuum fusion, inert gas fusion, and tin fusion method. A description of each method with examples of a few apparatuses are given below.

2.8.2 Vacuum Fusion Method

The basis of this method is fusing the sample in a vacuum furnace and extracting the evolved gases with or without using a vacuum and then determining the amount of the collected gases. The vacuum fusion method was first used by Walker and Patrick in 1912 to determine the amounts of oxygen, nitrogen, and hydrogen in a number of metals [48].

2.8.3 Inert Gas Fusion Method

This method is similar to the vacuum fusion method except this method uses inert gas instead of a vacuum. An inert gas is used to create an inert atmosphere in the sample container and as the carrier gas of the detection system [48]. According to the literature, the inert gas fusion method is simple and therefore less expensive and also faster than the vacuum fusion method.

Some of the apparatus based on the inert gas fusion method are described below.

Apparatus used by Hargrove

One of the earliest successful systems based on the fusion method was developed by Hargrove et al. to measure both nitrogen and hydrogen in 0.3 to 10 mg weight steel samples within 90 minutes [46]. Helium was used as the inert gas in the system. A schematic of the system is provided in Fig. 2.10. A high temperature furnace that could reach a temperature of 1800° C was used in the system to fuse steel. A schematic of the furnace is shown in Fig. 2.11. During fusing, the gases evolved passed to the chromatograph, and necessary calculations were carried out to quantify the amounts of hydrogen. Some of the results obtained using this method are given in Table 2.1. Note: NBS in the table stands for the National Bureau Standards.

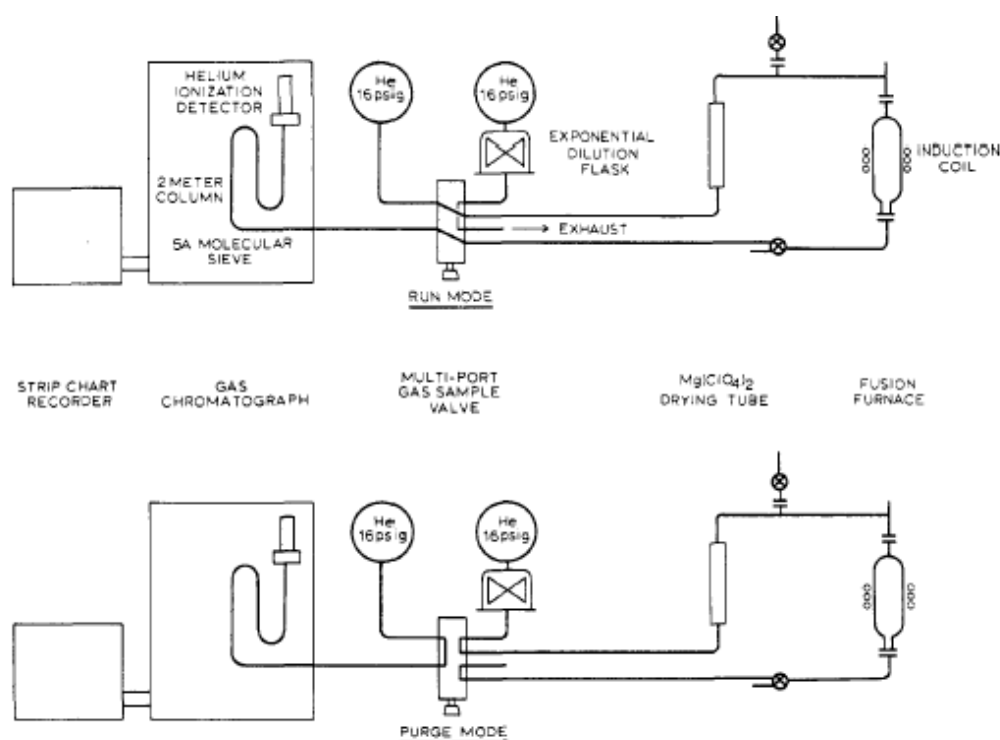


Figure 2.10: Fusion system used by Hargrove et al. [46].

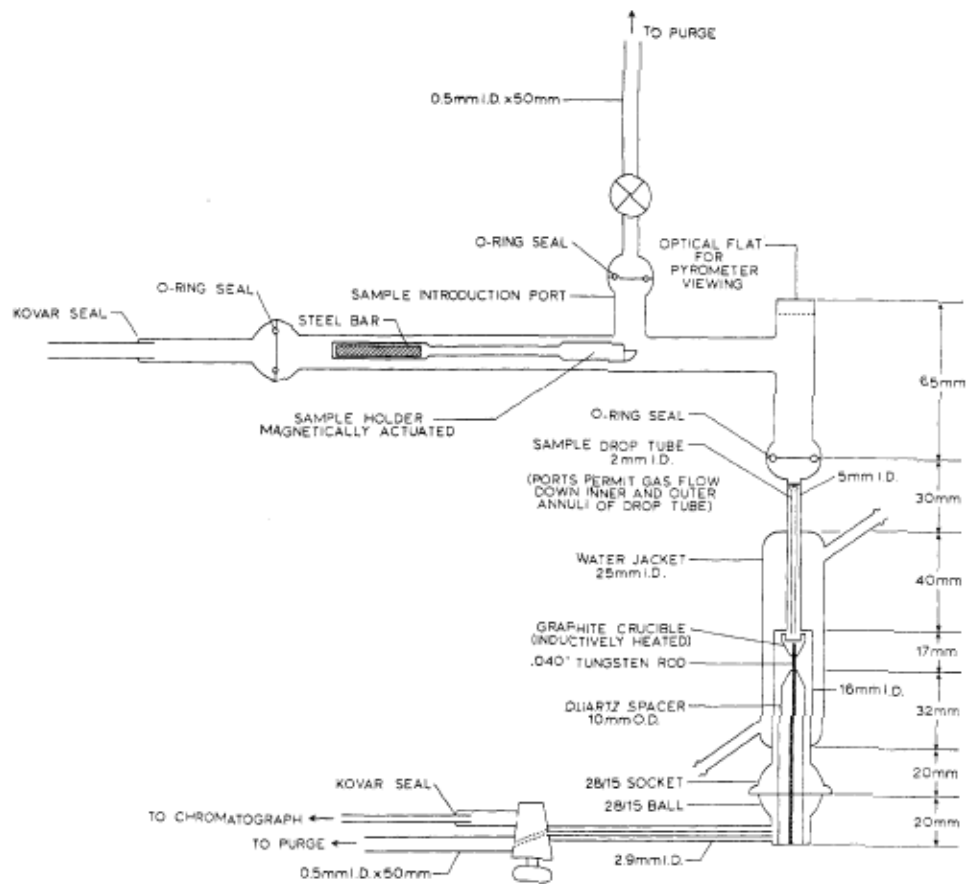


Figure 2.11: Furnace system used by Hargrove et al. [46].

Apparatus manufactured by Horiba Ltd.

The Horiba Ltd.'s (France) EMGA 621W Hydrogen analyzer has been designed to measure the hydrogen content in ferrous and non-ferrous metals. This is a fairly new system that can be found in the market today. In this system, a sample is placed in a graphite crucible, which is placed between the higher and the lower electrodes of an impulse furnace. A high current passes through the crucible creating an increase in temperature. The thermal conductivity detector analyzes the gas generated in the

Table 2.1: An example showing the readings obtained from the Hargrove's method [46].

Specimen mass, <i>mg</i>	NBS value, <i>ppm</i>	Measure values, <i>ppm</i>	Mean, <i>ppm</i>
0.2-0.7	32	39,32,29,34,28	32 ± 4

furnace after the dust and moisture are removed. It is also possible to stop fusion and extract progressively-mobile hydrogen content in the sample by heating the sample below the fusing point. Some of the specifications of this system are given in Table 2.2.

Table 2.2: System specification of the hydrogen gas analyzer described in [47]

Description	Range
Sensitivity	0.001 ppm
Measuring time	approx. 100 <i>seconds</i>
Sample weight, <i>g</i>	0.1 <i>g</i>
Accuracy	0.008 <i>ppm</i>

2.8.4 Tin Fusion Method

The tin fusion method is similar to the fusion methods that are described in the sections above; however, a molten tin (Sn) bath was used to fuse the sample. Tin allows fusion to take place at a temperature considerably below the melting point of the sample. For example, with steel, the tin fusion analysis can be usually performed at 1100-1500° C as compared to 1600° C, the melting point of iron [48].

In this method, first, the furnace is evacuated and the molten tin is degassed

before placing the sample in the tin bath. During fusion, hydrogen together with the other gases are extracted using a vacuum and transferred to a measuring system. The hydrogen amounts can then be determined by a suitable method. Some researchers have used silicon (Si) along with tin. According to them, silicon helps to depress carbon monoxide evolution.

Apparatus used by Mallet and Griffith

As described in [49], Mallet et al. used the tin fusion method to measure hydrogen in 2-4 g magnesium and magnesium-lithium alloys. The same system was used to by Griffith et al.[50] to measure the hydrogen quantities in aluminum alloys. The furnace section and the gas extraction system used in the tin fusion method are shown in Fig. 2.12 and Fig. 2.13, respectively.

According to Fig. 2.12, the furnace section consists of a T-shaped borosilicate glass furnace tube. In the vertical section of the furnace tube, about 200 g of tin in a borosilicate glass crucible was heated using a wire-wound furnace. The horizontal section was used for storage and preheating. A steel pusher weight for guiding the sample was also stored in this section. The gases evolved in the furnace section were continuously pumped with a mercury diffusion pump into a fixed calibrated volume where the pressure of the gas was measured with a McLeod gauge. The volume of the gas at standard temperature and pressure has been computed from the measured pressure and temperature and the size of the calibrated volume. Finally, the gas was pumped with a hand-operated pump into the analysis section to remove hydrogen from the system by diffusion through a palladium tube heated to 300° C.

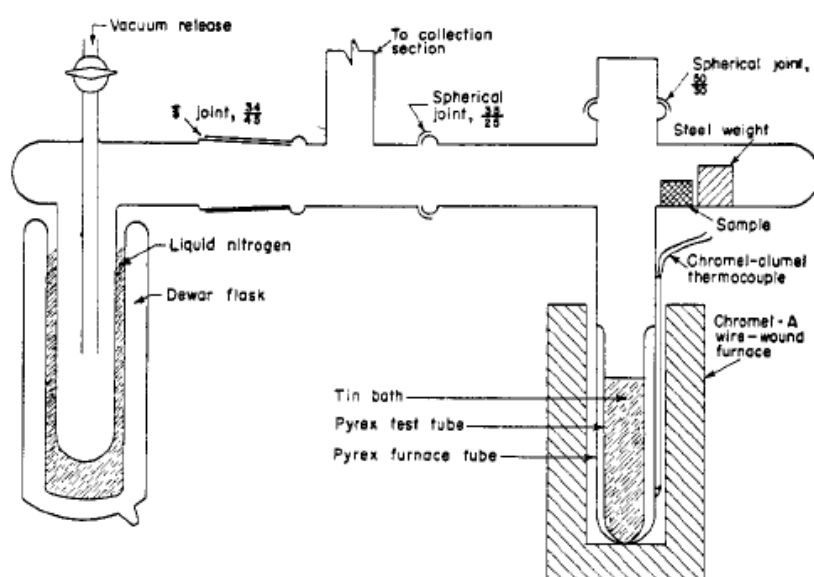


Figure 2.12: Furnace of the tin fusion system used by Griffith et al. [50].

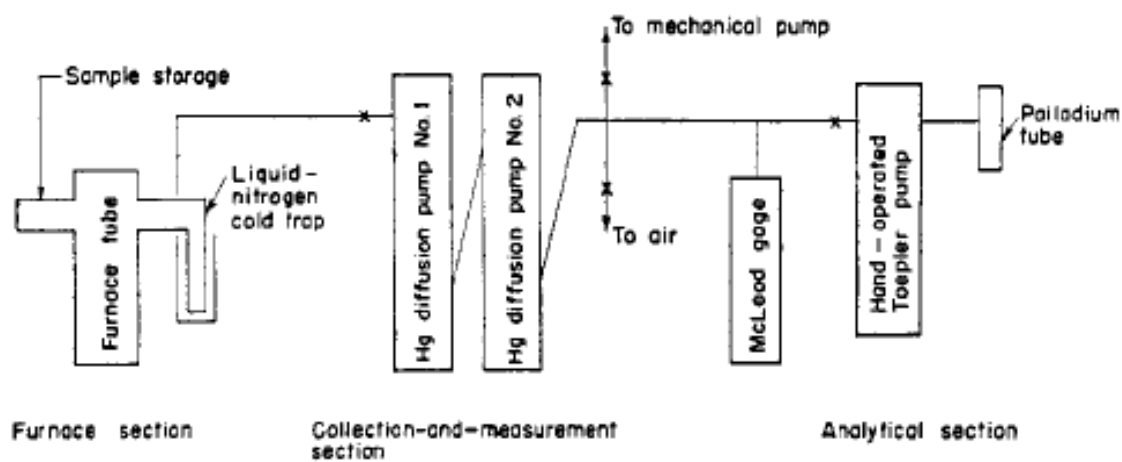


Figure 2.13: Gas extraction system system used by Griffith et al. [50].

Apparatus used by Carson

A schematic of the quartz tube that was used in the apparatus used by Carson et al. [51] is shown in Fig. 2.14. He compared the tin fusion method with the furnace control method (also known as the hot extraction method) using steel samples weighing about 2-3 g.

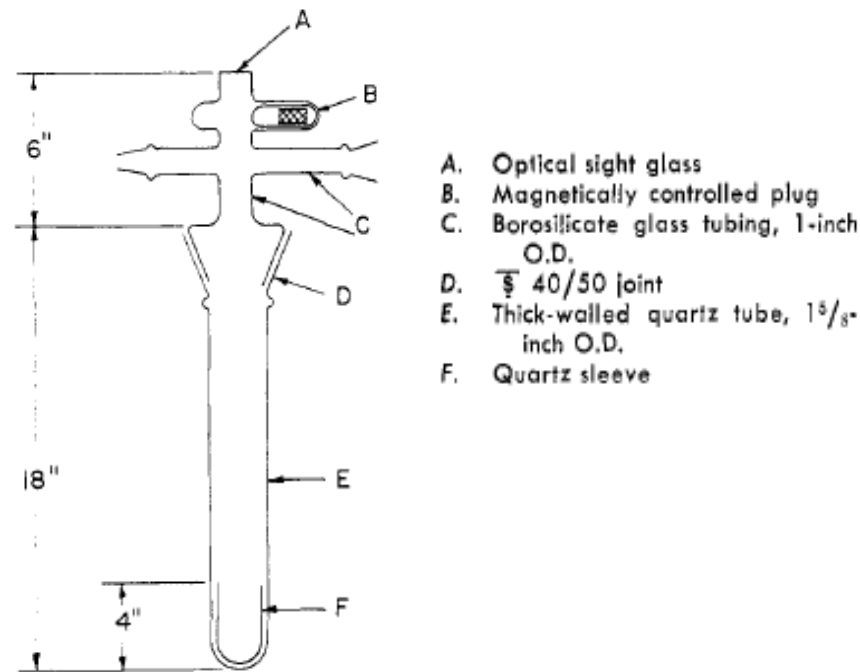


Figure 2.14: Tin fusion furnace assembly used by Carson [51].

2.8.5 Discussion

The fusion method is the only method that could be used to measure total amount of hydrogen in a test sample. The method has challenges because of the elevated operating temperature, which is higher than $1500^{\circ}C$. The accuracy of the fusion methods depends on the following factors:

- high temperatures caused creep of the seals and joints resulting in leaking.
- several gases could be evolved during fusing steel. Therefore, the accuracy of the final results will depend on the method that is used to differentiate and quantify hydrogen from the other evolving gases.
- It is known that hydrogen can also be trapped in molten steels. Therefore, steps should be taken to egress all hydrogen from the melt.
- The current, fusion based systems are capable only of using smaller size samples, which weigh only a few milligrams. Thus, it is doubtful that whether the measurable hydrogen quantities from such small samples represent the true amount of hydrogen in the original sample.

2.9 Hydrogen Amounts in Literature

2.9.1 Overview

This section provides some examples of the amounts from selected literature. The provided values are categorized based on the test method. It is important to note that direct comparison of the provided values is not possible because of the differences in following factors:

- method used to measure
- sample material and heat treatment process that the sample has been gone through
- sample preparation method
- hydrogen charging method

- temperature and pressure at which hydrogen was collected

Thus, most of the provided values can be used only to compare the trends and ratios.

Example: ratio between amount of hydrogen egress at 50° C and 400° C.

2.9.2 Amounts from Eudiometer Method

Case 1

The hydrogen amounts collected from a disk-shaped test sample made out of hot rolled AISI 1018 steel using the standard eudiometer method are given in Table 2.3 [8]. The collected amounts are also presented in Fig. 2.15, which represents a typical hydrogen collection graph for the eudiometer method. The samples were charged for 24 hours in a reaction kettle using NACE¹ solution saturated with hydrogen sulfide. Hydrogen measurements were carried out at room temperature. According to the test results, the average amount of hydrogen collected was 1.34 ml/100g $\pm$ 0.1. From the graph it is apparent that it took at least 72 hours to stabilize the hydrogen amounts under the given conditions. It has been taken 24 hours (one day) to collect about 86% of hydrogen from the mean amount collected from all the tests.

Case 2

Fig. 2.16 provides the standard eudiometer test results from six laboratories in the United Kingdom using five scenarios ("phases" as indicated in the reference) [52]. The five phases included

1: Welded in lab; cleaned on site; measured on site

2A: Welded on site; cleaned on site; measured on site

¹National Association of Corrosion Engineers

Table 2.3: Amounts of hydrogen collected in Case 1

Time (hours)	Hydrogen amount, <i>ml/100g of sample</i>
0	0
1	0.66
2	0.81
5	1.00
7	1.05
24	1.16
48	1.22
72	1.23
96	1.24
120	1.26
144	1.21

2B: Welded in lab; cleaned in lab; measured on site

3A: Welded on site; cleaned on site; measured on site

3B: Welded on site; cleaned in lab; measured in lab

The welded test samples were made out of steel. The measurements were carried out at 25° C. According to the results, it took minimum of fourteen (14 days) for complete evolution of hydrogen from the test samples. Table 2.4 gives the mean hydrogen amounts collected from the deposited metal samples after a fourteen day period. The calculated $C_V\%$ value (Coefficient of Variance) for the overall results given in the tables was approximately 7.4%. The C_V value was calculated using the following equation:

$$C_v = \frac{\sigma}{\mu} \times 100 \quad (2.15)$$

where σ is standard deviation and μ is mean.

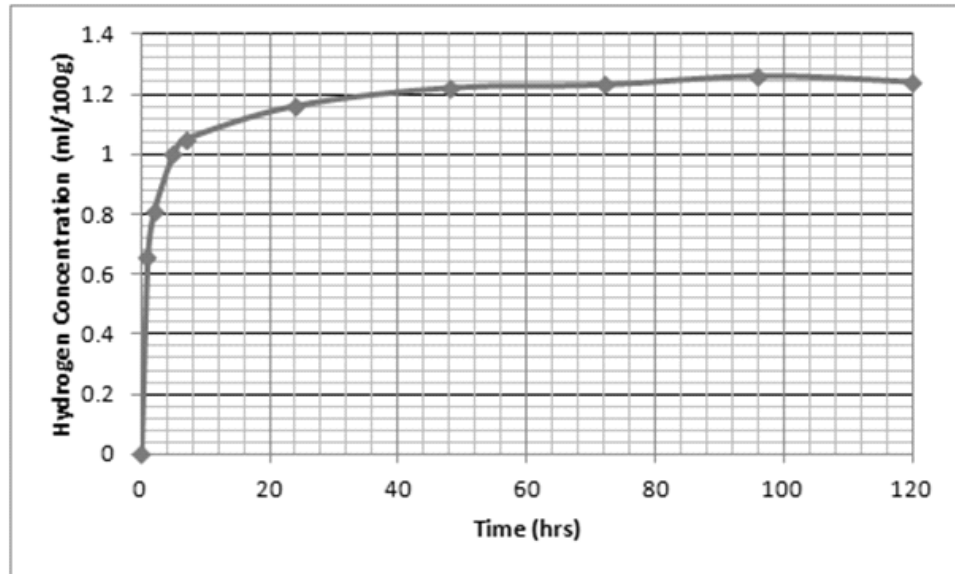


Figure 2.15: A graph indicating the hydrogen amounts from Case 1 [8].

2.9.3 Amounts from Hot Extraction Method

Case 3

The test results obtained using the apparatus described in Section 2.7.2 are provided in Table 2.5. As given in the table, the measured hydrogen amounts were compared with the eudiometer method based on the IIW² standard and JIS standard. The IIW standard uses mercury as the eudiometer fluid while the JIS standard uses glycerin as the eudiometer fluid. It is well known that the JIS method gives a lower amount of hydrogen (40%) than the IIW method as a result of capturing hydrogen bubbles that are released from the sample in glycerin [37].

A unity plot, which is given in Fig. 2.17 was made using the values given in Table 2.5. Accordingly, the relationship between the hydrogen amounts collected using the

²International Institute of Welding

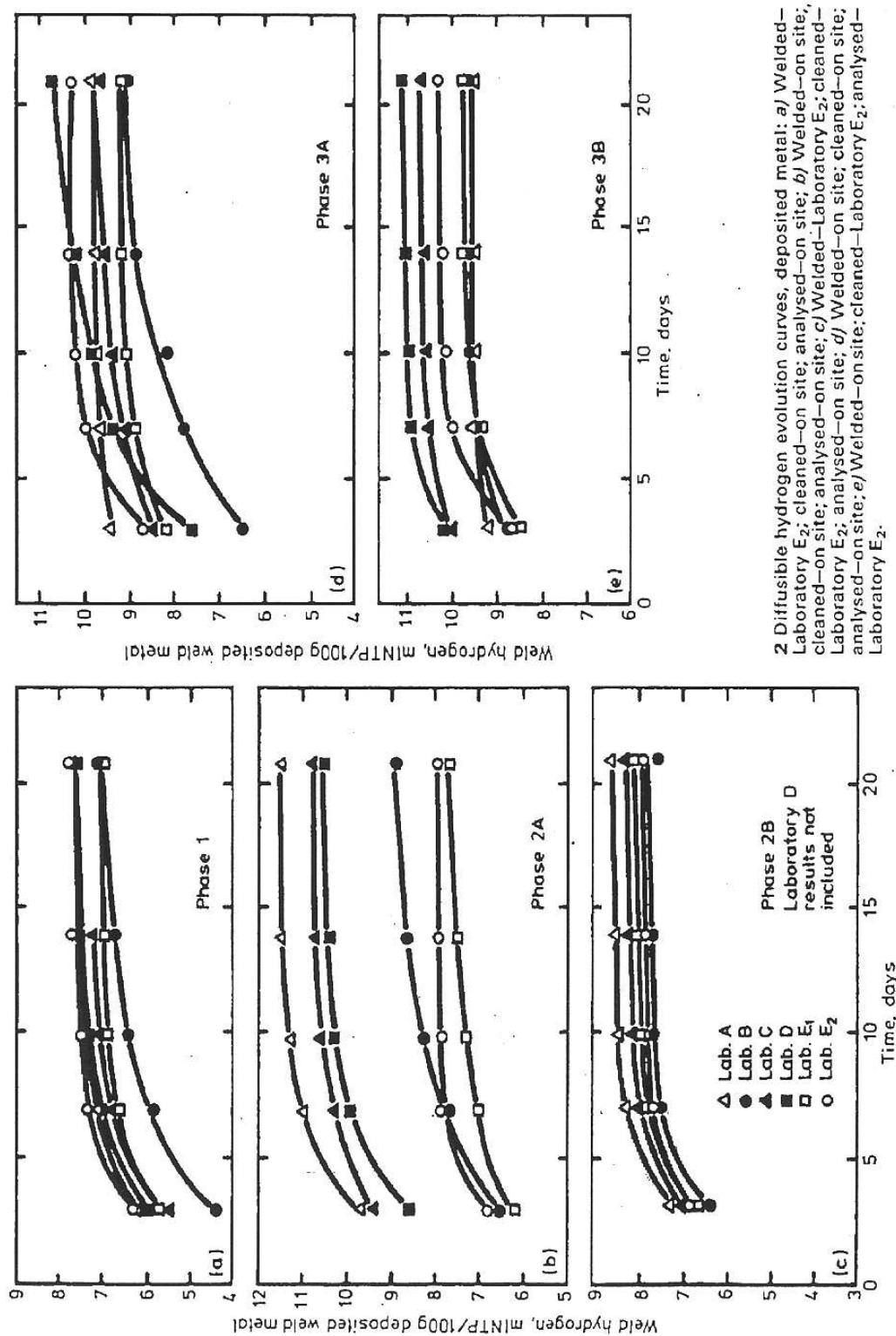


Figure 2.16: Eudiometer test results from 5 laboratories in the UK [52].

Table 2.4: Hydrogen amounts in *ml/100g of deposited material* after fourteen days period [52].

Lab	Phase 1	Phase 2A	Phase 2B	Phase 3A	Phase 3B
A	7.53	11.46	8.60	9.77	9.51
B	6.73	8.70	7.78	8.90	9.55
C	7.09	10.70	8.22	9.62	10.63
D	7.52	10.41	* reject	* reject	11.05
E1	6.99	7.50	7.98	9.32	9.98
E2	7.54	7.90	7.90	10.22	10.22
Mean	7.26±0.43	9.45±0.70	8.10±0.73	9.55± 0.76	10.16±0.72

two methods can be given from

$$H_{HotExtraction} = 1.18H_{Eudiometer} \quad (2.16)$$

where,

$H_{HotExtraction}$ = Diffusible Hydrogen obtained by hot extraction based invented method at 25° C

$H_{Eudiometer}$ = Diffusible Hydrogen obtained by eudiometer method

Note: Hydrogen amounts in the unity plot are given in ml/100 g of deposited materials.

The following can be also concluded from the measurements given in Table 2.5:

- When hydrogen amounts were collected from the same test sample at different temperatures, the amounts collected had declined with the increase of temperature. For example, after completing hydrogen collection at room temperature, when the temperature was elevated to 500°, 1000° and the to 2100° C, the ratio

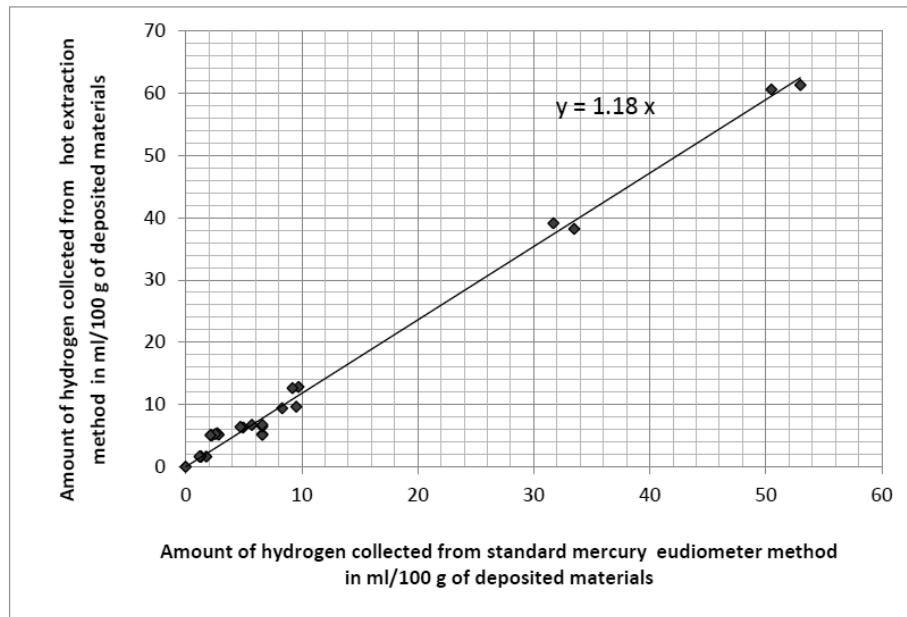


Figure 2.17: Unity plot for the the example given in Case 4.

among the measured hydrogen amounts were approximately 5:2:1. This shows that most of the hydrogen that resided in the samples were in the form of easily mobile or progressively mobile hydrogen compared to the amounts of trapped hydrogen.

- At room temperature, the hot extraction method collects more hydrogen compared to both standard methods (i.e IIW and JIS) as given in Equ.2.16.

Case 4

An early study on comparison of hydrogen amounts collected using four methods is provided in [56]. Table 2.6 contains the same extracted gas samples analysed by the four methods. The hot vacuum extraction method was used to extract the gas samples. The first method used a commercially available mass spectrometer. A

Table 2.5: Hydrogen amounts in *ml/100g of deposited material* obtained from [37].

	Amount	using	invented	method	Amount from	STD methods
Test	Room Temp.	500°C	1000°C	2100°C(fused)	IIW std	JIS std
A1	5.27	N/A	0.85	N/A	6.61	2.43
A2	5.12	N/A	0.85	N/A	6.61	2.43
A3	6.48	N/A	0.85	N/A	6.61	2.43
A4	6.74	N/A	0.85	N/A	6.61	2.43
A5	6.31	N/A	0.81	N/A	4.96	2.16
A6	6.73	N/A	0.78	N/A	5.71	3.70
A7	12.82	N/A	1.22	N/A	9.73	5.90
A8	12.63	N/A	1.40	N/A	9.21	4.30
A9	9.40	N/A	1.03	N/A	8.32	4.80
A10	9.66	N/A	1.01	N/A	9.54	3.06
A11	38.21	N/A	1.96	N/A	33.50	22.70
A12	39.12	N/A	2.02	N/A	31.70	24.90
A13	60.60	N/A	3.03	N/A	50.50	38.40
A14	61.32	N/A	3.21	N/A	53.00	36.00
A15	5.39	N/A	0.72	N/A	2.73	1.82
A16	5.14	N/A	0.81	N/A	2.17	2.56
A17	1.60	N/A	0.65	N/A	1.32	N/A
A18	1.64	N/A	0.60	N/A	1.78	N/A
B1	5.16	0.52	0.23	0.10	2.84	1.43
B2	5.03	0.51	0.22	0.09	2.27	3.12
B3	5.27	0.51	0.20	0.09	2.57	1.56
B4	5.05	0.57	0.18	0.08	2.14	1.37
B5	6.42	0.55	0.19	0.08	4.72	2.16
B6	1.70	0.40	0.18	0.07	1.31	N/A
B8	1.65	0.38	0.16	0.06	1.20	N/A

Table 2.6: Comparison of hydrogen amounts in ppm, obtained by various methods [56].

Sample Sample	Material Material	Palladium Membrane	Mass Spectrometer	Gas Chromatography	Catalytic oxidation and Absorption
A1	AISI 316	1.70	1.63	1.62	1.67
A2	"	1.59	1.50	1.60	1.58
A3	"	1.60	1.49	1.42	1.54
A4	6.74	1.73	1.51	1.61	1.48
A5	6.31	1.50	1.57	1.73	1.66
B1	Pure iron	0.47	0.38	0.41	0.55
C1	Titanium	72.5	71.7	69.0	72.4
D1	Steel	0.21	0.20	rejected	0.07
E1	3% Si-Fe	2.34	2.22	2.11	2.27
E2	"	2.29	2.09	2.36	2.22
E3	"	2.29	2.13	2.13	2.00
E4	"	2.28	2.03	2.21	2.24
E5	"	2.55	2.35	2.49	2.25

palladium membrane was used in the second method. In this method, the evolved gas was collected in a calibrated volume and the pressure was measured. After hydrogen was removed by diffusion through the heated membrane, a second pressure measurement was made. The pressure measurements were used in quantifying the hydrogen amounts. In the third method, a commercially available gas chromatograph was used. In the fourth method - catalytic oxidation and absorption- hydrogen was oxidized to water and the amount of water was used to predict the hydrogen amounts.

According to the authors, although excellent precision can be obtained by using all four said methods, the palladium membrane method is preferred because of versatility, speed and low cost.

Chapter 3

Literature Review (Part 2): Interaction of Steels with Mercury

3.1 Introduction

Only a handful of literature studies are available on the interaction of mild steels with mercury. Most of the research studies among them are related to the decontamination of mercury from steel surfaces (i.e. cleaning mercury contaminated steels). It is also apparent that research work has been recently carried out related to elemental mercury from hydrocarbon reservoirs that react with steel surfaces of processing equipment and piping [57].

Analysis of steel samples for mercury contamination in the past has shown that mercury deposits can occur in the following forms [58]:

- Mercury in the form of insoluble sulphides
- Penetration of mercury into surface deposits, such as rust layers, scales, or salt precipitates
- Mercury at previously damaged sites of the steel component, such as corrosion pits and cracks
- Mercury in the pores of the steel that are channeled to the steel surface
- Mercury at the grain boundaries as a result of transcrystalline diffusion

3.2 Mechanism

The mechanism of how mercury interacts with steel is not completely understood, but it is thought to be one or a combination of the following [59]:

- Physical adsorption of elemental mercury to the steel surface oxide or sulfide (i.e. mill scale and/or corrosion scale).
- Reaction with surface scale constituents and incorporation into surface corrosion or mill scale.
- Amalgamation or reaction with steel at the steel/corrosion scale interface.
- Incorporation by diffusion into the steel atomic lattice.
- Incorporation into the steel surface by diffusion into the steel grain boundaries and possible reaction with steel grain boundary constituents.

According to [59], diffusion of atomic mercury into the steel atomic lattice in a manner similar to hydrogen diffusion is impossible given the size of a mercury atom relative to steel's interstitial space. Amalgamation is difficult because solubility of iron (Fe) in liquid mercury is very low. Grain boundary interactions possibly account for high levels of surface accumulation but the mechanism of the retention of mercury by grain boundaries is not apparent. Thus, it is believed physical adsorption of mercury to exposed surfaces and chemisorption to surface scales are the most likely candidates. Chemisorption is a type of an absorption that involves a chemical reaction between the surface and the absorbate.

It is also believed that the process of absorption is reversible: thus mercury absorbed by steel can re-evaporate into gas or re-dissolve into liquids that come

into contact with the contaminated surface [60]. It has been observed that pressure vessels cleaned with detergent at a low mercury vapor level will, after being closed for some hours, continue to produce elevated mercury vapor concentrations in their interior spaces for many days, even with periodic ventilation [59].

3.3 Evidence from Industry

Literature studies dating from the 1950s describe mercury boilers (i.e. boilers made out of steel for boiling mercury) became plugged with crystalline deposits of iron over time [61]. The mercury boilers were used since 1912 in mercury power plants in USA. This deposit of iron was attributed to steel being attacked by the mercury at boiling temperatures ($565\text{--}635^{\circ}\text{C}$), only when steel was exposed to mercury for extended period of time. After extensive amount of research, it was found that the dissolution of iron by mercury could be eliminated by adding minute amounts of inhibitors such titanium and magnesium into the mercury. Thus, the problems were eliminated [62][63].

Mercury-contaminated steel pressure vessels and piping in gas processing facilities has also been reported in later years. Mercury and mercury compounds are found in all geological hydrocarbons including coal, natural gas, gas condensates, and crude oils. As a result, mercury can be distributed through hydrocarbon production, processing, and transport systems [65].

3.4 Depth Profiles of Mercury Adsorption

3.4.1 In Steel

The findings of the EDX (Scanning Electron Microscope with Energy Dispersive X-Ray) analysis of steel pipes that have been used in gas processing plant in Germany are provided in [58]. According to the findings, mercury adsorbed only to the surfaces and did not penetrate into the steel structure. Mercury was found mainly in an elemental form in the rust layer at a depth of between 50 and 200 μm .

A research study carried out using API 5L-X52 type steel coupons that were immersed in liquid mercury, which was at 25° C for one of six (6) different pre-determined adsorption periods (15, 30, 45, 60, 75 and 90 days), is described in [66]. Mercury as spherical droplets of mercury oxide (HgO) attached on the steel coupon surfaces has been observed at the end of each adsorption period, and it was found the mercury concentration ranged from less than 5 to about 45 atom% by EDX analysis on the coupon surface. Examination of the steel coupon surfaces using XPS (X-ray Photoelectron Spectrometer) analysis two weeks later found mercury in the oxide form with surface concentrations ranging from less than 0.5 to about 3.0 atom% of mercury. These differences suggest loss of mercury through vaporization due to high HgO vapor pressure, leaving much lower mercury levels on the coupon surface, and only in the oxide form. XPS depth profile analysis further showed that Hg was present predominantly on the topmost surface to only about 10 nm depth. Insignificant concentrations of less than 0.1 atom% Hg by XPS analysis were observed and persistent throughout the depth profile regardless of the HgO adsorption periods investigated. These data indicate that Hg, under the applied conditions, was present only on the top surface and did not penetrate significantly into the depth.

Figs. 3.1 through 3.3 show mercury levels in the depth profile at the end of 30, 75, and 90 days of mercury adsorption, respectively. Note that Hg levels in these figures are multiplied by 50 to better match the scale of the other elements' concentrations.

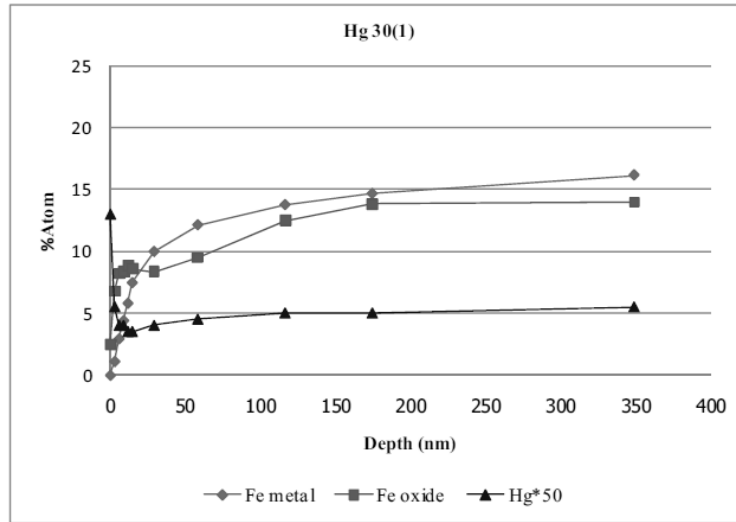


Figure 3.1: Hg in the depth profile of the 30 day HgO adsorption coupon [66].

3.4.2 In Pure Iron

The paper [67] describes a research study carried out using the Thermal Desorption Auger Spectroscopy (TDAES) on adsorption of mercury into pure iron. Dosing mercury at a low temperature (i.e. at 85 K) and room temperature (298 K) onto the clean iron caused mercury adsorption until a saturated layer was formed. It was found the layer was approximately 0.67 nm thick at 85 K and 0.23 nm thick at 298 K. These values correspond to nearly three mono layers of mercury on the clean iron surface at 85 K and one monolayer at 298 K.

The research study concluded that temperature plays an essential role in the sat-

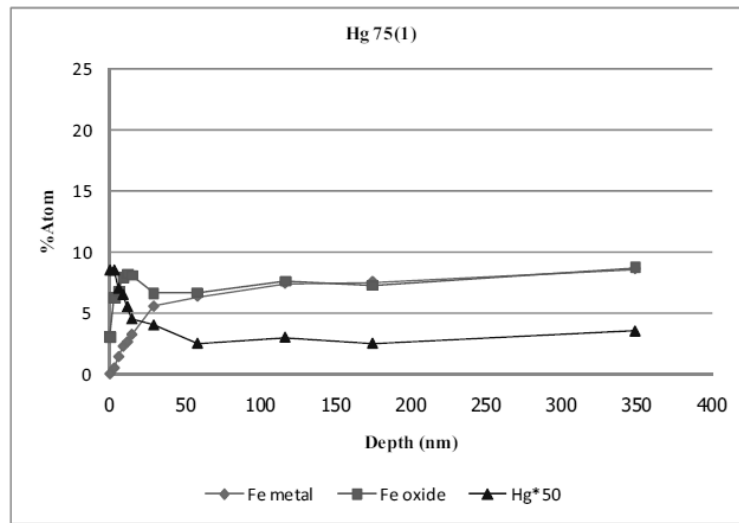


Figure 3.2: Hg in the depth profile of the 75 day HgO adsorption coupon [66].

uration capacity of the iron. At 85 K, the saturation thickness of mercury was much greater than at room temperature for the clean iron. It is believed that difference this may be caused by a rearrangement of mercury atoms on the surface at increasing temperatures, whereas at 85 K, the mercury adheres to the position at which it lands.

3.5 Chemical Analysis on Contaminants

Fig. 3.4 shows SEM images of cross sections of a pipe interior surface that has been used in a gas production unit. The process conditions during operation were approximately 50° C in a water-saturated gas with a 5 mole percent of CO₂, 4-5 ppm H₂S and a balance mostly of Methane. The length of service was approximately 5-6 years. The concentration of mercury in gas that flowed through the pipe during the service period was estimated from occasional measurements to have been between

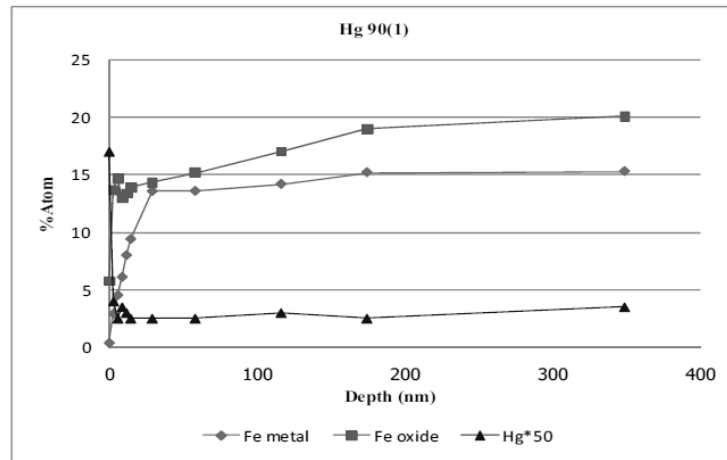


Figure 3.3: Hg in the depth profile of the 90 day HgO adsorption coupon [66].

500-800 $\mu\text{g}/\text{Sm}^3$ ¹.

The surface scale was removed from the pipe, and the powder sample was subjected to X-ray diffraction analysis (EDX). The analysis of the sample has identified the following crystalline phases [59]:

- HgS as a major phase
- FeOOH (goethite) as a major phase (poorly crystallized)
- FeCO₃ (siderite) as minor phase
- Fe₃O₄ (magnetite) as a minor phase

¹Sm³: Standard cubic meters

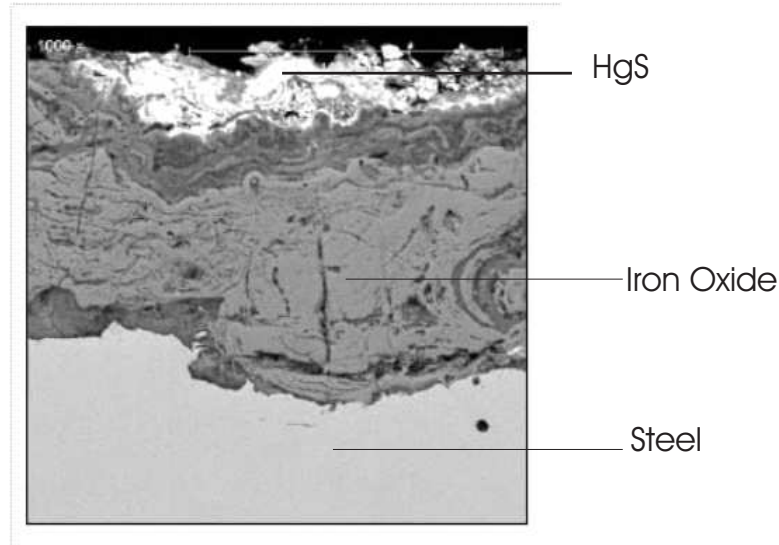


Figure 3.4: Metallographic Cross-Section of Pipe Scale

3.6 Summary

Fig. 3.5 provides a log plot of the solubility of iron in mercury (Hg), bismuth (Bi), and lead (Pb) with respect to inverse temperature. Fe-Hg binary phase diagram can be found in [64]. As shown, the solubility of iron in mercury is extremely low. Thus solubility at the boiling point ($565^{\circ}C$) of mercury is approximately 0.36 ppm. As described in [61], short-time experiments near the boiling point of mercury showed that iron and steels were unaltered by boiling mercury. However, long-time operation resulted in the dissolution of iron by mercury.

According to [68], plain carbon steels are virtually unattached by mercury under non-flowing or isothermal conditions. The presence of either a temperature gradient or liquid flow can lead to drastic attack. The corrosion mechanism seems to be one of dissolution, with the rate of attack increasing rapidly with temperature above

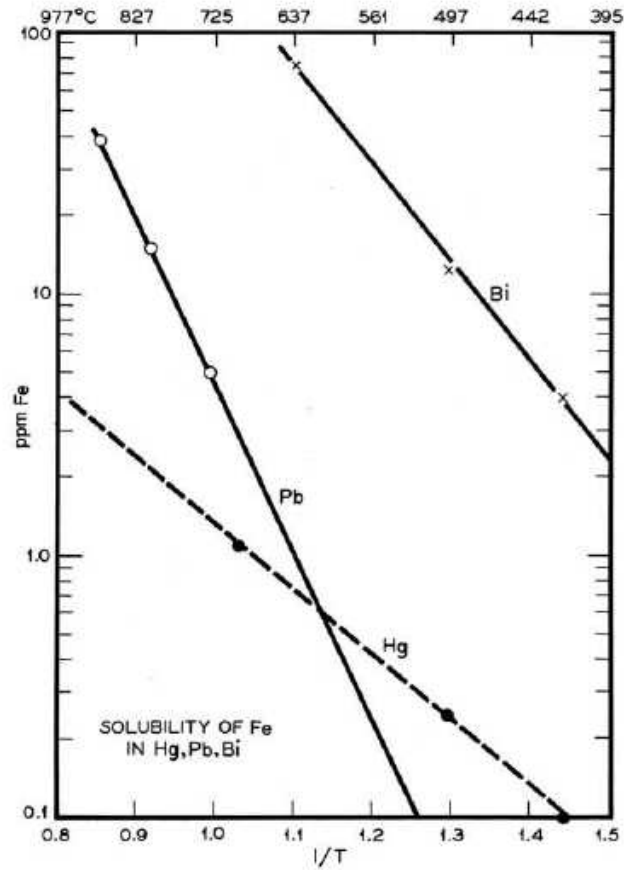


Figure 3.5: Solubility of iron in Hg, Bi and Pb [61].

500° C. Adding alloy elements such as chromium (Cr), titanium (Ti), silicon (Si) and molybdenum (Mo) into steel and adding 10 ppm titanium to mercury have helped in reducing the attack.

There are also reports on the dissolution of nickel (Ni) and chromium (Cr) in stainless steels by mercury. This was evidenced by the development of a dull luster rather than a shiny appearance on the surfaces of polished test samples, adherence of mercury on the test samples, and weight losses and metallographic changes on

the test samples exposed above 255 ° C. Metallographic and micro-analytical examinations have revealed a shallow reaction zone in 316L stainless steel exhibiting substantial Ni and Cr leaching from the exposed surfaces to hot mercury leading to significant porosity and transformation of the corroded material to ferrite [69].

In summary, according to the available information, contamination and attack of carbon steels by hot mercury that results in the dissolution of iron from steel is possible. However the evidence for dissolution of carbon or other elements in carbon steel from hot mercury is not found in the available literature.

Chapter 4

Equipment Development

4.1 Introduction

The main objective of this research work is to develop a new hydrogen measuring system that can measure the amounts of hydrogen in steels. This chapter describes the design and the construction of the new system, in details. It is important that the measuring system being developed can accurately measure mobile and progressively mobile hydrogen in a given type of steel. The system should overcome the weaknesses of the currently available systems, yet also be simple, robust, and easy to use.

4.2 Concept

4.2.1 Selection of a Technique

The hot vacuum extraction method, which is a direct technique, has been used for a long time. As described in Section 2.4, a direct technique based on hydrogen measuring methods provides more advantages compared to the measuring methods based on indirect techniques. Thus, the hot vacuum extraction method is used for the new hydrogen measuring equipment. As its name describes, this method applies elevated temperatures on a test sample placed in a vacuumed environment to promote hydrogen to egress from the test sample.

4.2.2 Use of Elevated Temperature

When elevated temperatures are used to promote charge hydrogen (that is hydrogen already in the sample) to egress out of a test sample, the egressed hydrogen amounts can be classified as easily mobile hydrogen (H_{PM}) and progressively mobile hydrogen (H_{EM}). Thus in a sample,

$$H_{total} = H_{EM} + H_{PM} + H_{Trap} \quad (4.1)$$

where H_{total} is the total amount hydrogen and H_{Trap} is the amount of hydrogen that is trapped inside the sample.

In this research work, easily mobile hydrogen is defined as the hydrogen that would egress out from a hydrogen-charged steel sample when the sample is heated up to 50° C. The progressively mobile hydrogen is defined as the hydrogen that would egress out from a hydrogen-charged sample when is heated beyond 50° C. Hydrogen that would not egress out by simply elevating the temperature is considered as trapped hydrogen. Usually, trapped hydrogen is difficult to take out by elevating the temperature and is therefore immeasurable. Therefore, the trapped hydrogen amount in a test sample can be estimated by subtracting the total of the mobile and the progressively mobile hydrogen volume from the total hydrogen volume as shown in equation 4.2. Total hydrogen is the hydrogen that egress from a steel when it is fused.

$$H_{Trap} = H_{total} - (H_{EM} + H_{PM}) \quad (4.2)$$

4.2.3 Use of Vacuum

It is believed that the vacuum helps hydrogen to come out of a sample because of the pressure difference between the inside and the outside of the test sample. However, no research evidence could be found in literature that establishes any useful relation between the vacuum pressure levels and hydrogen egression.

In this research study, change in the vacuum pressure was used to determine the amount of hydrogen that egresses from a test sample. It is also important to note that the design using a vacuum results in the most accurate use of the universal gas law.

4.3 Equipment Design

4.3.1 Design Considerations

After considering the findings from the literature review, the following have been identified as essential requirements for the new hydrogen measuring equipment:

- Able to measure various types of hydrogen (ie. easily mobile and progressively mobile) accurately and efficiently. Easily convertible to a unit that could measure total hydrogen
- Flexible enough to measure very small to very large volumes of hydrogen accurately
- Able to handle test samples (specimens) with different shapes and different sizes
- Safe to use

- Economical and simple to construct
- Included with its own leak detection system
- Suitable for industrial use

Currently available hydrogen measuring equipment is limited in most or all of these essentials.

4.3.2 Design Overview

A detailed schematic of the newly designed hydrogen measuring system is given in Fig. 4.1. The system consisted of a vacuum chamber, a heating mantel, a vacuum pump, two pressure gauges, a temperature indicating controller, a helium bottle, calibration volumes, manual flow control valves, connectors, and interconnecting capillary tubes.

As shown in Fig. 4.1, a test sample containing a vacuum chamber was connected to the rest of the equipment using a capillary tube. The capillary tube was branched into two major sections using a T joint. The T joint in the figure is marked with an “X”. One of the two branches of the T joint was connected to two pressure gauges using another T joint. As shown in the figure, one pressure gauge measured vacuum chamber pressure, and the other pressure gauge measured the helium pressure. Helium was used in the leak detection system, which is explained in Section 4.6.11.

The other branch of the T joint (marked with an X) was connected to a vacuum pump, a helium bottle, and three calibration volumes using a union joint. This was the only union joint used in the equipment. The vacuum pump was connected to the equipment in such a way that the pump was able to evacuate the entire system. The

helium bottle was connected in the same way to pressurize the entire system with helium. Needle type manual flow control valves were provided to isolate sections of the system as required.

The three calibration volumes were connected to the system using one branch of the union joint. The calibration volumes were used to collect the hydrogen that egressed from a test sample. Each calibration volume could be isolated from the others as well as from the entire system using manual flow control valves.

The hydrogen contained in a test sample egresses out when its temperature is elevated. The heating mantel was the heating source of the test sample. During the tests, the vacuum chamber that contained the test sample was placed inside the heating mantel. A temperature controller was connected to the heating mantel. The temperature controller was configured to automatically maintain the test sample temperature at a predetermined set temperature by manipulating the heat supplied by the heating mantel.

The details of the components mentioned above are discussed in the following sections.

4.4 Materials Selection

4.4.1 Overview

During the design stage of the new equipment for the measurement of hydrogen, it was required to select a suitable material to fabricate the components of the equipment. The components included the following:

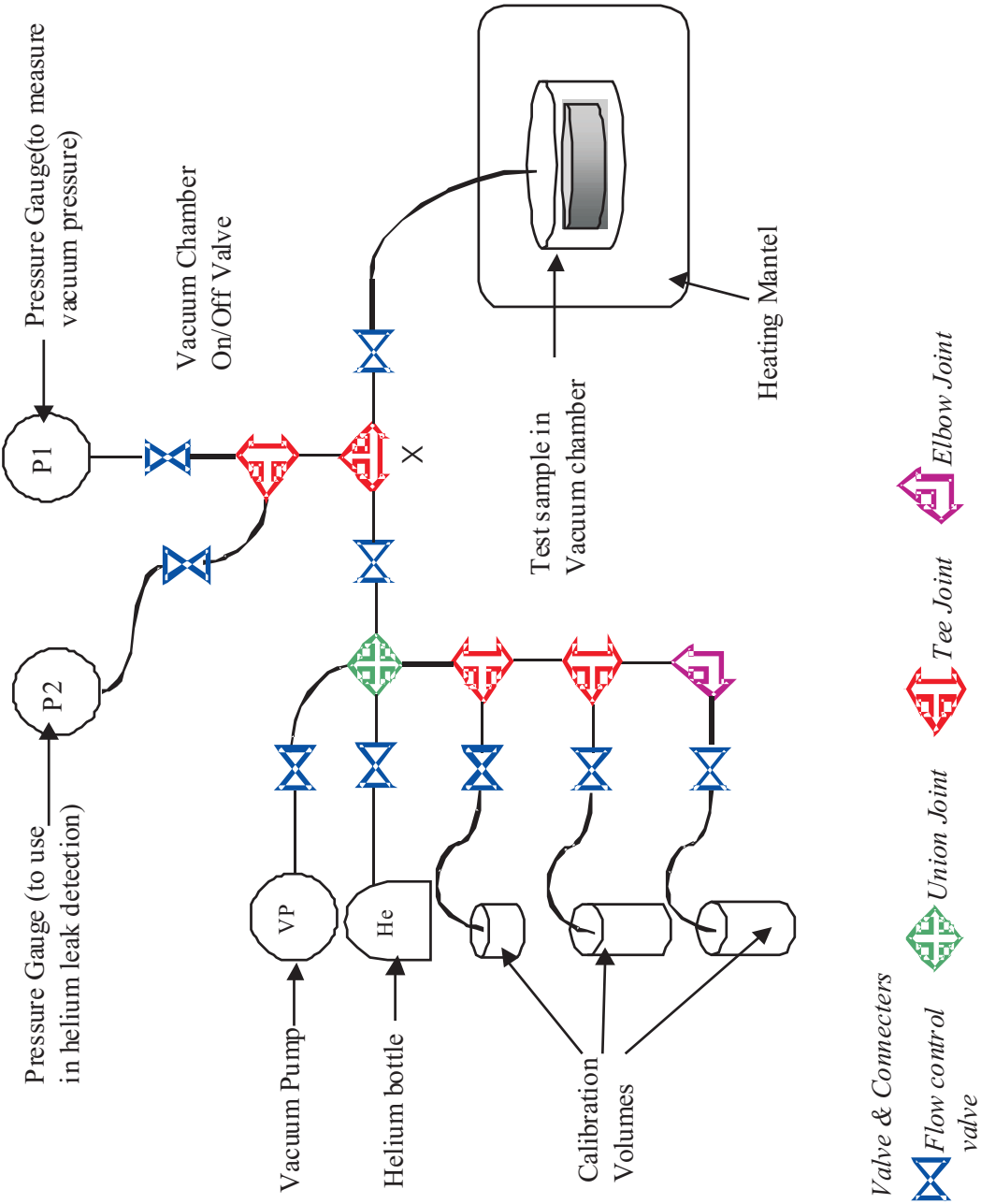


Figure 4.1: A detailed schematic of the newly designed hydrogen measuring system.

- A vacuum chamber, which holds the test sample during the test. The vacuum chamber is required to hold the vacuum at elevated temperatures.
- Calibration volumes, which collect hydrogen that egresses out from a sample.
- Other connections, such as connectors and tubes.

In previous research work, ceramics (e.g. borosilicates and quartz) have been commonly used to fabricate test sample holders (chamber). This choice was specifically made because of the elevated operating temperatures of the equipment. The recent publications mentioned stainless steels for the purpose. Caskey et al. [73] states, because of their relatively better hydrogen compatibility, austenitic type stainless steels are frequently a better choice for hydrogen service than ferritic or martensitic types of stainless steel.

After considering the advantages and disadvantages of few candidate materials, it was decided to use grade 316 L austenitic stainless steel to fabricate the required components in this research study because it has the following qualities:

- Relatively low outgassing rate
- Relatively low permeability to hydrogen
- Could withstand the expected elevated test temperatures
- Easy to handle (non-brittle, easy-to-form tubing)
- Fabrication processes that used in fabricating stainless steel components are readily available in-house
- High quality stainless steel connections are commercially available for purchase

- Reliable joining processes are available for connecting the components
- Corrosion resistance

The chemical composition and mechanical properties of Grade 316 stainless steel can be found in [72]. A brief description that summarizes the interaction of austenitic stainless steels with hydrogen and vacuum is provided below.

4.4.2 Hydrogen in Stainless Steel

Hydrogen permeability in stainless steel

Hydrogen permeation through stainless steels from the gas phase has been examined extensively on a wide variety of austenitic steels but only in a few ferritic or martensitic steels [73]. Accordingly, austenitic stainless steels have extremely low permeability to hydrogen. A graph that shows the permeability of hydrogen to different types of stainless steels at a wide temperature range is provided in [73].

Hydrogen permeation through austenitic stainless steels is also known to depend on surface conditions. It is believed that the oxide layer on the metal could make them less permeable to hydrogen.

4.4.3 Hydrogen Diffusivity

A graph that compares hydrogen diffusivity in stainless steels with pure iron at various temperatures can be found in [73]. Thus, the diffusivity in austenitic steels are less than extrapolated values for pure γ -iron and vary with alloy composition. It is also believed that hydrogen trapping in austenitic steels is not as strong as in ferritic stainless steels [73].

Summary

The movement of hydrogen in stainless steels is controlled primarily by the basic crystal structure (FCC or BCC). Thus, the hydrogen movement in the austenitic stainless steel is restricted by its the fewer free spaces in the FCC structure. Alloy composition appears to have a small but measurable effect on hydrogen permeability in the austenitic stainless steels. Surface oxides and chemically formed films on stainless steels inhibit hydrogen absorption. Although trapping occurs in both austenitic and ferritic stainless steels, the magnitude of the effect in austenitic steels is smaller [73][74][75].

4.4.4 Stainless Steel for Vacuum System

Danielson [75] states metals are arguably the most prevalent vacuum chamber materials, with stainless steel (SS) far ahead of other metals such as mild steel or aluminum (Al) alloys. This finding is mainly because of the low outgassing rate of stainless steels compared to other materials. Outgassing is a challenge for creating and maintaining clean high-vacuum environments because of the voluntary release of absorbed or dissolved gases from the material to the environment. Thus, a vacuum chamber that is made of a material with a high outgassing rate could release gasses to the vacuum, making it difficult to retain a vacuum. Table 4.1 provides the outgassing rates for a few materials. It is clear from the values that stainless steel is a better choice when compared to most materials.

Table 4.1: Approximate outgassing rates to use for choosing vacuum materials [75].

Vacuum Material	Approx.outgassing rates, <i>torr liter/sec/cm²</i>
Stainless Steel	6E-9
Aluminum	7E-9
Mild Steel	5E-6
Brass	4E-6
High Density Ceramic	3E-9
Pyrex	8E-9

4.5 Equipment Construction

This section describes the construction procedure of the measuring system. The new system uses heat and vacuum to collect and measure hydrogen; therefore, it is named the **Thermal Vacuum Hydrogen System (TVHS)**.

The construction of the TVHS was completed in several stages (steps). The stepwise procedure made the troubleshooting easy. The main components were constructed during the first stage. Purchasing commercially available items such as pressure gauges, thermocouples, temperature indicators, temperature controllers, connectors, and capillary tubes were also done in the first stage. Grade 316 stainless steel Swagelok[®] connectors and capillary tubes were selected. An actual test was done in stage 2 to confirm whether the design actually could capture gases egress from a test sample. In stage 3, all the components were assembled together, including the leak detection system. The main panel design and final TVHS construction were completed in stage 4. Further details on each stage are given in the following sections.

4.6 Stage 1: Construction of Main Components

The main components that are required to construct the TVHS were fabricated in the first stage. Construction details of each component are given below.

4.6.1 Vacuum Chamber

Design

The vacuum chamber, which contains a vacuum atmosphere, holds the test sample during a test. Thus, the vacuum chamber goes through a heating and a cooling cycle. The vacuum chamber should be able to sustain such heating and cooling cycles without leaking. A leak in the system could draw air from the atmosphere into the chamber, causing inaccurate results. Therefore, designing the vacuum chamber was a critical step.

The vacuum chamber was designed as a two-piece set that consists of a container to hold the test sample and a matching lid. The vacuum chamber was designed to closed and opened by tightening and loosening eight bolts that were placed along the perimeter of the container lips and the lid.

Materials

A solid block of grade 316 stainless steel was selected as the material to fabricate the vacuum chamber. Before fabrication, the stainless steel block was baked in a furnace at $300^{\circ}C$ for 7 days to minimize outgassing of any fabricated component constructed from it. Baking steel before usage is a common technique that has been used to reduce outgassing. A discussion on outgassing in vacuum systems in general can be found in [75] and outgassing of hydrogen from stainless steel vacuum chambers in particular can be found in [77].

Fabrication

When constructing a vacuum chamber, it is essential to minimize its joints because they are vulnerable to leaks. Joints such as threaded joints could leak with usage and time. Therefore, efforts were taken to minimise the number of joints as well as threaded joints that require frequent threading and unthreading. Thus, the container and the lid of the vacuum chamber were machined as single components from a cylindrical block of grade 316 Stainless Steel. Machining was completed using CNC (Computer Numerical Control) lathe technology. The constructed container, its lid, the gasket, and a disk-shaped test sample are shown in Fig. 4.2.

The container portion of the chamber was a cylinder of 50 *mm* in diameter and 28 *mm* in height with a flat bottom. The thickness of the vacuum chamber walls are 6.35 *mm* (0.25 inches). A large thickness was selected to minimise the possible stresses induced during handling and to avoid the possible effects of atmospheric pressure on the walls. During a test, the outside of the walls of the vacuum chamber experiences forces from the atmospheric pressure, but the pressure inside the chamber is much less than the atmospheric pressure as a result of the vacuum environment. As a result of the pressure difference, an inward force is created on the outside of the walls of the vacuum chamber. If the walls of the chamber are not strong enough, such a force could squeeze the chamber walls, reducing the chamber volume. This influences the internal vacuum chamber pressure and thereby leads to inaccurate measured hydrogen amounts.

A connector was required to connect the vacuum chamber to the rest of the system. This was accomplished by threading a commercially available grade 316 stainless steel Swagelok® connector to the top center of the lid. The selected Swagelok®

connector fit perfectly with the rest of the Swagelok[®] connectors used with the system. Even though this can be considered as a joint, it is inevitable during the design process. However, this joint is a permanent joint that never requires disassembling, and it is the only threaded joint in the vacuum chamber. A commercially available high performance vacuum sealant was applied around the Swagelok[®] connector area as a precautionary step to avoid leaking through this joint.

Thermocouple port

During a test, the temperature of the test sample inside the sealed vacuum chamber had to be measured. It was not feasible to make a thermocouple port by drilling a hole through the walls of the chamber to insert a thermocouple until it touches the test sample because the hole could become a vulnerable location for leaks. Therefore, a temperature port was made by drilling approximately 0.5 mm in diameter hole on the lid of the chamber. The depth of the hole was made about ninety percent of the thickness of the lid to avoid a through hole.

Test samples

The container could hold a test sample with any shape as long as it fit inside the dimensions of the container. The internal dimensions of the container were 37 mm in diameter and 22 mm in depth. A bigger chamber would be required for a bigger sample than the given dimensions. The most economical option for designing a bigger chamber would be to use a taller container with the same diameter and lip profile as the original container. This would allow the existing lid and its fittings to be used for the new container. Large test samples are always preferred over smaller test samples, so they can reasonably represent the average microstructure as well as provide a much larger amount of hydrogen for measurement. However, currently

available industrial type hydrogen measuring units can handle only very small test samples of about 6 grams [43]. The vacuum chamber constructed in this research work could handle test samples ranging from a few milligrams up to 125 g ($\sim 18 \text{ cm}^3$). In addition, the samples could be any regular or irregular shape.

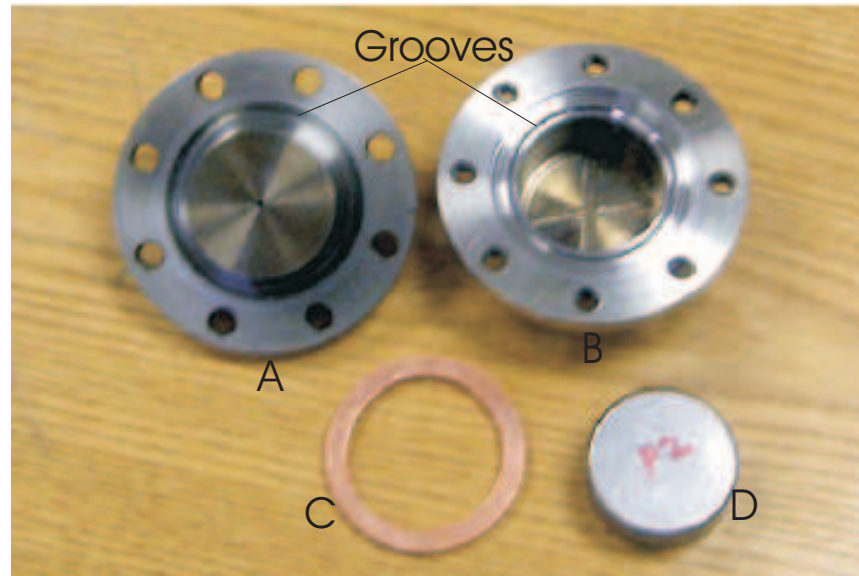


Figure 4.2: Parts of vacuum chamber assembly (A) Bottom view of lid (B) Top view of chamber (C) Gasket (D) Test sample.

4.6.2 Gaskets

A gasket was used between the vacuum chamber container and its lid before tightening the bolts. The gasket made it easier to obtain a proper seal between the container and its lid and minimizes the chances of any leakage. As shown in Fig. 4.2, about 2 mm deep grooves were cut into the surfaces of the container and its lid. The main purpose of the grooves is to hold the gasket without moving when tightening the bolts.

Material

Initially, gaskets made out of Teflon[®] were used, but their use was discontinued because they were able to seal only up to about 60° C. Later a solid deoxidized copper bar stock was used as the gasket material. Deoxidized copper is preferred over normal copper because when compared with normal copper, deoxidized copper does not give off oxygen at elevated temperatures. Egression of oxygen from the gasket into the vacuum chamber would affect the accuracy of the hydrogen measurements obtained from the equipment.

In general, softer gasket materials provide better sealing than those of harder materials. Therefore, a deoxidised copper block was annealed to make the material softer before machining the gaskets. Annealing was done by gradually heating the deoxidized cylindrical copper block to 600° C in a furnace and then slowly cooling it in the furnace using a controlled step down to room temperature.

The annealing process enhanced the ductility of the gasket. Table 4.2 shows the hardness values obtained for deoxidized copper and annealed deoxidized copper. As shown in these values, the annealing process provided about 20% reduction in the hardness of the annealed gasket compared to a gasket that is not annealed. Reduction in hardness is an indication of enhancement in ductility. Enhanced ductility helped the gasket to deform effectively during the tightening of the lid, thus reducing the chances of leaking.

Fabrication

A number of gaskets were machined using an in-house lathe machine.

Table 4.2: The hardness values obtained for deoxidized copper and annealed deoxidized copper gaskets.

Material Type	Hardness <i>Rockwell B scale</i>
Deoxidized copper gasket	54.1 ± 1.5
Annealed Deoxidized copper gasket	43.8 ± 1.7

Design improvements

Even though the annealed deoxidized copper gaskets provide a better seal, reproducibility in ensuring the expected seal was not observed. As there are no further improvements that could be carried out with respect to this material, additional improvements in the design were considered. As a result, two vee apexes were machined inside each flat bottomed groove on the lips of the container and the lid where the gasket rested. When the bolts were tightening, the vee apexes bit into the copper gasket from both sides that finally provided the expected seal. The vee apexes on the lid and the container were designed in such a way that they had a small offset. This allowed one copper gasket to be used twice as explained below.

Economical usage

It is economical to be able to use one gasket as many times as possible. When the expected seal was obtained by introducing the vee apexes, they bit into the copper gasket, engraving circles on both flat sides of the gasket. The engraved circles were visible when a gasket was taken out of the assembly after a test. However, the same gasket could be used twice by slightly offsetting the vee apexes on the lid and the container from each other. As a result, the engraved circles on both sides of the gasket became slightly offset from each other as well. This is illustrated in Fig. 4.3.

Now, the gasket could be used for a second time by flipping it upside down. This enables the vee apexes to be aligned again on the flat surfaces of both sides of the same gasket for the second time.

4.6.3 Calibration Volumes

Design

Calibration volumes were used to collect the hydrogen that egresses from a test sample. Those volumes were actually metal bottles machined with a constant known volume. The term “calibration” is used to highlight the accuracy of the known volumes and that these bottles are used to measure the volumes of hydrogen collected from the test samples. Three calibration volumes were used with the equipment designed in this research study. Two of these are equal in volume (5.06 ml each), and the third one is approximately half the size of the others (2.86 ml).

The hydrogen measuring systems studied during the literature review had only one calibration volume. One unique feature of the novel hydrogen measuring equipment presented in this thesis is its three separate calibration volumes. The three calibration volumes are able to be isolated from one another as well as from the whole system. This isolation feature enables one to adjust the total volume of the entire system within a wider volume range suitable to the hydrogen’s expected egress volume. The adjustment of the total volume of the system is done by engaging or disengaging one or more of the calibration volumes by closing and opening their connecting valve. The main advantage with this feature is its better measurement sensitivity and ability to operate the equipment accurately over a wide range of hydrogen egress conditions. The various combination of volumes that could be added in to the vacuum system was 2.86 ml, 5.06 ml, 7.92 ml, 10.12 ml, and, 12.98 ml.

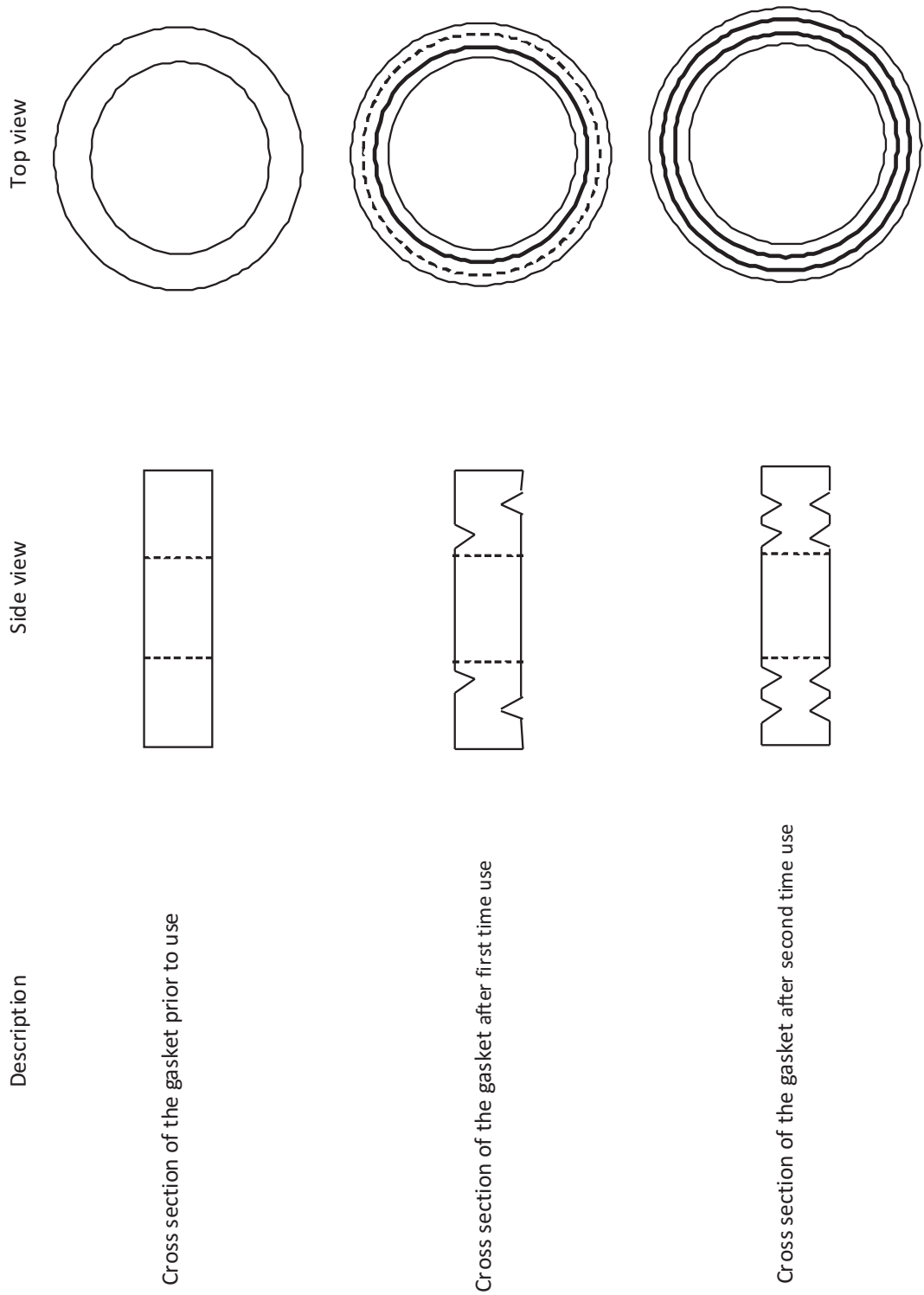


Figure 4.3: Cross sections of a gasket after each use.

Fabrication

Following the same fabrication process as the vacuum chamber, each calibration volume was machined as a single unit without any joints. The joints were more likely to become leak sources with time. Thus, each calibration volume was machined in a lathe from a single block of grade 316 stainless steel. Similar to the vacuum chamber, each calibration volume requires a connector to connect it to the rest of the system. This was accomplished by tightly threading a commercially available grade 316 stainless steel Swagelok[®] connector to the shoulder area of each calibration volume.

The wall thickness of each calibration volumes is 6.35 mm (0.25 inches). This thickness is required to withstand possible volume variations caused by constantly changing differential pressure between the internal vacuum and the atmospheric pressure.

4.6.4 Vacuum Pump

A rotary type vacuum pump, or roughing pump, was selected. The pump was able to produce a low vacuum up to -13 *psig* (-89.6 *kPag*). If a higher vacuum capability is required, the current pump would need to be operated in conjunction with a diffusion pump. This method enables a wide range of vacuum conditions to be explored.

4.6.5 Heating Mantel

The heating mantel was the only heat source in the system. It was capable of elevating temperatures of a test sample up to 500° *C*. A more sophisticated high temperature vacuum furnace would be required to reach temperatures higher than 500° *C*.

4.6.6 Temperature Controller

A commercially available temperature controller. It controlled the temperature of the heating source in two modes: simple on/off mode and PID (Proportional Integral and Derivative) controlled on/off mode. In the simple on/off mode, temperature control was done by switching on/off the 120 Volt power supply of the heating source based on directly measured furnace temperature. In the PID controlled on/off mode, temperature control was done by switching on/off the 120 Volt power supply of the heating source according to a predetermined PID algorithm applied to the difference between the required temperature and the measured temperature. As a result, the rate of change of temperature (Derivative) and accumulated temperature errors over time (Integral) of the furnace temperature are accounted for in addition to only the furnace temperature (Proportional). When the fluctuation of the final temperature and the time required to reach the set temperature are considered, PID on/off mode is preferred over the simple on/off mode.

4.6.7 Temperature Indicator

A commercially available digital temperature indicator was installed in the system. The indicator has six channels. There are six thermocouples each connected to one channel. A selector switch is available to switch the display to show the readings obtained from each thermocouple one at a time. The six thermocouples connected to the temperature indicator measure temperatures over the following locations:

- In the vacuum chamber (1 channel)
- Two locations inside the panel (2 channels)
- Room temperature (1 channel)

- Two locations of the capillary tube that is connected to the vacuum chamber and the rest of the system (2 channels)

According to the universal gas law, the volume of gas is a direct function of temperature and pressure; therefore, an accurate determination of gas volume requires an accurate measurement of temperature at each volume section of the system.

4.6.8 Thermocouples

Commonly available, general purpose type K thermocouples were selected because of their wide temperature measuring range and accurate resolution.

4.6.9 Valves, Connectors and Capillaries

The measurement system consisted of nine flow control valves and six connectors. As shown in Fig. 4.1, the six connectors comprised one union joint, one elbow joint, and four T joints. Commercially available Swagelok[®] type valves and connectors made out of 316 stainless steels were used in the design. During the design stage of the hydrogen measuring equipment, thorough analysis was done to minimize the number of valves and connectors. Each valve and connector adds at least two joints to the system. These joints are vulnerable to leaks, so it is essential to minimize the number of valves and connectors but allow the possibility of sectionalizing (i.e. isolate different sections) the system. Sectionalizing is important for detecting leaks easily. This is discussed further in Chapter 5.

The system used grade 316, 1/8 *inch* (3.175 mm) diameter stainless steel capillary tubes throughout. The purpose of the capillaries is to effectively transport hydrogen from the vacuum chamber to each calibration volume. However, the lengths of the

capillaries were selected to minimize the total volume and physical volume of the measuring system.

Similar to the capillary tubes, each flow control valve and connector adds a certain volume to the total system. In other words, the number of valves and connectors used affects the sensitivity of the measurements obtained from the system especially during the measurement of very small quantities of hydrogen. Therefore, it is important to minimize the number of valves and connectors.

4.6.10 Pressure Gauges

After carefully considering the requirements, two commercially available, industrial type digital pressure gauges were selected for the measuring system. The first gauge had a pressure range of -15 *psig* to + 15 *psig* (103.4 *kPag*). It was selected to measure the vacuum drop caused by egress of hydrogen from a test sample. The smallest pressure that can be measured using this gauge is 0.001 *psig* (0.0068 *kPag*). Therefore, the selected pressure gauge is precise enough to measure even a minute pressure drop. Furthermore, there is an output signal available on this pressure gauge to send pressure data to an automatic data recording device.

The second gauge had a pressure range of 0 to +200 *psig* (0 to 1379 *kPag*). This gauge with its higher pressure range is required to measure the helium pressure during the leak detection. The leaks are indicated by a drop in helium pressure over a certain period of time. More details of the leak detection system are given below.

4.6.11 Leak Detection System

Technique

A leak can be defined as an unintended crack, a void, or porosity in a wall or joint of a system that allows contained fluids and gases to escape. The most common leaky locations of closed systems are usually found at interconnecting joints, gaskets, welded and brazed joints, or as a defect in material [70]. A leak detection process in a system is usually a quality control step that assures device integrity, and it should preferably be a one-time, non-destructive test [70].

Undetected leaks in a measuring system lead to inaccurate results. Therefore, the hydrogen measuring system was designed with a built-in leak detection system. Several leak detection techniques are available, spanning from very simple to more complex approaches. Some of the most common leak test methods that are used in the industry include underwater bubble tests, bubble soap paint, pressure and vacuum decay, and tracer gas (halogen, helium, and hydrogen) detectors [70].

The leak detection method used in this research study was based on the pressure decay method. The pressure decay method identifies the existence of a leak by a continuous drop in the pressure. In this method, the system to be tested is pressurized with a high pressure gas. Then, the system is isolated from the gas supply. Then the internal pressure of the system is monitored over time. A pressure drop in the system is an indication of a leak, and the rate of the pressure drop is an indication of the size of the leak present in the system. If the pressure drops at a slow rate, it is an indication of a small (minor) leak. If the pressure drops at a faster rate, it is an indication of a large (major) leak. If the pressure remains unchanged for a predetermined time interval, the entire system is considered leak-free.

Leak location

The pressure decay method does not identify the location of the leak, but several simple methods are available to identify the leak locations. Such methods include the sniffing technique or the bubble soap paint method. The sniffing technique uses a detector probe or sniffer to locate the leak location. The sniffer senses leaks in a system that is pressurized with a tracer gas. The bubble soap paint method applies a soap solution to possible areas of leaks in a pressurized system. The escaping gas converts soap solution to soap bubbles. A visual inspection of the bubbles can be used to identify the leak location.

Pressurised medium

Helium (He) was selected as the pressurising medium of the detecting system; thus, the system consisted of a helium (He) supply and a pressure gauge. Helium has been used successfully in leak detections over the years because of its physical properties: it is neither toxic nor flammable. It is an inert gas that does not react with other metals and compounds. Helium has very low viscosity and low relative molecular mass, so it passes easily through cracks and voids. Under the same environmental conditions, it flows through an orifice 2.7 times faster than air [70]. Helium can be considered as the most suitable medium for checking leaks in systems that contain hydrogen. The molecular size of a helium gas is much smaller than that of hydrogen gas. Thus, it can be concluded that a system that is leak-proof for helium is leak-proof for hydrogen. A comparison of the molecular sizes of a few gases are provided in Table 4.3.

Table 4.3: Molecular sizes of few gases [71].

Gas	Approx. molecular size, pm
He	28
H_2	50
O_2	120
N_2	130
CH_4	224

Leak detection

The designed leak detection system has the flexibility to run the leak detection test before and after the hydrogen measurement of a test sample. A post leak detection test verifies that no new leaks have occurred during the test and is able to validate the accuracy of the test results. During leak detection in this research, first, the measuring system was pressurized with helium gas for a predetermined pressure. If the pressure remained unchanged for a 15-minute interval, it was considered no leak was present in the measuring system. Conversely, a drop in helium pressure indicated one leak or multiple leaks. In addition, the rate of drop in the pressure indicated the magnitude of the leak.

The most common leaks noticed were minor (smaller) leaks that are always difficult to locate. Minor leaks are indicated by slower pressure drops shown by the pressure gauge. Such minor leaks were located effectively by checking the system section by section and isolating certain sections of the system by closing the manual flow control valves located between sections. Once the section was isolated, the joints in the section were checked for leaks using Snoop[®] which is a commercially available liquid soap-like leak detection spray. Once the checking for leaks was completed in

one section, the next section was tested. The nine flow control valves in the system were capable of sectionalizing the system. During the design stage, a thorough analysis was done to optimise the number of flow control valves. Although it would seem that providing as many flow control valves as possible would make it possible to divide the system into smaller sections thereby making the minor leak detection faster and easier, too many valves could create too many interconnecting joints in the system. Too many joints could make the system more vulnerable to leaks. On the other hand, providing fewer flow control valves makes it difficult to sectionalize the system into smaller sections.

Once the leak was found and location was repaired and the system was again pressurised with helium to make sure no leaks remained. Once it was confirmed there were no further leaks, the system was vacuumed and then checked for retention of the vacuum. This could be considered as a vacuum decay test or a pressure rise test. This was the final leak detection step prior to a test. However according to the initial observations, if helium leak detection does not shows leaks in the system, it is rare to find a leak using the vacuum.

4.7 Stage 2: Initial Test Assembly

The main components required for constructing the novel hydrogen measuring system were acquired during Stage 1. In Stage 2, an actual test was done using a few components that were just enough to capture hydrogen egress from a test sample. This test was important before proceeding to the final construction stage to confirm whether the design actually could capture gases egress from a test sample. First, the setup was tested without any test sample for any leaks. The same setup was tested

again with a hydrogen charged test sample to see whether it captured hydrogen from the sample. The test was done on a laboratory table as shown in Fig. 4.4 and explained below.

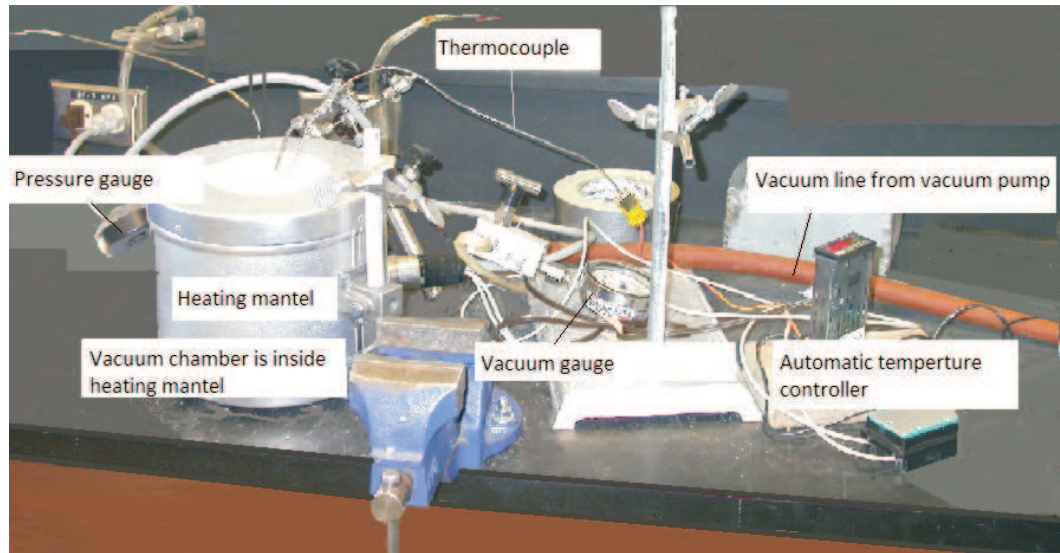


Figure 4.4: Preliminary test assembly.

First, a capillary tube was connected to a vacuum gauge (pressure gauge). Then the tube was divided into three branches using a union joint. One of the three branches was connected to the vacuum pump. The other branch was connected to a calibration volume. The third branch was connected to the lid of the vacuum chamber. A gasket was placed on the grooves of the lip of the container. The vacuum chamber lid was placed in alignment with the gasket. The container was then closed without any test sample in it. The eight bolts were carefully tightened. The assembled vacuum chamber was then placed inside the heating mantle (also called a mantle heater). Once the primary assembly was completed, the vacuum was introduced to the system. Then, the vacuum pump was isolated from the system and turned off.

The vacuum gauge indicates the vacuum pressure. The initial atmospheric pressure, vacuum chamber temperature, and vacuum gauge pressure were recorded. The three readings were recorded against time over a period of approximately two hours to detect any leak at the room temperature. Then, the temperature of the vacuum chamber was increased to 250° C and maintained for approximately an hour. Finally, the temperature was brought back to room temperature and left for one hour. Atmospheric pressure, vacuum chamber temperature, and vacuum gauge pressure were observed during the time. The observation showed there were no leaks in the vacuum chamber pressure at room temperature or at 250° C.

Then, the test procedure explained above was repeated with a hydrogen charged test sample placed inside the vacuum chamber. A drop in vacuum pressure reading was observed during the test that is completed at 250° C with the test sample. It is concluded the pressure drop was caused by gases egressing from the test sample at 250° C.

The two test procedures above confirmed that the novel hydrogen measuring design served the purpose. Therefore, it was decided to assemble all components to complete the equipment.

4.8 Stage 3: Assembly of All Components

The initial test assembly completed in the Stage 2 proved that the concept of the novel hydrogen measuring system was successful. Therefore, the next step was to assemble all the components together, including the leak detection system.

During the design stage, a layout drawing of the component assembly was pre-

pared. The layout drawing is shown in Fig. 4.1. During preparation of the layout drawing, the main focus was on answering the following questions:

- Where and how does the hydrogen that egresses from a test sample flow?
- Where and how should the system be evacuated (i.e. vacuumed)?
- How should the leak detection system be integrated?
- How should vacuum and helium pressures be measured?
- Where should the vacuum pump be located?
- Where should the vacuum chamber be located?
- Where should the calibration volumes be located?
- How should the entire system be isolated (i.e. sectionalized) into smaller sections?
- Where should the flow control valves be located?
- How should the number of flow control valves be minimized?
- How should the number of joints (tee joints, union joints, and elbow joints) be minimized?
- How should the total length of the capillary tubes used in the system be minimized?

To answer the questions above, several ways of assembling the components are taken into consideration.

4.8.1 Capillary Lengths

Capillary tubes are the veins of the system: they connect the main components together. However, capillaries that are too long make systems bulky. Moreover, every unit length of a capillary tube increases the total system volume. When measuring very small volumes, the system total volume becomes inversely proportional to the measurement sensitivity of the pressure reading. Conversely, the distance between two components depends on the length of the capillary tube between them. Therefore, very short capillary lengths limit the working space around them. A workable space between components is preferred to properly tighten the screw Swagelok[®] connectors belonging to the components. It is vital to adequately tighten all the connectors to have a leak-free system. Furthermore, in the final stage, the whole system is required to be mounted on to a panel. Appropriate capillary tube lengths need to provide enough flexibility when mounting or troubleshooting the system. Hence, capillaries that are too small could loosen the joints, resulting in bending moment forces, leading to leaks.

4.8.2 Check for Leaks

After all the components were assembled, a high performance vacuum sealant was applied to each joint. After the sealant was cured, the system was checked for leaks. Leak detection was done without a test sample inside the vacuum chamber because egress of gases from the test sample could be mistaken for a leak. A completely leak-free component assembly was confirmed before assembling the system onto a panel. This is discussed below.

4.9 Stage 4: User Interface Panel Design and TVHS Construction

4.9.1 Objective

During Stage 3, all the components of the system were connected together and laid on a flat surface. The system looked like a complex mesh at that point. Thus in this stage the system needed to be converted to a user friendly unit by mounting it on a panel box.

4.9.2 Panel Box Frame

Once an approximate form of the system was sketched, the panel box frame was designed and constructed to mount the panels which were later used to mount the components. The panel box frame was designed to be 60 x 40 x 30 cm (height x width x depth) in size. It was constructed with one inch (2.54 cm) steel L angle bars. First, steel L angle bars were cut to the required panel dimensions (60 x 40 x 30). Then, the cut pieces were welded to form a rectangular frame. The frame was spray painted to protect it from corrosion. Holes were drilled on the frame to screw bolt the front control panel, two side panels (left side and right side), and the three side covers (top, back, and bottom).

4.9.3 Side Panels

The two side panels and the three side covers were cut to the required dimensions. Then, they were bolted to the panel box frame. The two side panels and all the side covers including the back panel were cut out of 1/32 inch (0.8 mm), plain grade 304 stainless steel sheets. The back panel was perforated to provide enough venti-

lation to remove any heat generated from the temperature controller, temperature indicator, and the power supplies mounted inside the panel box. Heat buildup inside the panel could elevate temperature inside the capillary tubes and controlled volumes. An increase in temperature of these components affected the accuracy of the measurements. This is further discussed in Chapter 5.

4.9.4 Front User Interface Panel

A complete internal flow diagram of the system was drawn on the front user interface panel. All manual control valve knobs were positioned on this diagram at appropriate locations to help the user locate the control valves easily. Only the valve knobs were visible on the user interface panel where each valve was secured behind the panel, inside the panel box. The system was made more user-friendly by showing the name tags of each component beside them. The flow diagram and the name tags were engraved into the front user interface to improve the appearance of the equipment. This was a tedious task that required attention to capture details. It was done in several steps.

First a 1/32 inch (0.8 mm), plain grade 304 stainless steel sheet was cut to fit the front side of the panel box. The valves, pressure and temperature indicators, and temperature controller to be mounted on the operator interface panel were marked on it. Then, the stainless sheet was removed from the panel box and the cutouts for the valve knobs, pressure and temperature indicators, and temperature controller were made. A 1:1 scale drawing was prepared showing all the information required on the operator interface panel. The drawing along with the steel panel was handed over to the University of Calgary Engraving Centre. Engraving was done on a special plastic sheet. The stainless steel front panel with all the cutouts was used as a pattern to

transfer locations of the cutouts to the plastic sheet. The information on the drawing was transferred to the engraving machine to initiate automatic engraving. Once the engraving was completed, both panels (the engraved plastic panel with cutouts on top of the stainless steel panel with cutouts) were bolted to the front of the steel panel box frame. The bottom and side panels were mounted at the same time.

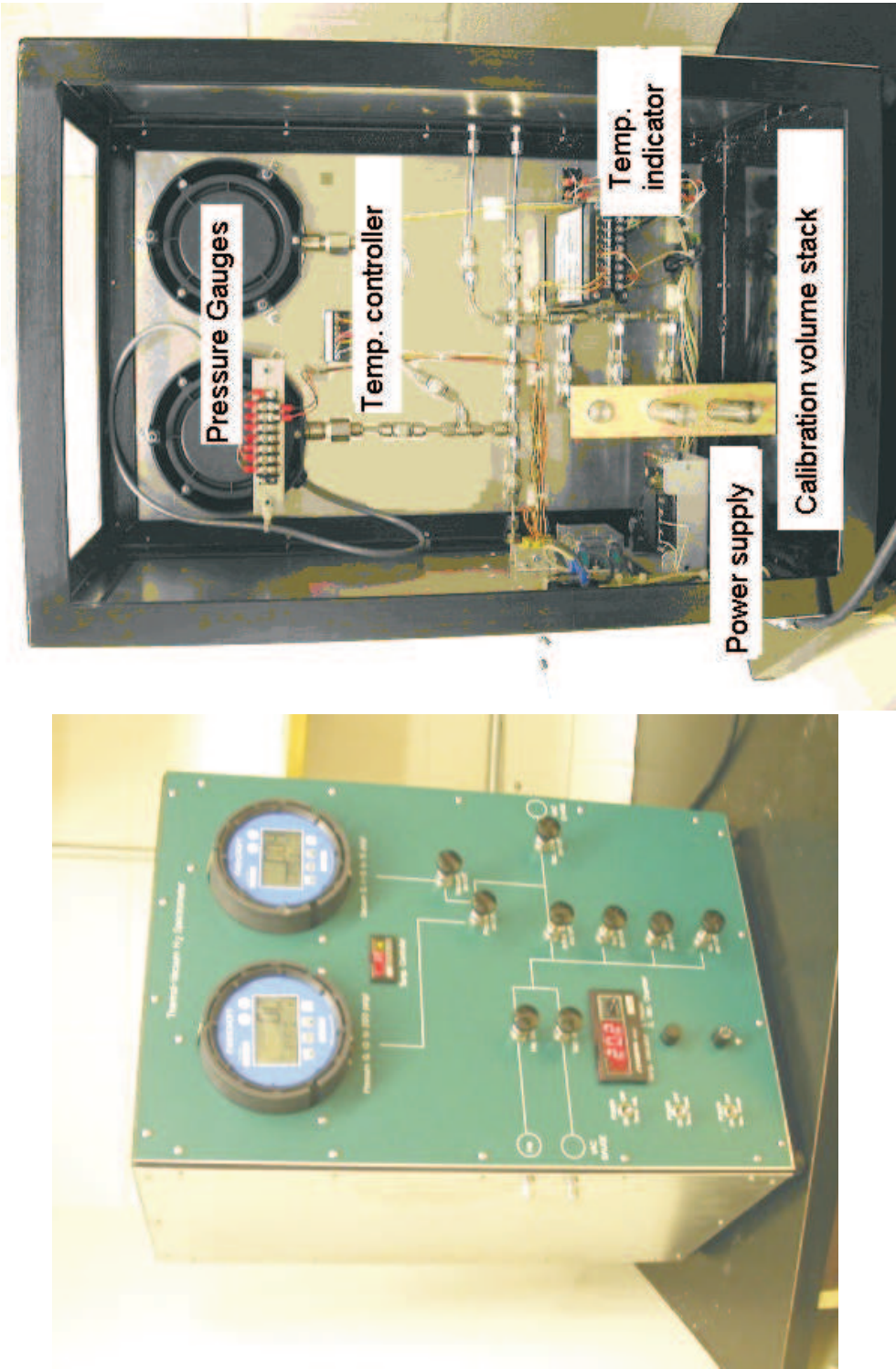
4.9.5 Final Assembly

The previously assembled internal system described in Stage 3 was installed inside the rectangular panel box. As planned, all the volume control valves, two pressure gauges, temperature controller, and the temperature indicator were mounted on the front operator interface panel at locations where the cutouts were made. This assembly allowed the user to control and access information from the front. The vacuum chamber port and three thermocouple ports were mounted on the right side panel board. The shared inlet port for the vacuum pump and helium bottle were mounted on the left side panel. The three controlled volumes were secured on a wooden block and mounted on the bottom side cover. The most important task was to properly tighten all the gas carrying connector joints to be leak proof.

The final view of the constructed front user interface panel, the two side panels, and the inside view of the TVHS are given in Fig. 4.5 and Fig. 4.6 respectively. A schematic diagram of the TVHS is shown in Fig. 4.1.

4.9.6 Wiring

Once all the components were mounted on the panels, wiring was done. Electrical wiring for the temperature controller, temperature indicator, thermocouples, heating



A B

Figure 4.5: (A) Front and (B) inside view of the TVHS.

mantel, and pressure gauges were completed. Two fuses were located on the bottom left corner of the operator panel for easy access to replace them when required.

After completing the wiring, the top and the back side covers were mounted. The construction of the novel Thermal Vacuum Hydrogen System (TVHS) concludes here.

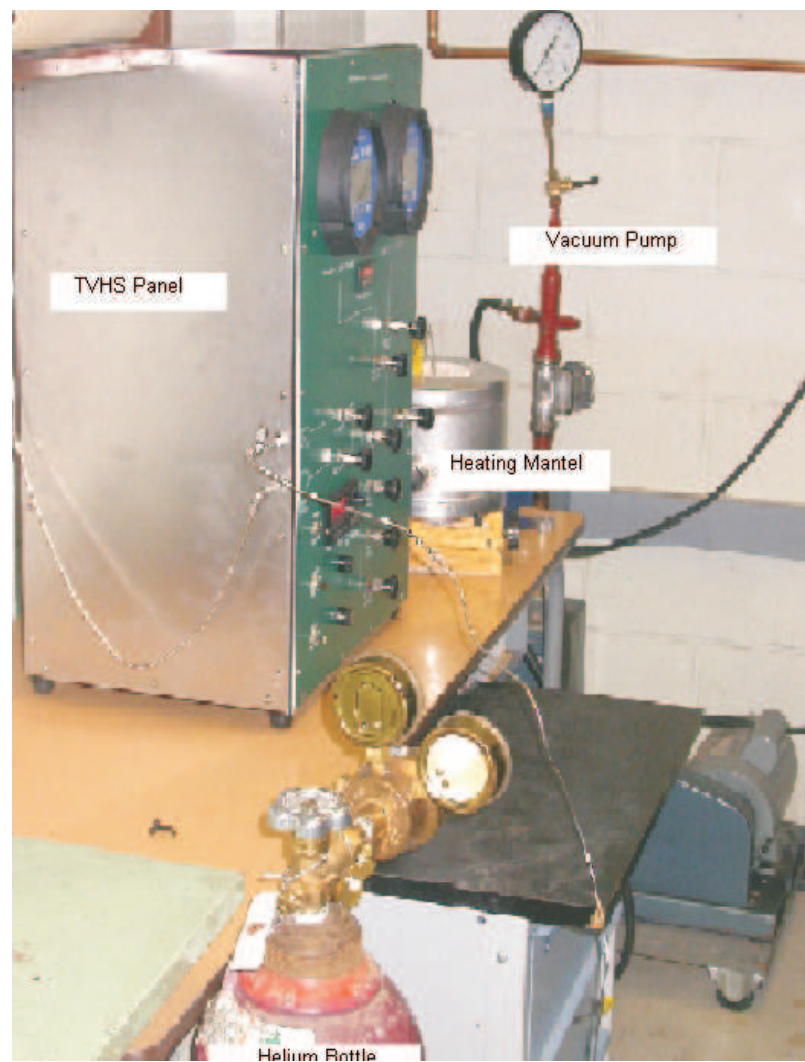


Figure 4.6: Side view of the TVHS.

Chapter 5

Problems Encountered and their Solutions

5.1 Introduction

A new hydrogen measuring system called the Temperature Vacuum Hydrogen system (TVHS) was designed and constructed. Despite the careful attention and time spent focusing on the details during the design and construction stages, several problems occurred during the initial test trial stage. Problems such as leaking in the vacuum chamber were expected during the trial tests. However, problems such as drift of the vacuum pressure gauge readings as a result of atmospheric pressure and temperature fluctuations were unexpected.

This chapter describes the following issues that were identified during the initial hydrogen measurements and the solutions applied to mitigate them.

- Leaking
- Difficulties in temperature stabilization
- Problems related to gaskets
- Problems related to using different thickness samples
- Problems caused by variation of temperature in some parts of the system
- Drift in pressure gauge reading

5.2 Leaking

5.2.1 Issue

The TVHS was used the vacuum decay method to quantify the hydrogen amounts at elevated temperatures and pressures below the atmospheric pressure (vacuum). In this type of system, even a minute void or a gap can cause problems because of the following reasons.

- A minute void or a gap could be expanded at elevated temperatures, and act like a bigger void.
- Internal low pressure from the vacuum tends to draw air from the atmosphere into the system through any minute void as gas under pressure always moves from a higher to a lower level.

Therefore, any void or gap that could lead to a leak must be avoided at all times.

5.2.2 Prevention of Leaks

The best way to eliminate leaks was by eliminating joints. A joint in the TVHS system is where two components are connected together. The TVHS is an integrated system; therefore, it was impossible to eliminate all the joints. Accordingly the following steps were taken to minimize the number of joints in the system:

- a Minimize the number of joints
- b Make the joints permanent
- c Minimize the exposure of the joints to mechanical and thermal stresses

a. Minimizing the number of joints:

The TVHS consists of several components. During construction, a layout drawing was prepared to assist in assembling these components. The layout drawing was used to visualize the overall layout of the system; thus, it helped in minimizing the number of joints by combining the joints with each other. Thus, some single joints were replaced by using commercially available connector types (tee, union and elbow) that could connect two or more components together. For example, a union type connector was used to connect four components that previously required multiple single joints.

Minimizing the number of joints was also achieved by minimizing the joints within each component. The components such as the calibration volumes were machined as a single component (i.e. “machine as one piece”) from a block of metal. This “machine as one piece” method eliminated threaded or welded joints within the component.

b. Making the joints permanent

As a second method of avoiding leaks, the joints that could not be avoided were made permanent. Accordingly, all the remaining joints inside the TVHS panel were made to be permanent joints. Permanent joints do not require repeated assembly and disassembly of the connectors, which wear the threads of the connectors. Worn threads become loose joints, leading to leaks, hence requiring frequent replacement. Frequent replacement of connectors transfer stresses to adjacent joints and make them susceptible to leaking again. By making the joints permanent, these problems were avoided.

c. Minimizing the exposure of the joints to mechanical and thermal stresses

Mechanical stresses

Sometimes, mechanical stresses were induced on the joints during handling the equipment. One such occasion was during disassembly of the vacuum chamber. The movements during this event induced stresses on some of the joints in the TVHS. One way of minimizing these stresses was careful (soft) handling of the components.

Thermal stresses

Thermal expansions and contractions in joints made them susceptible to leaks. It was noticed that the joints inside the TVHS panel did not undergo major temperature fluctuations that could cause thermal stresses on joints. According to the temperature measurements obtained during the tests, the temperature inside the panel (where most of the joints were located) remained at a maximum of 0.5°C higher than the room temperature. The room temperature was controlled at $20 \pm 1^{\circ}\text{C}$ during the tests. Therefore, thermal stresses on joints inside the TVHS were considered negligible, and additional steps for minimizing the exposure to thermal stresses were not required. However, as explained the section below, there was one location outside the TVHS susceptible to leaks resulting from thermal stresses that required preventative actions.

5.2.3 Preventing Vacuum Chamber Leaks

Two joints in the vacuum chamber were identified as the most suspectable locations for developing leaks. A brief explanation of why these locations were susceptible to leaks and how this problem was overcome are provided below.

Joint in the vacuum chamber:

One of the locations identified as susceptible to leaks was one joint on the vacuum chamber, which is marked as **A** in Fig. 5.1. This was a permanent joint on the lid consisting of part of a Swagelok® fitting screwed into a tapped screw-hole on the lid. Despite the fact that it is a permanent joint, it leaked many times during the trial experiments. This joint was subjected to mechanical stresses when the vacuum chamber lid was opened and closed during each test. In addition, at the end of each test, the gasket that bit into the lid was removed by tapping on the lid. Thus, the joint went through mechanical stresses

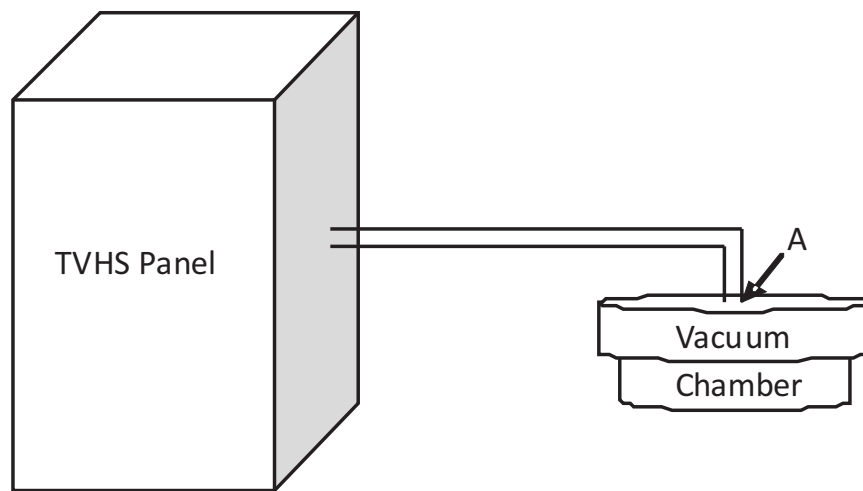


Figure 5.1: A joint in the vacuum vacuum chamber lid marked in **A**.

Elimination of thermal stresses was not practicable. Therefore steps were then taken to reduce the mechanical stresses by improving the gasket removal procedure, which would otherwise need to be removed by tapping on the lid. The improved gasket removal procedure, explained in Section 5.4.1, helped to reduce the induced stresses and, as a result, the leaks at this location.

Lid and container assembly:

The vacuum chamber became susceptible to leaks if its lid was not properly installed onto the container. This location was considered as a non-permanent joint because, during each test, the location had to go through assembly and disassembly of the lid. The following improvements were made to minimize leaks at this location.

a. Effective bolt tightening procedure

There were a total of eight bolts in the vacuum chamber assembly to assemble the lid and the container together. Proper tightening of these eight bolts was essential in retaining the vacuum inside the system. Thus an effective bolt tightening procedure was developed and it is given in 6.1.

b. Improvements to the gasket material

As explained in Section 4.6.2, gaskets made out of annealed material provided a better seal than that were not annealed.

c. Design improvements of the vacuum chamber

As explained in Section 4.6.2, two vee apexes were machined on the grooves of the vacuum chamber. During the tightening of the bolts, the vee apexes bit into the copper gasket, providing a deformed local friction seal.

5.2.4 Vacuum Leak Sealant

A vacuum leak sealant was applied on all joints in the TVHS as an additional precautionary step. There are several industrial type vacuum leak sealants available on the market. Kurt J Lesker company's KL-5 vacuum leak sealant was selected because of its special characteristics, which were suitable for the joints in the TVHS. According

to the manufacturer, KL-5 is a silicone resin that can be used for sealing leaks in high and ultra high vacuum systems. Residual gas analysis by the manufacturer has indicated no evidence of hydrocarbons or other contamination arising from KL-5 used on vacuum systems.

According to the manufacture's specifications, KL-5 can be successfully used from -200°C to 450°C and can withstand repeated temperature cycles. This temperature range was adequate for this research study.

Most of the industrial type vacuum sealants that were considered initially had a complex application procedure. Before applying, multiple portions had to be mixed according to the manufacture's recommended ratios. Also, they were successful only if they were cured at elevated temperatures before using. Curing at the elevated temperature was not feasible for the joints inside the TVHS panel. Unlike those sealants, KL-5 cured at room temperature within 24 hours. Also, KL-5 came in a bottle as a transparent liquid that could be applied on the joints with a small paint brush.

Cured sealant was easily removed with any acetate, ketone, or ester solvent.

5.2.5 Issues with Leak Detection

As described in Section 4.6.11, the leak detection included checking for pressure decay with pressurized helium followed by checking decay in the vacuum. Unlike the vacuum, one of the issues with using a gas such as helium in the leak detection is the sensitivity of the gases to room temperature fluctuations. Thus, when monitoring for leaks, it was required to differentiate whether the pressure drop was due to a minor (small) leak or due to a small drop in the room temperature. During the

tests, this was done by monitoring both pressure and room temperature for about fifteen minutes. Then, the pressure and temperature readings were plotted with the time. The graphs helped to differentiate a leak from a pressure change as opposed to one caused by a change in the temperature.

The second issue with using a pressurized gas for leak detection was, unlike a vacuum, positive pressure could expand minute gaps and voids unnecessarily or even create new gaps and voids in weaker areas. In addition, the pressure on the joints loosened them by inducing stresses. This can be explained further by taking the vacuum chamber as an example. The vacuum chamber is similar to a container with a lid without threads. If the container is filled with pressurized gas, the lid tends to loosen from the internal positive pressure. However, if a vacuum is introduced to the system, the lid tends to compress from the differential pressure between atmospheric on the lid and vacuum within the chamber.

When the two issues above were considered, leak detection using a vacuum (i.e. vacuum decay method) showed more benefits in detecting leaks, especially in a system designed for containing a vacuum. Regardless of the benefits of using vacuum, helium was used in leak detection and the following explains why. The TVHS was designed to collect and measure hydrogen. Therefore, it needed to contain hydrogen. For such a system, leak detection using helium is better than using a vacuum, because the size of a helium gas atom is smaller than the size of a hydrogen gas atom. Therefore, the smallest void that helium would leak from, causing a pressure drop will not allow oxygen or nitrogen entry, nor any movement of hydrogen. If the vacuum decay method is used as the only method of leak detection, during a leak event, atmospheric air would be drawn to the system from the void, causing the

leak. The size of the smallest void that air could leak from can be considered as the size of the diatomic oxygen gas atom because this is slightly smaller than that of the nitrogen gas. Therefore, a void detected by the vacuum decay method would be much larger than that of the hydrogen atom. Thus, hydrogen would be able to leak from such a void.

Another issue with both the pressure decay method and the vacuum decay method is both leak detection methods identify only whether there is a leak. If there is a leak, some other techniques such as the soap bubble method or a sniffer is needed to use to locate the leak. This makes the leak detection process time consuming.

5.2.6 Identifying a Leak from Test Data

The embedded helium leak detection system of the TVHS was helpful in detecting leaks before starting a test as well as once a test was completed. If a leak was identified before a test, it could be repaired before starting the test, so the leak could not affect the measurements. If a leak was identified after a test, the test results were not usable. Thus, the test results had to be discarded, which was a waste of time and resources. The following paragraph explains a method that could be used to identify a leak from the test data during an experiment. However, this method should be used with caution as explained there.

As explained in Chapter 6, during a test, the vacuum pressure during that tests duration needed to be recorded. Fig. 5.2 shows a graph that was plotted using the recorded test data. The y-axis of the graph indicates the vacuum pressure in the system during the test. The x-axis indicates the test duration. Thus, the graph

shows how vacuum pressure has been continuously dropped during this test.

The vacuum pressure in the system can be changed as a result of the combination of the following factors:

- a collection of egressing hydrogen from the test sample
- a leak
- a change in the temperature of the system
- a change in the system's volume

At the beginning of a test, the temperature of a test sample was at room temperature. During a test, the test sample temperature was elevated and maintained for a certain time period until the hydrogen egressed out from the sample. At the end of the time period, the temperature of the test sample was brought back to room temperature. Thus, at the end of the test, the temperature of the sample was at the original or starting temperature. Therefore, the effects from the changes in the temperature would not become a contributing factor in the continuous change in the vacuum pressure.

During a test, the changes to the volume of the system could happen from changes in the temperature. For example, during a test, the vacuum chamber tends to expand because of an elevated test temperature, resulting in thermal expansion of the metal comprising the chamber. However, at the end of a test, when the chamber is brought back to room temperature, the volume of the chamber goes back to the original state because of contraction. This is applicable to the whole TVHS system. Therefore, the effects from the changes in the volume would not become a contributing factor to the continuous change in the vacuum pressure.

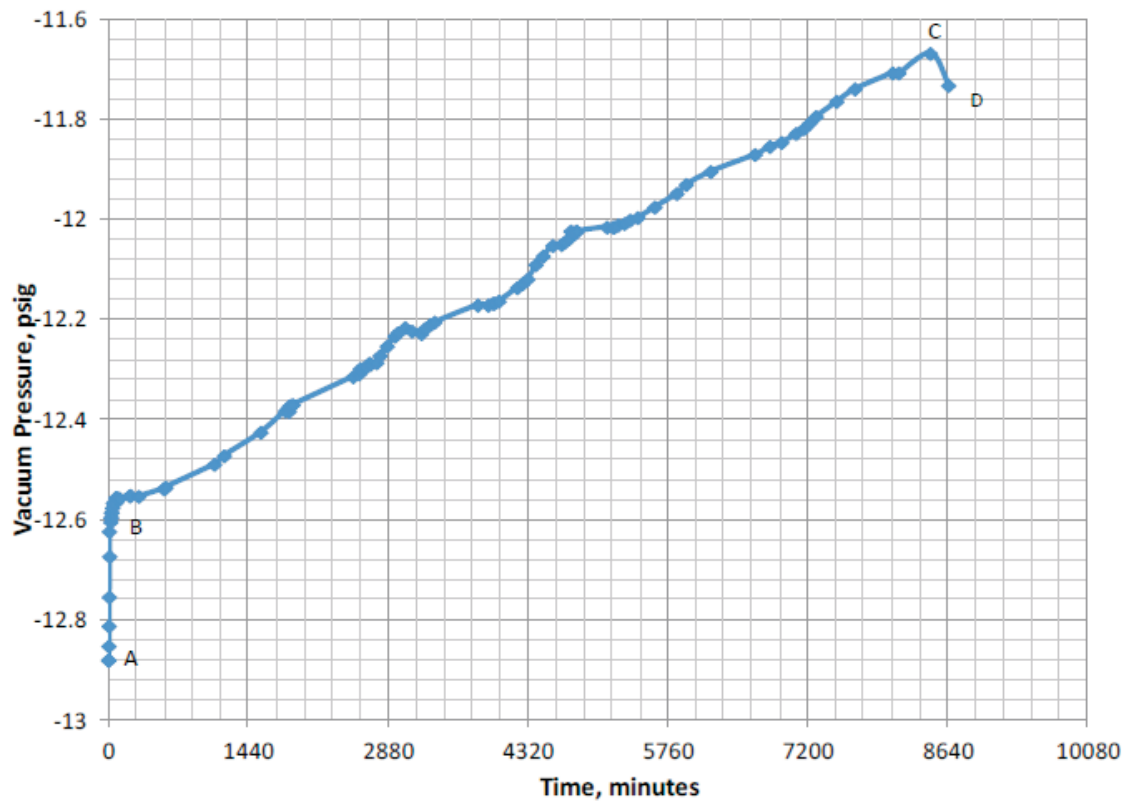


Figure 5.2: A typical vacuum decay graph that indicates a leak in the TVHS system.

This finding leads to the conclusion that the vacuum pressure in the system is changed either from the collection of hydrogen in the system or from a leak. A leak allows atmospheric air to enter into the system. A successful test also allows hydrogen to collect inside the system. This means that, during both events, the change in the vacuum pressure is caused by the collection of a gas (i.e. air or hydrogen) inside the system over the time. Therefore, both events cause a vacuum drop in the system and could show similar test results. According to the initial observations, it is difficult to distinguish the difference between the two events from looking only at the vacuum pressure drop readings, unless the readings are plotted as a vacuum decay graph.

The vacuum decay graph in Fig. 5.2 shows that the vacuum pressure continuously decays over an extended period of time. The rate of the vacuum decay during the test, which is indicated by the slope between B to C in the figure, has not changed for more than 5 days. Even if the line between B to C is extrapolated, the slope does not show any indication of flattening (leveling) off. In general, this is an indication of a leak. Even though hydrogen also egressed from the sample during this test, because of the higher leak rate, it means that the leak was governing the vacuum decay. If there was no leak during the test, the slope of the line between B to C would start flattening or at least should show signs of flattening when the test was run for an extended period of time. This is because in general the amounts of hydrogen that egress from a sample should come to an end. Thus plotting the vacuum decay graph during a test would help in identifying a leak in the system before the end of a test.

However one should be cautious when the method above is used for a test sample with very high amounts of hydrogen. For such samples, the egression of hydrogen for an extended period could be real as a result of the longer durations that may required to egress out higher volumes of hydrogen. It is previously known, however, that the test sample used for the example above had an amount of hydrogen between 1 to 2 ppm. As a result, flattening of the slope of the graph could be expected within a period of five days. In this example, the initial information on the approximate amount of hydrogen helped in confirming there was a leak in the system. Therefore, this method can be used as a useful tool to identifying leaks especially during the tests that are repeated.

5.2.7 Other Indications of Leaks

Fig. 5.3(A) shows a deoxidized copper gasket before it was used (i.e. before assembled it in the vacuum chamber). Fig. 5.3(B) shows the same gasket after being used in the vacuum chamber. The used gasket given shows a discoloration around the gasket, specifically, on the outer-side of the marks that are created by the vee apex bite. However the inner side of the vee apex bite mark showed no discoloration, and this area was similar to the gasket surface before use. This observation could be considered as an indication that no leak had occurred in the vacuum chamber during that test. The reason can be explained as below.

The discoloration of the outer circle of the gasket is caused by oxidation of the copper at the elevated test temperature. That means atmospheric air has entered into the two gaps between the gasket/ lid and the gasket/container, but the seal between the vee apex and the gasket has stopped further traveling of oxygen in the air into the direction of the chamber. Therefore, the inner side of the vee apex bit mark has not shown any discoloration because of not being exposed to any oxygen. The inner side is open only to the vacuum atmosphere. During the tests, this observation was used as an alternate method in confirm that no leaks occurred to the vacuum chamber.

5.3 Difficulties in Temperature Stabilisation

5.3.1 Issues

In the initial stages, when the TVHS was under development, a variac was used to control the heat input to the heating mantel. At that time, the variac was directly connected to the heating mantel. The power to the heating mantel was manually



Figure 5.3: A deoxidized copper gasket (A) before use (B) after use.

adjusted by setting the dial in the variac to a corresponding resistance value. The manually controlled variac method had the following drawbacks:

- To set a temperature, the corresponding resistance value for that temperature had to be known the before a test.
- The temperature was only able to be controlled with a tolerance of $\pm 1^\circ \text{C}$ with considerable effort.
- The method took a longer time to stabilise as higher temperatures were required, this being especially true when the temperature was required to reach more than 150°C .

Due to these practical difficulties in using the manually controlled variac method, the temperature control method of the TVHS was upgraded to an automated temperature controller. During the tests, once the required temperature was manually set (registered), the controller started to bring the temperature of the sample to the

required value. However, it was found during the initial trial tests that the temperature of the sample always reached a higher temperature (overshoot) than the registered required value. After the overshoot, the temperature slowly dropped to the required value and stabilised at that value. For example, if 150°C was selected, the test sample temperature first reached about 153°C and then with time it stabilised at 150°C .

5.3.2 Solutions

Besides reaching a higher temperature than required, the overshooting of the temperature also increased the time to stabilise the temperature at the set value. Various tuning methods were tried on the controller to make the overshoot smaller. Among them, the only method that helped in successfully eliminating the overshoot was increasing the temperature in two steps. For example, if the required test temperature (set temperature) was 150°C , 147°C was registered as the initial set temperature. That made the temperature overshoot to 150°C or a couple of decimal points lower than 150°C , i.e. 147°C . At that point, the set temperature was increased to 150°C making the temperature stabilize at 150°C without any overshoot of this temperature occurring.

This method helped to stabilize the test temperature more efficiently. Thus, this method was used during the tests.

5.4 Problems Related to Gaskets

Practical issues arose during usage of the gaskets; the solutions are given below.

5.4.1 Gasket Removal

The copper gaskets needed to be used multiple times. Using the gasket only once was not economical. Therefore, at the end of a test, the gasket was removed carefully to avoid damaging it.

It was found that the copper gaskets tended to adhere to the lid of the 316 stainless steel vacuum chamber, especially during the tests that were performed at higher temperatures. The biting of the gasket into the vee apex in the lid of the vacuum chamber made it difficult to remove the gasket at the end of a test for reuse. Different methods were tried to take off the gasket. Initially, it was attempted to lift the adhered gasket using a flat side of a small screwdriver, but that damaged the edges of the gasket. Then, the adhered gasket was loosened by tapping on the outer surface of the lid. Once the gasket was loosened, a little push was given to its sides using a screwdriver. This method allowed the adhered gasket to be taken off without damage. However, with time, it was found that tapping loosened the permanent connections between the vacuum chamber lid and the rest of the system between the chamber and the TVHS where leaking started to occur. Therefore, the tapping method was not able to be used.

After trying different methods, it was decided to take advantage of the higher coefficient of thermal expansion of the gasket material. Deoxidised copper, which is the gasket's material, has a higher coefficient of thermal expansion compared to grade 316 stainless steel, which is the lid's material. Table 5.1 gives the linear thermal expansions coefficients of the three metals. The higher thermal expansion coefficient of deoxidized copper made the gasket loosen from the lid when it was heated. Then, a little push with a screwdriver took it off. This method helped to remove the gaskets

without damaging them so they could be reused. To heat the gasket, a hand-held specimen blow drier, which was available in the laboratory, was used. The shape and the function of this drier is similar to a hair drier.

Table 5.1: Linear thermal expansions coefficients of the three metals [78].

Material Type	Coefficient of thermal expansion 10^{-6} m/m K ($10^{-6} \text{ in/in}^{\circ}\text{F}$)
Deoxidized Copper	17.7 (9.9)
Grade 316 stainless steel	16.0 (8.9)
Grade 304 stainless steel	17.3 (9.6)

5.4.2 Maximum Temperature

Tests were carried out to find the maximum temperature that deoxidized copper gasket could withstand without losing its sealing ability. If the ability to sealing was lost, the atmospheric air could be drawn in to the vacuum chamber. At elevated temperatures, copper could soften and therefore the sealing ability could be lost.

The tests that were carried out were similar to a vacuum decay leak test. The vacuum chamber was assembled with a deoxidized copper gasket as described in Chapter 4. However, no test samples were required in the vacuum chamber for these tests. Vacuum was applied to the whole system. Once the vacuum was stabilized, the system was checked for leaks using helium and the vacuum. Once it was confirmed there were no leaks, the vacuum chamber was heated to 250°C . Then, the temperature was held at that value for 5000 minutes, roughly 3.5 days. This time was selected to give the copper gasket enough time to stabilize at that temperature. Also, that was the maximum time duration for which most of the hydrogen mea-

surement tests were planned to run. During that time, the vacuum pressure was recorded and the vacuum was checked for decay. Because there was no test sample inside the vacuum chamber, a decay in the vacuum should represent a leak. Once it was confirmed there was no vacuum decay at 250° C, the temperature was increased to 300° C and the steps were repeated. Then the tests were continued at 350° C, 400° C, and 450° C.

No vacuum decay was found at any of those temperatures except at 450° C. After the vacuum decay was noticed, the system was checked to find the location of the leak. For that, the system was pressurized with helium. It was found the helium was leaking from the gap between the vacuum chamber container and the gasket.

After this step, two tests were repeated at 400° C and 450° C. Again, decay in the vacuum was observed at 450° C. That finding concluded the deoxidized copper gasket could be used only up to 400° C. This finding made the test temperature of progressively mobile hydrogen measurements using the deoxidized copper gasket limited to 400° C.

Because the hydrogen measuring test temperature was limited to 400° C, it was decided to find a secondary gasket material that could withstand higher temperatures. As a result, it was decided to fabricate a few gaskets using grade 304 L stainless steel.

5.4.3 Stainless Steel Gaskets

As mentioned, a number of gaskets were fabricated out of grade 304L stainless steel. "L" stands for the low carbon grade. The mechanical properties of Grade 304 stainless steel are quite similar to grade 316 stainless steel except grade 304 has slightly lower

hardness [72]. Also, it is widely available in different forms and is more economical than grade 316.

During fabrication, a different approach was used for the stainless steel gasket. Unlike the copper gaskets, stainless steel gaskets were cut from a quarter inch stainless steel sheet. Stainless steel sheets were more economical than solid stainless steel blocks. A abrasive water jet cutting machine was used for cutting. As mentioned before, the copper gaskets were turned from a solid round bar. The cutting process produced gaskets much faster than the lathe process.

Once the gaskets were fabricated, they had to be heat treated to make them softer; otherwise, the gaskets would not bite into the vee apex of the vacuum chamber, and the sealing would not be successful. In addition, the gaskets could also damage the vee apex. Annealing was selected as the heat treating process to soften the gaskets. During annealing, the gaskets were placed inside the furnace, heated to 875°C , and held at that temperature for four hours. Finally, the furnace was switched off to provide a slow cooling. The temperature and time for the annealing process were selected from previous experience.

The hardness values of the gaskets before and after the annealing process were measured to determine how much the annealing process helped in softening them. At the same time, the hardness of the lip area of the sample container of the vacuum chamber was also measured to compare with the gasket's hardness value. Ideally the gasket material needed to be softer than the hardness of the lip area of the sample container.

The Rockwell B scale of the Rockwell macro-hardness tester was used to measure

the hardness. The hardness values were taken in six places and the average was calculated. Accordingly, the measured hardness of the lip area of the container was HR B 93 (i.e. Rockwell B scale). The pre and post annealed stainless steel gaskets had a hardness of HR B 87 and HR B 81, respectively.

Double-annealing method

The annealing process made the gasket softer, but it was questionable whether it was soft enough. Therefore it was decided to double-anneal the gaskets to make them even softer to give them better sealing ability. During the re-annealing process, the gaskets were heated to 900° C and held at that temperature for two hours. Then, they were allowed to cool down slowly by switching off the furnace. The re-annealed gaskets had a hardness of HR B 76. It was decided this level of softness was adequate. According to previous observations, to provide a better sealing, the gasket material hardness should be at least 10 to 15 units lower than the component.

5.5 Problems due to Test Samples with Various Thicknesses

5.5.1 Issue

As explained in Chapter 10, 4 mm (thinner sample) and 12 mm (thicker sample) thick test samples were used in this research work. The difference in the sample thickness made the inner free volume of the vacuum chamber different during a test. This difference became an issue when vacuum decay graphs needed to be compared. This is explained in detail below.

How does inner free volume change?

The inner free volume of the vacuum chamber can be represented from the following:

$$\text{Inner free volume of the vacuum chamber} = \text{Volume of the empty vacuum chamber} - \text{Volume of the test sample}$$

Thus, the inner free volume of the vacuum chamber changed with the volume of the test sample. If the test sample volume was larger, the inner free volume of the vacuum chamber was lesser and vice versa. The volume of the tests sample was a function of the diameter and thickness. All the test samples that were used in the tests had the same diameter. Thus, the inner free volume of the vacuum chamber changed with the thickness of a test sample.

How does test pressure relate to sample thickness?

The change in the sample thickness resulted in a different test pressure even with the same amount of hydrogen. This phenomenon is explained below.

Fig. 5.4 shows a simplified version of the hydrogen measuring system with a thicker (on the left) and a thinner previously hydrogen-charged test sample before starting a test. At this stage, it can be assumed that hydrogen has not started to egress out from the sample.



Figure 5.4: A simplified version of the hydrogen measuring system with a thicker and a thinner previously hydrogen-charged test sample before starting a test.

V_1 : volume of the thicker sample

V_2 : volume of the thinner sample

V_{total} : total volume of the system without any sample

For this initial stage, according to the universal gas law,

For the thicker sample:

$$P_o \propto 1 / (V_{total} - V_1)$$

for the thinner sample:

$$P_o \propto 1 / (V_{total} - V_2)$$

Fig. 5.5 indicates a snapshot of the system parameters during a test. During the test, hydrogen egressed out from the test sample and started accumulating in the system. This changed the internal pressure of the system.



Figure 5.5: A snapshot of the TVHS system parameters during a test.

For simplicity, it can be assumed during the time duration, a similar amount of hydrogen (V_{H1}) is collected in the system for both cases. As the total volume of the system (V_{total}) is a constant, the initial pressure P_o of the system changes with the accumulation of hydrogen. Thus,

P_1 : the internal pressure of the system with the thicker sample with accumulation of V_{H1} amount of hydrogen

P_2 : the internal pressure of the system with the thinner sample with an accumulation of V_{H1} amount of hydrogen

As explained before, when the free volume of the system is considered:

$$V_{total} - V_2 > V_{total} - V_1$$

Therefore, even after accumulating a similar amount of hydrogen,

$$V_{total} - V_2 + V_{H1} > V_{total} - V_1 + V_{H1}$$

With the accumulation of hydrogen, the pressure of the system increases, but only as long as the same amount of hydrogen is always accumulated:

$$P_1 > P_2 \text{ as}$$

$$P_1 \propto 1/(V_{total} - V_1) + V_{H1}$$

$$P_2 \propto 1/(V_{total} - V_2) + V_{H1}$$

Accordingly, even though the same amount of hydrogen is accumulated during a test, differences in the initial volume result in a difference in the final pressures. This is not an issue when calculating the final amounts of hydrogen in comparing the values. However, this difference becomes an issue when the vacuum decay graphs need to be compared with each other.

5.5.2 Solution

The solution for this issue was to make the inner free volume of the vacuum chamber constant for all the tests regardless of the thicknesses of the samples. This was achieved by introducing dummy samples with the test samples.

Phenomenon

As mentioned, 12 mm and 4 mm thick samples were used during the tests. If two tests (referred as case) are considered, the inner free volumes during each test can

be considered as follows:

$$V_{case1} = V_{total} - V_{12mmsample}$$

$$V_{case2} = V_{total} - V_{4mmsample}$$

where V_{total} is the total volume of the system without any sample.

Also,

$$V_{12mmsample} > V_{4mmsample}$$

Thus,

$$V_{case2} > V_{case1}$$

To make the inner volumes of the chamber constant in the two cases, a dummy sample was placed in the vacuum chamber along with the test sample. That meant when a 4 mm thick test sample was used in the test, a 8 mm thick dummy sample was placed inside the chamber along with the test sample. The choice of 8 mm thick dummy samples made the total thickness of the test sample and the dummy sample 12 mm. Thus,

$$\dot{V}_{case2} = V_{case1}$$

where now

$$V_{case1} = V_{total} - (V_{12mmsample})$$

$$\dot{V}_{case2} = V_{total} - (V_{4mmsample} + V_{8mmdummysample})$$

As shown above, when a 12 mm thick test sample was used in the test, a dummy sample did not need to be placed inside the chamber along with the test sample, because the total thickness (i.e. sum of the thickness of test sample and the dummy sample) needed to be 12 mm. Thus by selecting the total thickness of 12 mm, it saved the effort of preparing an additional dummy sample for the 12 mm thick samples.

Advantage

The use of dummy samples made it possible to compare the vacuum decay graphs of different thickness samples with one another during a test. As explained before, the change in the volume of the system from the different thickness samples became an issue when it was necessary to compare the pressure decay graphs. Even though this volume change was not an issue during the final measured hydrogen value, the comparison of the pressure decay graphs can be useful as a quality assurance step during the tests. Comparison of the graphs that were plotted during tests provides an early insight for the tests' outcomes. This ability to compare would be useful if this method were adopted in industry to measure hydrogen.

5.5.3 Preparation of Dummy Samples

Dummy samples were prepared using a similar process to that used to prepare the test samples. The test sample preparation process is explained in Chapter 10. The disk-shaped dummy samples were cut from a grade AISI 1018 cylindrical steel bar, which is the same material that was used to prepare test samples.

It was important that the dummy samples did not introduce any hydrogen into the system. Thus, the dummy sample could not contain any amount of hydrogen, including any residual hydrogen that could be introduced to the steel bar during its fabrication process. If the dummy sample contained any residual hydrogen, that hydrogen could also egress out during tests and could add to the amounts of hydrogen that egressed out from the test sample being measured. This could lead to inaccurate measurements during the tests. Thus, any amounts of hydrogen that resided in the dummy samples had to be removed before being used. This was done by baking the dummy samples for seven days at 300⁰ C.

5.5.4 Use of Dummy Samples

During the hydrogen measurement tests, a dummy sample was placed inside the vacuum chamber with the test sample. As explained above, an 8 mm thick dummy sample was used with a 4 mm thick test sample. A 12 mm test sample was used without a dummy sample.

During the initial stage, some tests were carried out using 6 mm thick test samples. With those samples, 6 mm thick dummy samples were prepared and used.

5.6 Problems from Temperature Variation

5.6.1 Issue

It was noticed that the temperature of some components of the TVHS system were different during a test. This became a concern as an accurate determination of gas volume requires an accurate measurement of temperature at each section of the system: according to the universal gas law, the volume of a gas is a direct function of temperature. This issue is explained in detail below.

Heat sources

Two heat sources that contributed to heating of the components of the TVHS were identified.

One of these heat sources was the heating mantel. The heat that dissipated from the heating mantel transferred to the capillary tube, which was connected between the vacuum chamber and the rest of the TVHS system. As a result, the capillary tube started to heat up during the tests. For example, Table 5.2 provides the temperature of each location during a hydrogen measurement test. At the time

of the measurement the room temperature at the moment of the measurement was 19.6° C.

Table 5.2: The temperature of each location of the TVHS during a hydrogen measurement test.

Location	Temperature, °C
In the vacuum chamber	150
Two locations inside the panel	19.9, 19.9
Two locations the capillary tube which was connected to the vacuum chamber and the rest of the system.	25.4, 28.3

The heat that dissipated from the heating mantel by convection was able to be partly reduced by covering the mouth of the heating mantel using an industrial type heat insulation material. In addition the reduction in heat dissipation helped the set temperature for the test sample to be reached faster.

The second heat source was the electronic components that were inside the TVHS panel. The components started heating up during usage, which resulted in an increase of the inside temperature of the TVHS panel by 0.1 to 0.5° C.

Hydrogen amounts at elevated temperature

If the hydrogen amounts were calculated at 150° C, the volumes related to each of the locations needed to compensate for the related temperature. The following simplified model explains how to calculate the amounts of hydrogen and then how to convert them to hydrogen volumes at standard temperature and pressure.

Fig. 5.6 shows a simplified version of the TVHS system during a test. As explained earlier, during a test, the components inside the TVHS, the capillary tube,

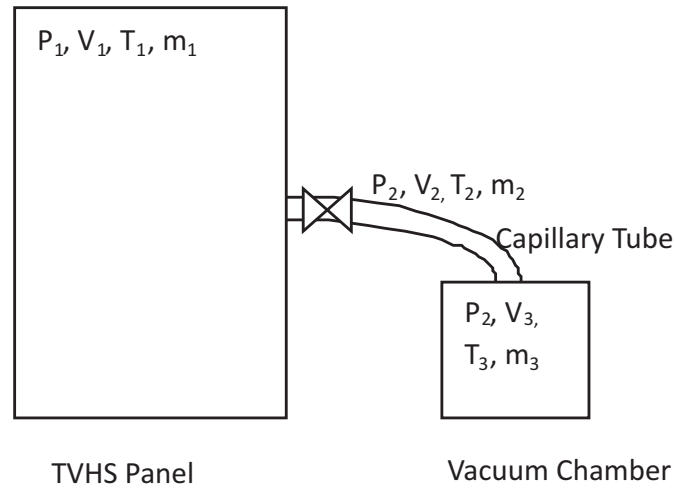


Figure 5.6: A simplified version of the TVHS system during a hydrogen measuring test.

and the vacuum chamber were at different temperatures. These temperatures are represented by T_1 , T_2 , and T_3 where

$$T_3 > T_2 > T_1$$

Note: Even though during a test, temperature was measured at two locations of the capillary and two locations inside the TVH;, to make the model simple, here only one temperature is considered at each location.

V_1 , V_2 , and V_3 represent the volumes of the tubing inside the TVHS, the capillary tube, and the vacuum chamber, respectively.

P_1 is the pressure inside the tubing of the TVHS. P_2 is the pressure inside the capillary and the vacuum chamber. Because the capillary is opened to the vacuum chamber, they both have the same pressure.

m_1 , m_2 and the m_3 are the masses of hydrogen in the tubing inside the TVHS, the capillary tube, and the vacuum chamber, respectively.

According to the universal gas law,

$$PV = nRT \quad (5.1)$$

where

P: pressure

V: volume

n: number of moles

R: universal gas constant

T: temperature

$n = m / M$ where

m: mass and M: mole mass

Therefore, Equ.5.1 becomes

$$PV = (m/M)RT \quad (5.2)$$

From the Equ. 5.2, when the TVHS panel is considered

$$P_1 V_1 = \frac{m_1}{M_{Hydrogen}} RT_1 \quad (5.3)$$

where $M_{Hydrogen}$ is the mole mass of the hydrogen.

Similarly for the capillary tube,

$$P_2 V_2 = \frac{m_2}{M_{Hydrogen}} RT_2 \quad (5.4)$$

For the vacuum chamber,

$$P_2 V_3 = \frac{m_3}{M_{Hydrogen}} RT_3 \quad (5.5)$$

During tests, when the valve between the capillary and the TVHS panel is opened,

then

$$P_1 = P_2$$

$$m_1 = P_1 V_1 M_{Hydrogen} / RT_1$$

$$m_2 = P_1 V_2 M_{Hydrogen} / RT_2$$

$$m_3 = P_1 V_3 M_{Hydrogen} / RT_3$$

$m_{total} = m_1 + m_2 + m_3$ where m_{total} is the total mass of hydrogen.

$$m_{total} = P_1 V_1 M_{Hydrogen} / RT_1 + P_1 V_2 M_{Hydrogen} / RT_2 + P_1 V_3 M_{Hydrogen} / RT_3$$

$$m_{total} = \frac{P_1 M_{Hydrogen}}{R} \left(\frac{V_1}{T_1} + \frac{V_2}{T_2} + \frac{V_3}{T_3} \right) \quad (5.6)$$

For standard pressure and temperature, considering the total mass of hydrogen

Equ.5.6 can be written as

$$V_{std} = \frac{m_{total} R T_{std}}{M_{Hydrogen} P_{std}} \quad (5.7)$$

Where V_{std} : Volume of hydrogen at standard pressure and temperature, by

combining Equ.5.6 and Equ.5.7

$$V_{std} = P_1 \frac{T_{std}}{P_{std}} \left(\frac{V_1}{T_1} + \frac{V_2}{T_2} + \frac{V_3}{T_3} \right) \quad (5.8)$$

According to IUPAC (International Union for Pure and Applied Chemistry),

standard temperature and pressure

$$T_{std} = 273.15 \text{ K } (0^\circ \text{ C})$$

$$P_{std} = 101.3 \text{ kPa } (14.69 \text{ psi})$$

$P_1, V_1, T_1, V_2, T_2, V_3, T_3$ can be measured during the test. Thus, V_{std} can be

calculated. The V_{std} gives the standard amount of hydrogen that is converted from

the amount of hydrogen collected at 150° C .

It is important to note that the thermocouples read only the temperatures at the places where their tips are attached. They do not read the temperatures of adjacent locations. For example, the capillary tube that was connected to the vacuum chamber and the rest of the system had a temperature gradient, but due to the current setup, the TVHS could read only the temperature of two locations. Thus, when calculating the hydrogen amounts, only two temperature values would be used. This would lead to an error in the amounts of hydrogen as the calculation has not considered the temperature gradient. This is applicable to the entire TVHS system. Thus, when calculating the hydrogen amounts, to be more accurate, the TVHS should be divided into more sections, and the temperature should be read in each of the sections. In such a case, the Equ.5.8 can be expanded to:

$$V_{std} = P_1 \frac{T_{std}}{P_{std}} \left(\frac{V_1}{T_1} + \frac{V_2}{T_2} + \frac{V_3}{T_3} + \frac{V_4}{T_4} + \frac{V_5}{T_5} + \frac{V_6}{T_6} \dots \right) \quad (5.9)$$

Although dividing the system into sections makes the measured amounts accurate, the calculations and the physical system become more complex. The physical system becomes complex from the addition of more thermocouples.

Correction for volume expansion

The elevated temperatures make the volumes expand. Thus, to be more accurate, the volumes of each section at which the temperature is measured (those are the locations where the temperature is higher than room temperature) should also be measured. The initial volumes of the TVHS were determined (calibrated) at the room temperature as previously explained. When that procedure is considered, it is obvious that measuring the volumes of individual sections at elevated temperatures is not practicable.

5.6.2 Solution

Because of the reasons explained above, it was found if the system was brought back to the initial room temperature at the end of a test, correcting the volumes for different temperatures was not required during the calculations. Thus, the expansion of the volume of each individual section from elevated temperatures can be disregarded.

Thus, when Equ.5.9 is considered, it can be simplified to

$$V_{std} = P_1 \frac{T_{std}}{P_{std}} \frac{V_{total}}{T_{room}} \quad (5.10)$$

where

$T_{room} = T_1 = T_2 = T_3 \dots$ where T_{room} is the room temperature.

$V_{total} = V_1 + V_2 + V_3 \dots$ where V_1, V_2 , and V_3 are the volumes of individual sections at room temperature

Additional precautions

The selected perforated stainless steel plate on the back of the TVHS panel helped to reduce the heat inside the TVHS that was generated as a result of heating up the electronic components. In addition, the top panel of the TVHS was partly lifted and opened for better circulation of air. This also helped to further reduce of the temperature.

5.7 Problems Caused by Drifting Pressure Gauge Reading

5.7.1 Issue

Observations

In the TVHS, the primary vacuum pressure gauge was used to read the decay in the vacuum pressure during a test. During initial hydrogen measuring tests, the vacuum decay graphs show some areas of noticeable fluctuations in the vacuum pressure. Such two areas are shown in the Fig. 5.7 by two gray color circles. Further, some tests that were run for longer durations showed a continuous decay in the vacuum, suggesting there was a leak in the system. When the system was checked however, no leaks were found. During those tests, it was expected there would be a gradual decay in the vacuum decay (i.e. slow leveling off the curve) with time, and identical tests would give similar test results (i.e. calculate final volumes of hydrogen).

During troubleshooting, the first speculation was that the drift in the primary vacuum gauge was due to an effect from electrical noises. Electrical noise, or interference, can be defined as undesirable electrical signals that distort or interfere with an original (or desired) signal [79]. Noise can be generated from inside the system itself (internal noise) or from an outside source (external noise).

Thus, the vacuum gauge manufacturer was contacted to learn details of the effect of electrical noise on gauge reading. According to the manufacturer, the gauge was designed and constructed in a way that readings would not be affected by internal or external noises. In addition, during construction of the TVHS, the other electronic devices inside the TVHS were properly grounded during the construction to minimize external noise.

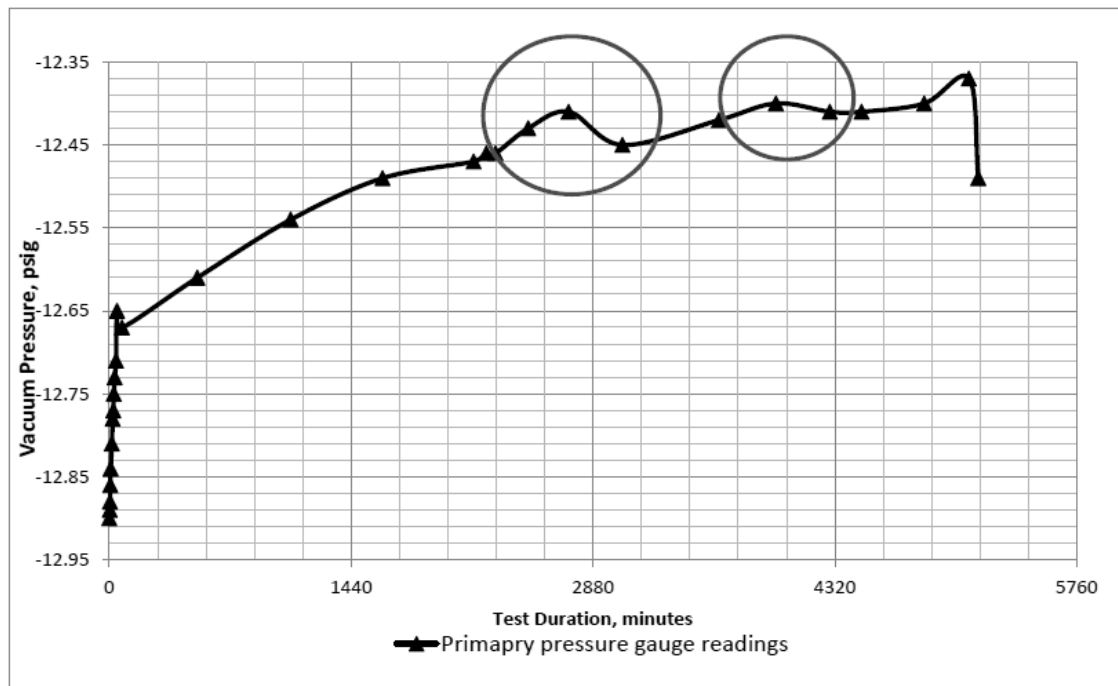


Figure 5.7: Typical vacuum decay graph using data from primary vacuum gauge.

Testing

After careful consideration of the pattern of the pressure fluctuations, it was thought there could be an effect on the primary vacuum pressure gauge readings from the atmospheric pressure and the atmospheric temperature. This was required to be sorted before continuing with the hydrogen measuring tests. The simplest way to accomplish this was by leaving the sealed primary vacuum gauge for an extended period and checking for any variations in the vacuum gauge reading by observing the changes in the atmospheric pressure and temperature. Thus, the effect of atmospheric pressure and temperature on the primary vacuum pressure gauge was found as follows.

First the vacuum was introduced into the TVHS, and the primary vacuum gauge was isolated from the rest of the system by closing the vacuum gauge on/off valve. The primary vacuum gauge was isolated from the rest of the system because it was required to check only the effects of atmospheric pressure and room temperature on the vacuum gauge during this test. The test was carried out during a period of stormy weather. During stormy weather, the atmospheric conditions (i.e. pressure and temperature) changed more drastically than during a normal day.

Once the vacuum was introduced to the vacuum pressure gauge, the drift of the vacuum pressure with the atmospheric temperature and atmospheric pressure were recorded for about eight thousand minutes (approximately five and half days). The stormy weather made the atmospheric pressure and temperature drastically fluctuate during the test duration.

5.7.2 Effects of Room Temperature

Fig. 5.8 indicates how the room temperature and the change in the vacuum pressure changed over the test duration. The change in the vacuum pressure is shown from the line with diamond shapes, and changes in the room temperature are shown from a line with dot shapes. The primary y-axis indicates the change in the vacuum pressure. The change in vacuum pressure is how much the vacuum pressure reading drifted from the initial vacuum pressure.

Change in vacuum pressure = the vacuum pressure shown on the gauge at a certain time - Initial vacuum pressure

For example, if the vacuum pressure shown on the primary pressure gauge at a certain time is -12.7, and if the initial vacuum pressure is -12.9 psi, the change

in vacuum pressure is 0.2 psi. Accordingly, a positive (+) value of the change in vacuum pressure is an indication of decay in the vacuum. In other words, decay in vacuum pressure is really an increase in the positive pressure. Conversely, a negative (-) value for the change in vacuum pressure is an indication of an increase in vacuum pressure, which is really a decrease in the positive pressure.

The secondary y axis of the Fig. 5.8 indicates the change in room temperature. The change in room temperature is how much temperature changed during the test compared to the room temperature at the beginning of the test.

Change in the room temperature = Measured room temperature - room temperature at the beginning of the test

A positive value in the temperature difference indicates an increase in the room temperature while a negative value indicates a decrease in the room temperature.

The graph does not show any strong correlation between the two parameters (i.e. change in the vacuum pressure and change in the room temperature).

Areas marked in gray color ovals

Fig. 5.9 shows the same graph in Fig. 5.8 drawn in a different scale. The span of the primary x-axis (i.e the axis indicates the change in the pressure) and the secondary y-axis (i.e. the axis change in temperature) are increased in Fig. 5.9. According to the figure, at most of the locations, the two curves follow the same pattern. Some of the most obvious locations are marked in gray ovals. In these locations, with the increase of change in room temperature, the change in the vacuum pressure reading has drifted positively, and with the decrease of change in room temperature,

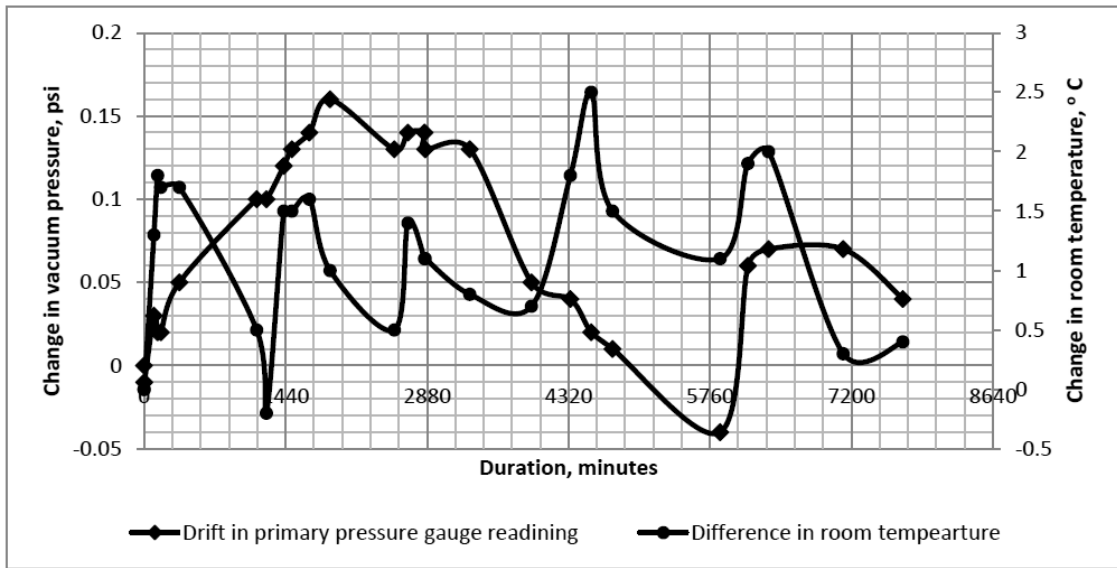


Figure 5.8: Effect of atmospheric temperature on primary vacuum pressure gauge reading.

the change in the vacuum pressure reading has drifted negatively. This observation indicates that the locations that are marked in gray ovals follow a pattern in which the pressure is directly proportional to the temperature. This finding showed that the room temperature affects the primary vacuum gauge readings.

Unmarked areas

The unmarked areas of Fig. 5.9 have not followed the pattern explained in the above paragraph. That is an indication that the pressure gauge reading is affected by other parameters besides the room temperature. This is further discussed in Section 5.7.4.

5.7.3 Effects of the Atmospheric Pressure

Fig. 5.10 shows how the primary vacuum pressure gauge reading and the atmospheric pressure change with time. In the graph, the x-axis indicates the vacuum

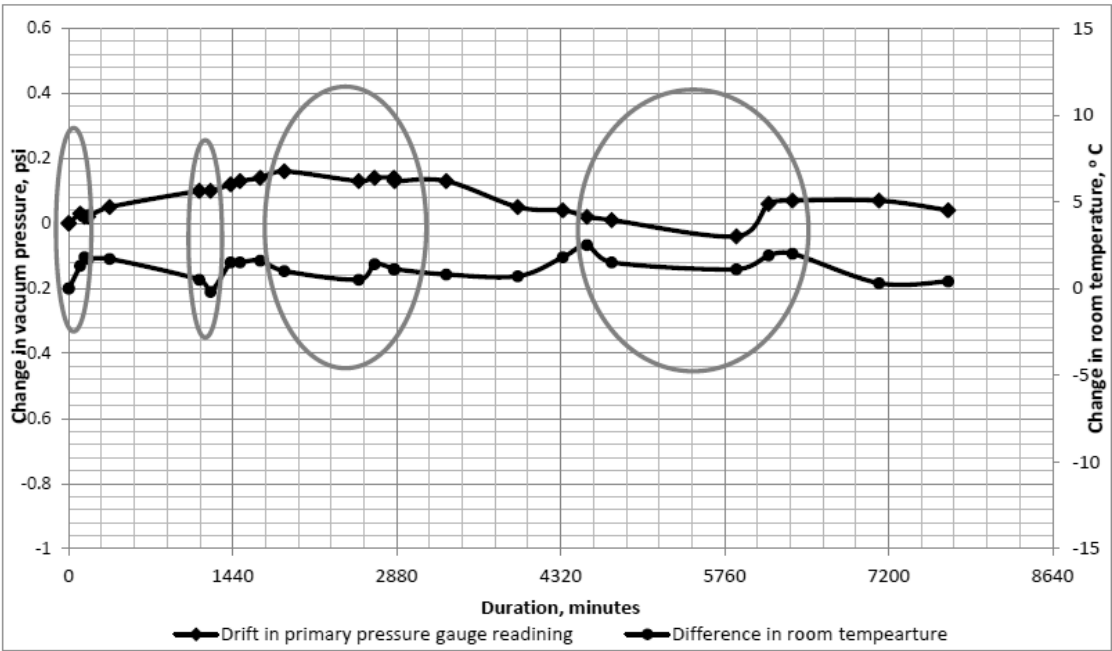


Figure 5.9: Effect of atmospheric temperature on primary vacuum pressure gauge reading in a larger scale graph.

pressure difference. Similar to Fig. 5.8, the line with the diamond shapes indicates the change in the vacuum pressure reading. The line with triangles indicates the change in atmospheric pressure. The primary y-axis of the graph indicates the change in vacuum pressure. As described above, the change in the vacuum pressure reading indicates how much the primary pressure gauge reading drifted from the initial vacuum pressure. The secondary y-axis indicates the change in the atmospheric pressure. The change in the atmospheric pressure was determine relative to the atmospheric pressure at the start of the test.

$$\text{Change in atmospheric pressure} = \text{atmospheric pressure at a certain time} - \text{atmospheric pressure at the beginning of the test}$$

Thus, a positive (+) atmospheric pressure would indicate an increase in the atmospheric pressure when compared to the atmospheric pressure at the beginning of the test. A negative (-) atmospheric pressure would indicate a decrease in the atmospheric pressure when compared to the atmospheric pressure at the beginning of the test.

According to Fig. 5.10, the shape of the change in the primary pressure gauge reading curve has followed an inverse pattern of the change in atmospheric pressure curve. That means, when there is an increase in the atmospheric pressure, the vacuum pressure reading has drifted negatively. Similarly, when there is a decrease in the atmospheric pressure, the vacuum pressure reading has drifted positively.

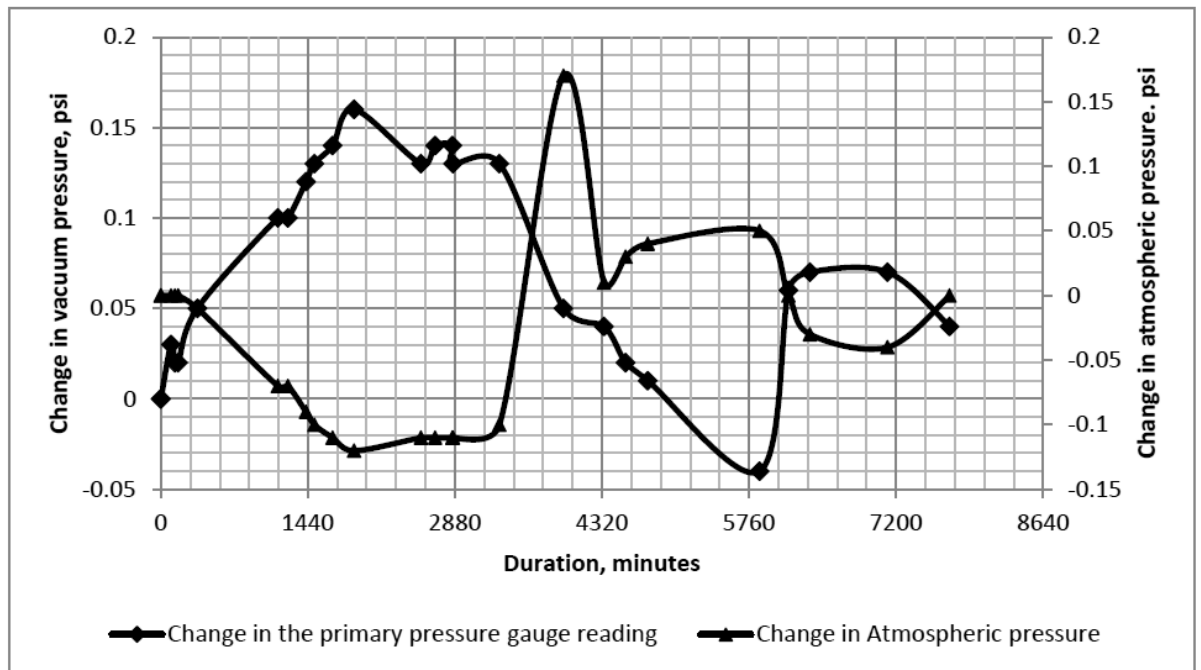


Figure 5.10: Effect of atmospheric pressure on primary vacuum pressure gauge reading.

5.7.4 Combined Effect of Temperature and Pressure

Fig. 5.11 is a combination of Fig. 5.8 and Fig. 5.10. Thus, Fig. 5.11 shows how changes to both room temperature and the atmospheric pressure were affected on the vacuum pressure gauge reading.

The combined effect of the room temperature and the atmospheric pressure can be explained using the areas that are marked with three black ovals A, B, and C. As explained in Section 5.7.3, it is obvious that the atmospheric pressure has an inverse effect on the primary vacuum gauge reading. When the marked areas are considered, this is indicated by the portion of the graph inside the ovals A and C. However, the two points marked with gray color arrows in the ovals A and B clearly show how the change in the room temperature has caused the shape in the portion of the graph inside oval A.

Therefore, the above test results concluded that the primary vacuum gauge readings are extremely sensitive to the changes in the room temperature as well as the atmospheric pressure.

5.7.5 Solution

It was clear that the fluctuations (drifts) of the primary vacuum gauge readings that were seen during the initial hydrogen measuring tests (explained in Section 5.7.1) were a result of the effects of the changes in the room temperature and the atmospheric pressure on the primary pressure gauge. Thus, it was necessary to find a solution to eliminate the effects of the room temperature and atmospheric pressure on the primary vacuum gauge before continuing the hydrogen measuring tests.

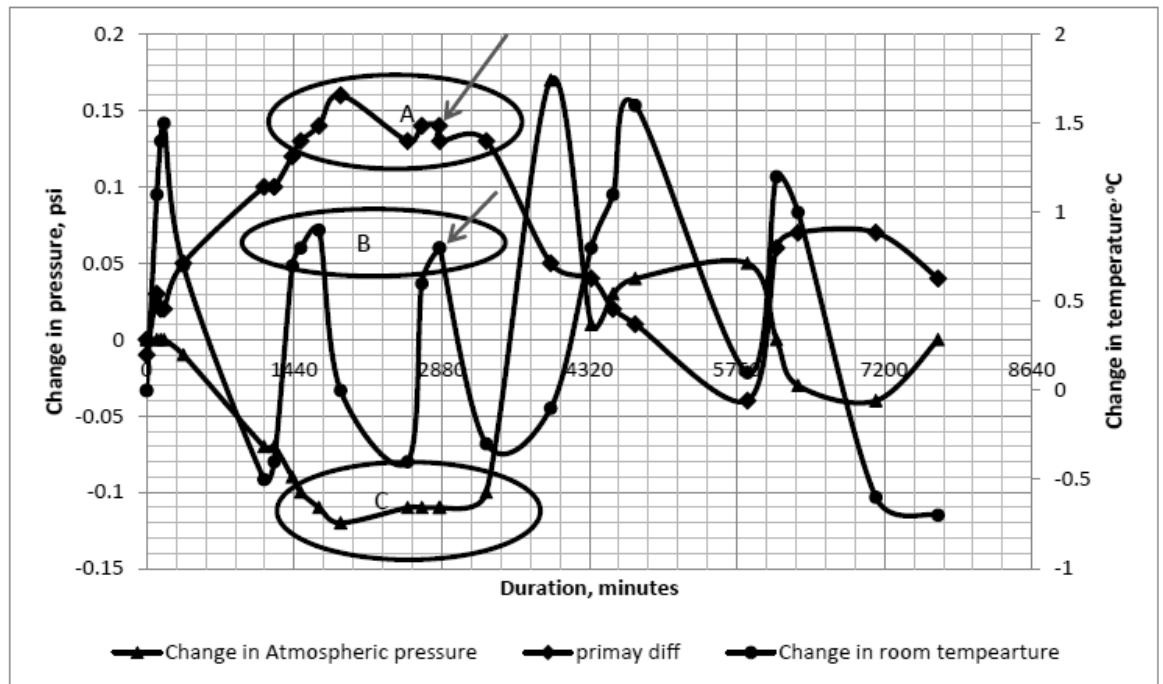


Figure 5.11: Combined effect of atmospheric temperature and pressure on primary vacuum pressure gauge reading.

Control atmosphere

One of the possible solutions for this issue was to control the temperature and pressure of the room in which the TVHS was located. Keeping the room temperature constant was achieved without many difficulties, but controlling the room pressure in a common laboratory was not feasible.

It was then thought that one could build a sealed containment with thicker walls around the primary vacuum gauge to reduce the effect of the atmospheric pressure on it. This was also not practical owing to the way that the gauge was mounted on the TVHS panel.

Secondary gauge

After considering the possible solutions, the solution that was implemented was to use a separate vacuum pressure gauge to observe the effects of the atmospheric pressure and temperature on the gauge. Once this information was known, it was possible to correct the vacuum pressure readings that were obtained in the hydrogen measuring tests.

To implement this solution, a vacuum pressure gauge identical to the primary vacuum gauge was purchased. This gauge was named “the secondary vacuum gauge.” Before using the secondary vacuum gauge in the system, its performance was compared with the existing primary vacuum gauge. Fig. 5.12 shows how both gauges’ vacuum pressures drifted over a period of about eight thousand minutes as a result of the effects from room temperature and atmospheric pressure. Accordingly, the secondary gauge readings drifted in an identical fashion to the primary gauge readings.

TVHS modification

The secondary vacuum gauge was added to the TVHS as a modification to the system. It was externally connected to the system by completing the necessary modifications to the vacuum inlet and electrical wiring of the TVHS.

Correction

The following section explains how the secondary vacuum gauge was used to correct the readings of the primary vacuum gauge reading during the hydrogen measuring tests. During a test, the secondary vacuum gauge was applied with a vacuum at a similar level as the rest of the TVHS. Thus, in the beginning of a test, both vacuum gauges showed a similar reading. Then, the secondary gauge was isolated from the

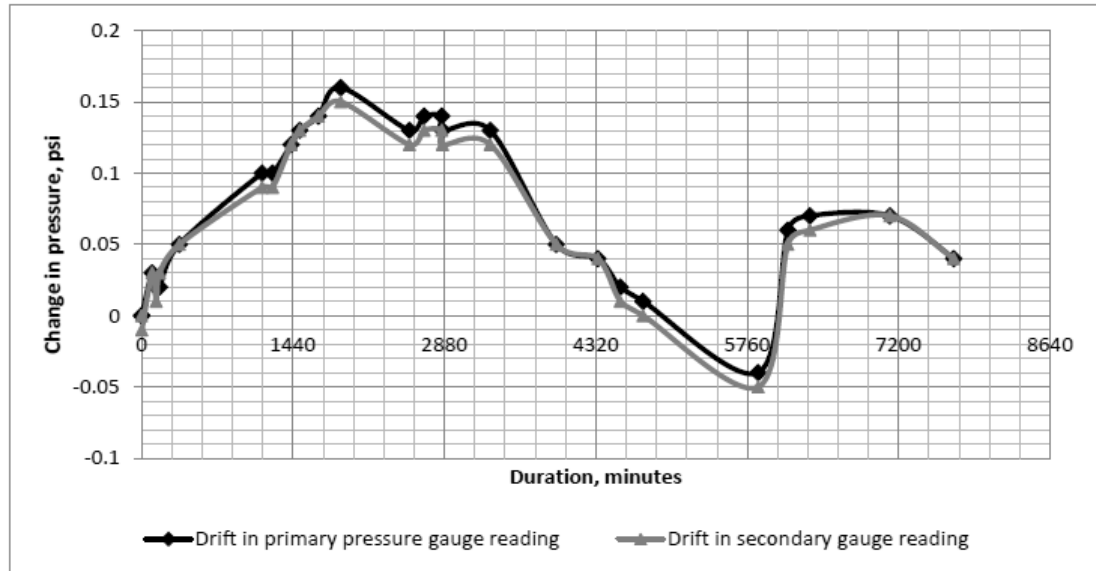


Figure 5.12: Behaviour of the primary and secondary gauges.

rest of the system by closing the connected flow control valve to it. Therefore, any drift in the secondary gauge reading would be caused only by the change in the room temperature and the atmospheric pressure. The primary gauge reading has two components. One is the decay in the vacuum as intended. The second component is the effect caused by the change in the room temperature and the atmospheric pressure. During the correction, the change in the secondary gauge reading was subtracted from the primary gauge reading. This made the primary gauge reading free from any effects from the change in the room temperature and atmospheric pressure. Fig. 5.13 shows the test results of a hydrogen measuring test before and after applying the correction for vacuum pressure gauge reading.

Fig. 5.14 shows the same graph shown in Fig. 5.13. In addition to the two vacuum decay curves, Fig. 5.14 shows

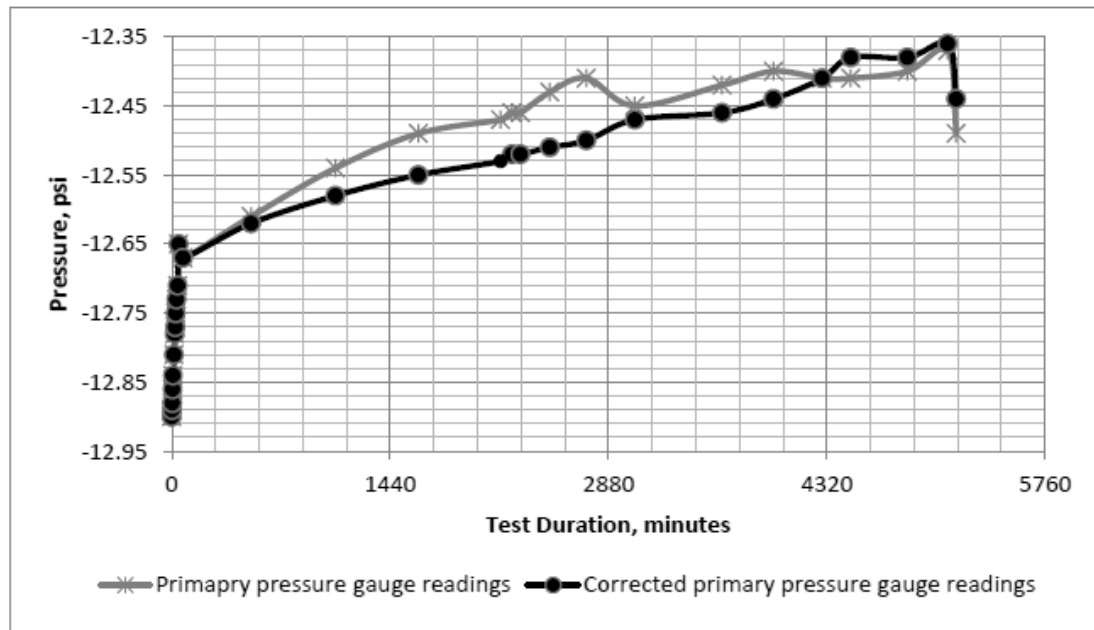


Figure 5.13: Example of test results of a hydrogen measuring test before and after applying the correction for vacuum pressure gauge reading.

- How atmospheric pressure changed over the test duration from the black color curve with plus signs
- How the secondary gauge reading changed over the test duration from the gray color curve with squares.

The secondary y-axis of the graph provides the values of the change in the pressure. The secondary pressure gauge reading is shown on the black color broken line, and this is affiliated to the primary x-axis as it indicates the vacuum pressure, not the change in the pressure. Fig. 5.15 is the same graph given in Fig. 5.14 to show how room temperature changed over the test duration.

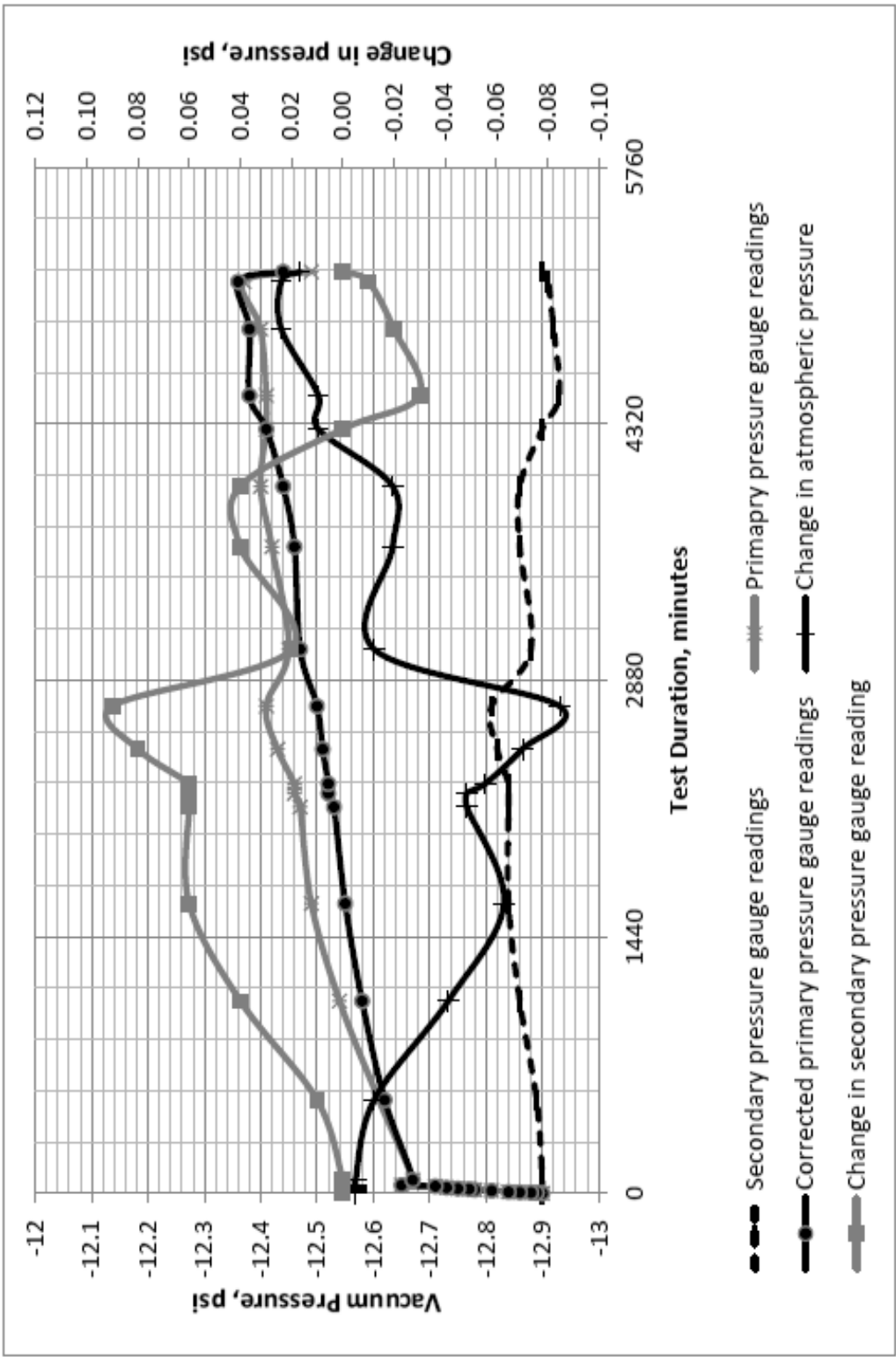


Figure 5.14: Example of how atmospheric pressure changed during the test.

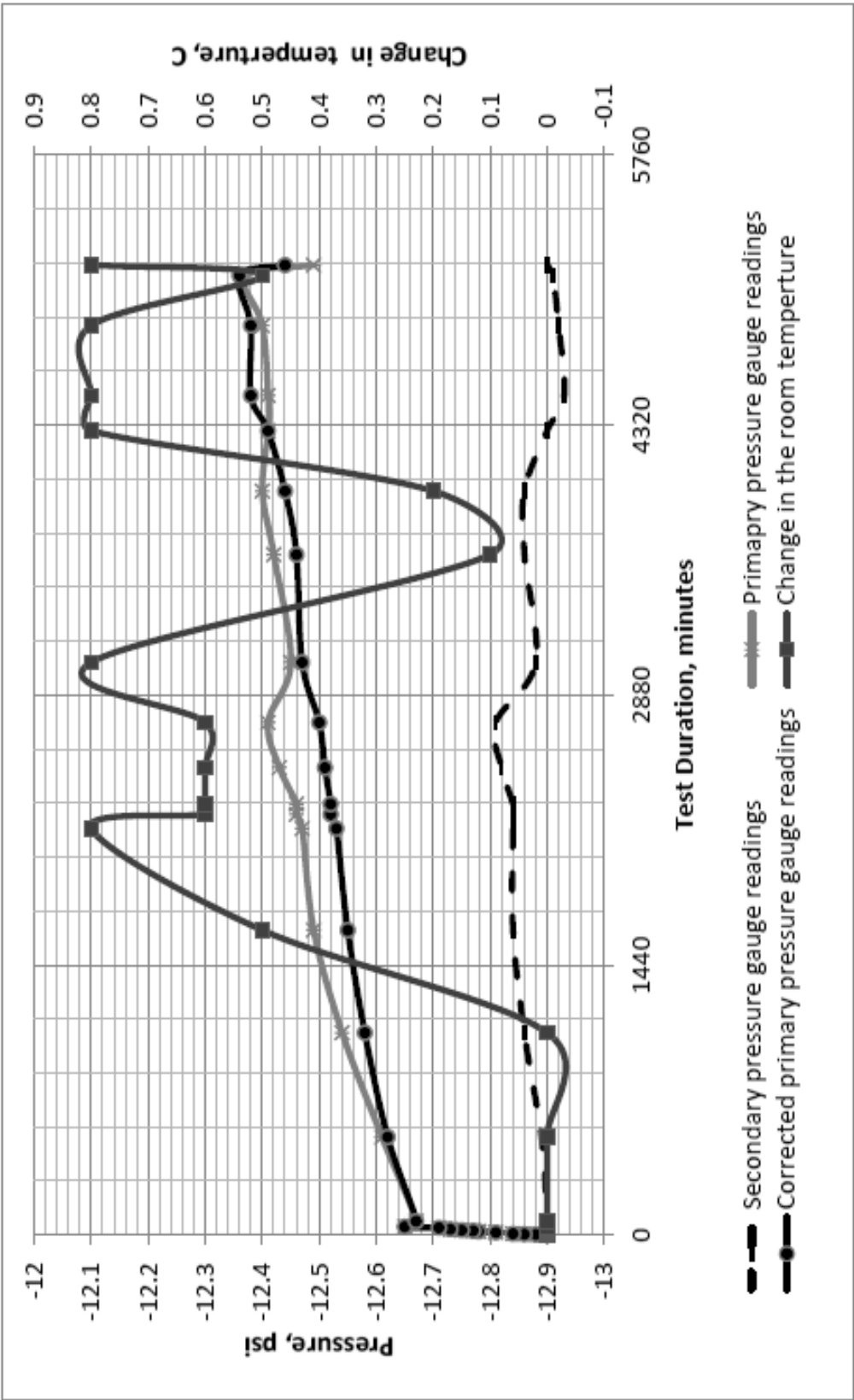


Figure 5.15: Example of how room temperature changed during the test.

5.8 Summary

This chapter described the practical problems raised during the initial trial tests and their solutions. Most of these problems were not considered during the design stage of the TVHS. Among the solutions, the most significant outcome was the introduction of a secondary vacuum gauge to the system. This helped in solving the major issue of the drifting of the vacuum gauge reading.

Other notable improvements were the introduction of a dummy sample to make the free volume constant and making the decision on take the readings required to quantify the hydrogen amounts only when the system was cooled down to room temperature. The latter helped in simplifying the calculation procedure for determining hydrogen amounts.

Chapter 6

Hydrogen Measuring Procedure using the TVHS

6.1 Introduction

This chapter describes the method of measuring hydrogen amounts in steel test samples using the newly developed Thermal Vacuum Hydrogen System (TVHS). The method is explained as a stepwise procedure. The lessons learned during the initial trial tests helped in establishing this procedure.

The following steps are included in the stepwise procedure:

- Cleaning the vacuum chamber and test sample
- Assembling the vacuum chamber
- Detecting and repairing leaks when required
- Introducing the vacuum
- Elevating the temperature
- Recording the primary and secondary vacuum gauge readings
- Bringing the system back to room temperature
- Determining the amounts of hydrogen

6.2 Main steps in Measurement

6.2.1 Cleaning

The first step of the measuring process was cleaning the interior of the vacuum chamber. Cleaning was done by wiping the interior of the chamber with a clean, dry cloth. The purpose of the cleaning was to remove dust, particles, or moisture. If moisture entered the measuring system, it could begin to evaporate at the elevated test temperatures. The evaporation could result in changing the vacuum pressure, which could appear to be caused by hydrogen and would lead to inaccurate results. For the same reason, no solvents or solutions were used for cleaning.

Likewise, the test sample was cleaned using a clean, dry cloth. The cleaned test sample was then placed inside the container of the vacuum chamber.

6.2.2 Assemble of Vacuum Chamber

Once the test sample was placed inside the vacuum chamber's container, the next step was to assemble the rest of the components in the vacuum chamber. These components included the vacuum chamber's lid and gasket.

To begin assembling the components, first, a gasket was placed inside the groove of the container lip. Next, the container with the test sample was attached to the bench vise that was secured on the working table adjacent to the TVHS. The two flat machined areas on the side of the container provided a better grip during attaching. The bench vise was secured in a way that it could be rotated and moved easily. Being able to move the bench vise made it possible to move the container that contained the test sample, and that helped in aligning the holes on the lips of the container

with the holes on the lip of the lid. Otherwise, it would be difficult to align the holes because the lid did not have any freedom to move as it was permanently attached to the THVS panel.

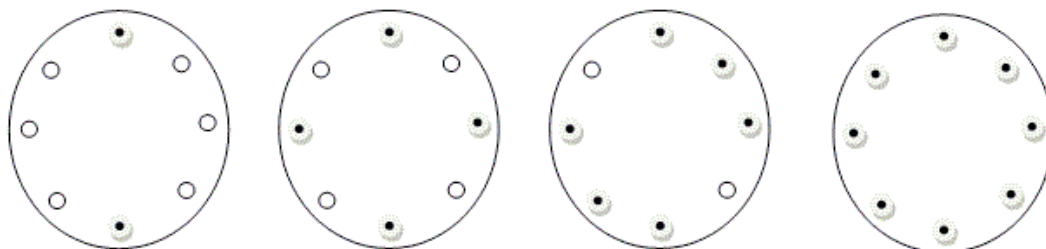
After aligning the holes, the bolts were threaded into the holes. There were a total of eight steel bolts. A steel washer was used with each bolt. Properly tightening these eight bolts was essential in retaining the vacuum in the vacuum chamber. Initial trial experiments showed that the vacuum chamber assembly was one of the most vulnerable places for leaking when the bolts were not properly tightened. Therefore, a bolt tightening procedure was developed to apply a specified amount of torque progressively to each bolt.

Bolt tightening procedure

In this procedure, first, all the bolts were threaded into the holes and hand tightened. Then, as shown in Fig. 6.1(A), the bolts at the 12 o'clock and 6 o'clock positions were partially tightened using a torque wrench that provided a torque of approximately a 60 lbf-in. Similarly, the bolt pairs in front of each other were partially tightened. Each pair that was selected for tightening at each time is shown in the figure by a black dot. Once all the bolts were tightened to a torque of 60 lbf-in, the torque was increased to 80 lbf-in and the steps that were carried out for 60 lb/in were repeated. At the end of this step, all the bolts were tightened up to approximately 80 lbf-in. Next, a similar technique was followed for tightening the bolts up to 100 lbf-in. The clock positions were selected to balance the force so the lid could be attached to the container by gradually biting down on the gasket without leaving any space.

In the last step, the bolts were tightened up to 120 lbf-in. Unlike the other steps, in this step, the torque was applied to each consecutive bolt. The bolt selection for

(A) Bolt pair selection for 60, 80, and 100 lbf-in



(B) Consecutive bolt selection for 120 lbf-in

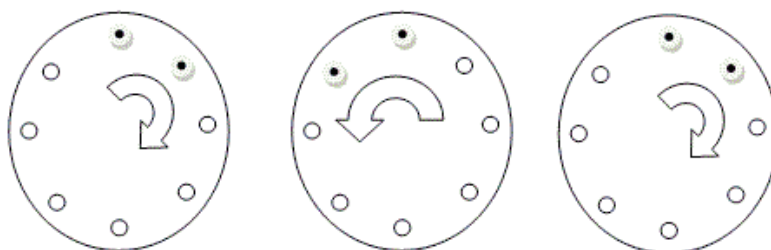


Figure 6.1: Schematic explaining bolt tightening procedure.

this step is shown in Fig. 6.1(B). This was repeated for three times: first, clockwise; then, anti-clockwise; and again clockwise. At the end of this step, the lid bit further into the gasket without leaving any gaps.

Small amounts of industrial type anti-seize compound was applied to the threads of each bolts before carrying out the lid-tightening procedure. The compound was used to avoid seizing or galling of the tightened bolts especially after being exposed to a high temperature test. The selected compound was able to used up to 815° C without it decomposing.

Once the vacuum chamber was assembled, the next step was to search for leaks

in the TVHS system, which included the assembled vacuum chamber.

6.2.3 Search for Leaks

During leak detection, the system was first pressurized with helium gas up to approximately 60 psi (413 kPa). This was done by opening the *helium on/off* valve (i.e. **A** in Fig. 6.2) and introducing helium into the TVHS system. Once the helium pressure reached 60 psi, the helium flow was stopped by closing the *helium on/off* valve. Before pressurizing the system with helium, it was important to close the *vacuum on/off* valve (i.e. **B** in Fig. 6.2) and the *vacuum gauge on/off valve* (i.e. **C** in Fig. 6.2). Closing the *vacuum on/off* valve prevented unnecessary pressurizing of the vacuum pump and its connections. Closing the *vacuum gauge on/off* valve prevented damaging the vacuum pressure gauge by pressurizing it with helium because the gauge was rated for +15 psig to -15 psig pressures.

Once helium was introduced into the system, the helium pressure was observed from the helium pressure gauge of the front panel of the TVHS. The helium pressure was observed for about fifteen minutes. If the pressure did not change during that time, it was concluded that there were no leaks in the system. A drop in the helium pressure indicated a leak in the system. In that case, the location of the leak was found and fixed. As mentioned in Section 4.6.11, it was easy to identify a location of major leaks because they made an audible leaking noise. The most common type of leakage in the system was minor leaks that were difficult to locate. The fastest and easiest way to locate a minor leak was by isolating (sectionalizing) the TVHS system into several smaller sections and checking for leaks in each isolated section. Isolation was done by closing the manual flow control valves in the section that needed to be isolated.

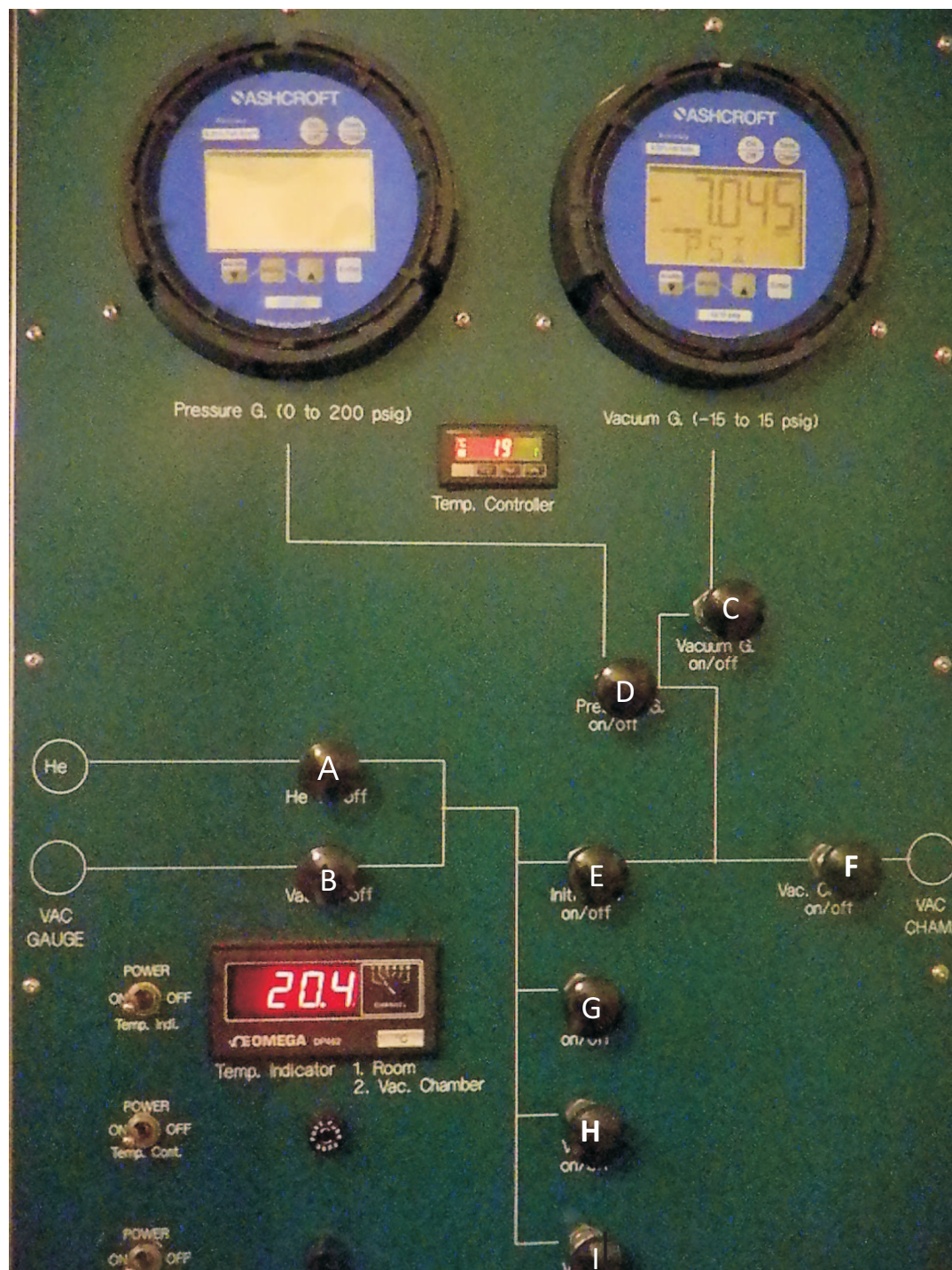


Figure 6.2: A photo of the front panel of the TVHS, showing the valve location.

Leak location

The following example explains how the location of a minor leak was identified. Assume after the whole system was pressurized with helium up to 60 psi, the helium pressure gauge indicated a continuous drop in the pressure. One of the most susceptible locations for a leak in the TVHS was the joint where the capillary connected to the vacuum chamber which is marked with an **A** in Fig. 5.1. Therefore, this location was checked first for leaks. To do that, the vacuum chamber was isolated from the rest of the system by closing the *vacuum chamber on/off valve*. If the leak location was actually location **A**, the drop in the pressure should have stopped because the location was at this point disconnected from the rest of the system. In this case, location **A** and other joints in the isolated section were checked for leaks using Snoop[®] to identify the location, hence confirming the leak in this section. If there was a leak in a joint, the liquid Snoop[®] turns into bubbles. The bubbles were formed by escaped helium going through the Snoop.

Note: Normally, the moment a valve was closed to isolate a section, a slight increase in the helium pressure was indicated by the pressure gauge because of the reduction in the total volume of TVHS. This should not be mistaken for any leaks being present in the isolated section.

Once the leak location was identified, the leak was repaired. Leaks in the system commonly occurred as a result of loosening of a joint or improperly assembly of the vacuum chamber. Loosened joints were repaired by re-tightening the connectors. Once re-tightening was completed, vacuum sealant was applied over the joint as a precautionary measure. The vacuum sealant was able to flow into minute gaps to seal them off.

After the repair was completed, the system was again pressurised with helium to make sure no leaks remained. Once it was confirmed there were no further leaks, the system was vacuumed and then checked for retention of the vacuum. This was the final leak detection step before starting a test. A leak during leak detection using the vacuum was indicated by a drop in the vacuum pressure; thus, the leak location had to be found to be repaired. However, when the system was under vacuum, Snoop[®] could not be used to locate the leak because Snoop[®] as a liquid could be sucked into the system from a minute void in the leak location helping to temporarily plug the void. Therefore, to find the leak's location, the system had to be re-pressurized with helium and Snoop could then be used to locate the leak.

6.2.4 Introducing Vacuum

Once it was confirmed there were no leaks in the system, measuring was started. For measuring, first, the vacuum was again introduced into the system by opening the *vacuum on/off* valve and switching on the vacuum pump. During this step, the *helium on/off* valve (i.e. **A** in Fig. 6.2) and the *helium pressure gauge on/off* valve (i.e. **D** in Fig. 6.2) remained closed.

After the vacuum was established, the *vacuum on/off valve* was closed and the pump turned off. Also, if the hydrogen amount being measured was approximately known, one or two of the three calibration volumes were also disconnected from the system by closing the respective *calibration volume on/off valve/ valves* (i.e. **G**, **H** and **I** in Fig. 6.2). This enhanced the sensitivity of the measuring system.

Once the vacuum was established, the next step was to elevate the temperature of the test sample.

Hydrogen loss

In general, it could take approximately up to 20 minutes to complete this stage since the time that a sample was charged with hydrogen. According to available experiment results, the amounts of hydrogen that could egress out from a test sample (i.e. the amount of hydrogen that loss prior to measurement) during this time duration could be negligible, providing the sample is at the room temperature and atmospheric pressure. See Fig. 12.12. Theoretical calculations using the Fick's second law for non-steady state diffusion also showed that the amount of hydrogen lost could be about 0.05 cm^3 .

6.2.5 Elevating Temperature

The heating mantel provided heat to the test sample. To do so, the sample contain in the vacuum chamber was placed carefully inside the heating mantel, by not introducing any stresses on the joints between the TVHS panel and the vacuum chamber. Stresses on the joints could lead to leaks. A thermocouple was placed in the thermocouple port of the vacuum chamber to measure the test sample temperature.

The heat that was provided to the test sample was controlled by the temperature controller. To do this, first, the required temperature was registered in the temperature controller, thus enabling the temperature controller to provide power to the heating mantel until the test sample reached the set temperature. Once the set temperature was reached, the temperature controller maintained the temperature at the set point. At the end of the test, the temperature controller was switched off to allow the test sample to cool down to room temperature.

Before elevating the test sample temperature, the following initial readings were

taken down. These readings were required later for determining the hydrogen amounts.

- Initial room temperature
- Initial atmospheric pressure
- Initial vacuum pressure
- Set temperature

6.2.6 Primary Vacuum Gauge Readings

The primary vacuum gauge was directly connected to the vacuum chamber; changes in pressure inside the vacuum chamber were thus indicated by reading the gauge. Before introducing vacuum into the system, the primary pressure gauge reading showed 0 psig (0 kPag). During each test, the system was vacuumed to -12.9 psig (-88.9 kPag), which was considered the initial vacuum pressure.

With the increase of the temperature and elapse of time, the hydrogen in the test sample progressively came out. This was shown from the primary vacuum pressure gauge reading as decay in the vacuum pressure. Table 6.1 provides the readings obtained during a test. The values show how the primary vacuum gauge reading changed with the increase in the temperature and time.

At the end of a test and before taking the final vacuum pressure reading, the test sample was brought back to room temperature to avoid any volume variations from the expansion of the vacuum chamber as a result of elevated temperatures. This phenomenon is described in Section 5.6. To bring the temperature down, the temperature controller was switched off and the vacuum chamber was taken out

from the heating mantel. When the test sample reached the room temperature, the following final readings were recorded:

- Final sample temperature
- Final room temperature
- Final primary vacuum gauge reading

6.2.7 Secondary Vacuum Gauge Readings

As explained in Section 5.7.1, a secondary vacuum gauge was later added to the THVS. The main function of this pressure gauge was to compensate for the changes in the atmospheric pressure and temperature affecting the primary pressure gauge reading. Thus, each time the primary pressure gauge reading was recorded, the secondary pressure gauge reading was also recorded. These secondary gauge readings were used to correct the primary pressure gauge reading. This is further explained in Section 5.7.1.

6.2.8 Determining Hydrogen Amounts

Once the steps above were completed and the required readings were obtained, the amount of hydrogen that egressed out from the test could be calculated. This is explained in Chapter 7.

Table 6.1: Example of the data recorded during a test.

Test Duration <i>minutes</i>	Primary pressure gauge reading <i>psi</i>	Secondary pressure gauge reading <i>psi</i>	Temp. inside vacuum chamber $^{\circ}C$	Atm pressure <i>psi</i>	Room temp. $^{\circ}C$
0	-12.90	-12.90	20.8	12.78	20.8
5	-12.86	-12.90	96.9	12.78	20.8
6	-12.85	-12.90	99.0	12.78	20.8
8	-12.82	-12.90	102.2	12.78	20.8
9	-12.80	-12.90	103.8	12.78	20.8
12	-12.77	-12.90	106.1	12.78	20.8
15	-12.69	-12.90	107.5	12.78	20.8
17	-12.73	-12.90	109.5	12.78	20.8
21	-12.71	-12.90	111.0	12.78	20.8
30	-12.68	-12.91	115.0	12.79	20.8
34	-12.67	-12.91	123.8	12.78	20.8
44	-12.67	-12.91	131.9	12.78	20.8
53	-12.66	-12.91	138.6	12.78	20.8
56	-12.65	-12.91	143.5	12.78	20.8
77	-12.65	-12.91	147.3	12.80	20.8
128	-12.65	-12.92	150.1	12.82	20.8
510	-12.65	-12.91	150	12.83	20.8
607	-12.64	-12.92	150	12.84	20.6
711	-12.64	-12.92	150	12.83	20.6
725	-12.64	-12.92	150	12.84	20.8
748	-12.64	-12.93	150	12.85	20.8
824	-12.62	-12.92	150	12.83	20.8
1024	-12.61	-12.90	150	12.85	20.8
1084	-12.60	-12.90	150	12.83	20.8
1307	-12.60	-12.90	150	12.83	20.8
1382	-12.59	-12.90	150	12.83	20.8
1645	-12.53	-12.90	150	12.83	20.8
2010	-12.51	-12.85	150	12.83	20.8
2190	-12.50	-12.83	150	12.81	20.8
2280	-12.49	-12.83	150	12.78	20.8
2540	-12.49	-12.84	150	12.78	20.8
2631	-12.48	-12.84	150	12.78	20.8
2838	-12.51	-12.85	150	12.78	20.8
3034	-12.50	-12.89	150	12.79	20.8
3459	-12.49	-12.89	150	12.83	20.9
3574	-12.47	-12.89	150	12.84	20.9
3782	-12.48	-12.87	150	12.84	20.9
4313	-12.48	-12.89	150	12.86	20.9
5051	-12.49	-12.91	150	12.89	20.8
5224	-12.61	-12.90	150	12.89	20.8

Chapter 7

Determination of Hydrogen Amounts using the TVHS

7.1 Introduction

This chapter describes the calculation procedure that determines the hydrogen amount as a volume at standard pressure and temperature. Three computer programs were developed to make the calculation process efficient. The chapter also discusses the calibration methods of the components that are used in the TVHS.

7.2 Concept

The concept for determining the amount of hydrogen that egressed from the test sample is explained below.

Fig. 7.1(a), shows the TVHS system before the temperature of the test sample was elevated. The test sample was inside the sealed vacuum chamber and vacuum was applied to the TVHS system. If the total volume of the system is V_{total} ,

$$V_{total} = V_{ipanel} + V_{icapillary} + V_{ichamber} \quad (7.1)$$

where

V_{ipanel} is the internal volume of all the components inside the panel before starting the test.

$V_{icapillary}$ is the internal volume of the capillary tube that connects the TVHS panel to the vacuum chamber before starting the test.

$V_{ichamber}$ is the free volume of the vacuum chamber prior to start the test. The term *free volume* refers to the rest of the volume inside the vacuum chamber after placing the test sample inside.

The volumes above were known before starting the test. These volumes are subject to change during tests because of thermal expansion.

Application of Equ.5.10 to the conditions above gives

$$V_{itotalSTD} = \frac{P_i V_{itotal} T_{STD}}{P_{STD} T_i} \quad (7.2)$$

where P_{STD} and T_{STD} are the standard pressure and temperature and P_i and T_i are the initial vacuum pressure and initial temperature.

Fig. 7.1(b) shows the TVHS system at the end of a test before switching off the power of the heating mantel. Thus, at this moment, the test sample is at an elevated temperature. Therefore,

$T_1 > T_i$ where T_1 is the elevated temperature. $P_i \neq P_1$ from accumulation of hydrogen in the system.

The elevated temperatures expand the internal volumes of the vacuum chamber and the capillaries. Therefore,

$$V_{1capillary} > V_{icapillary}$$

$$V_{1chamber} > V_{ichamber}$$

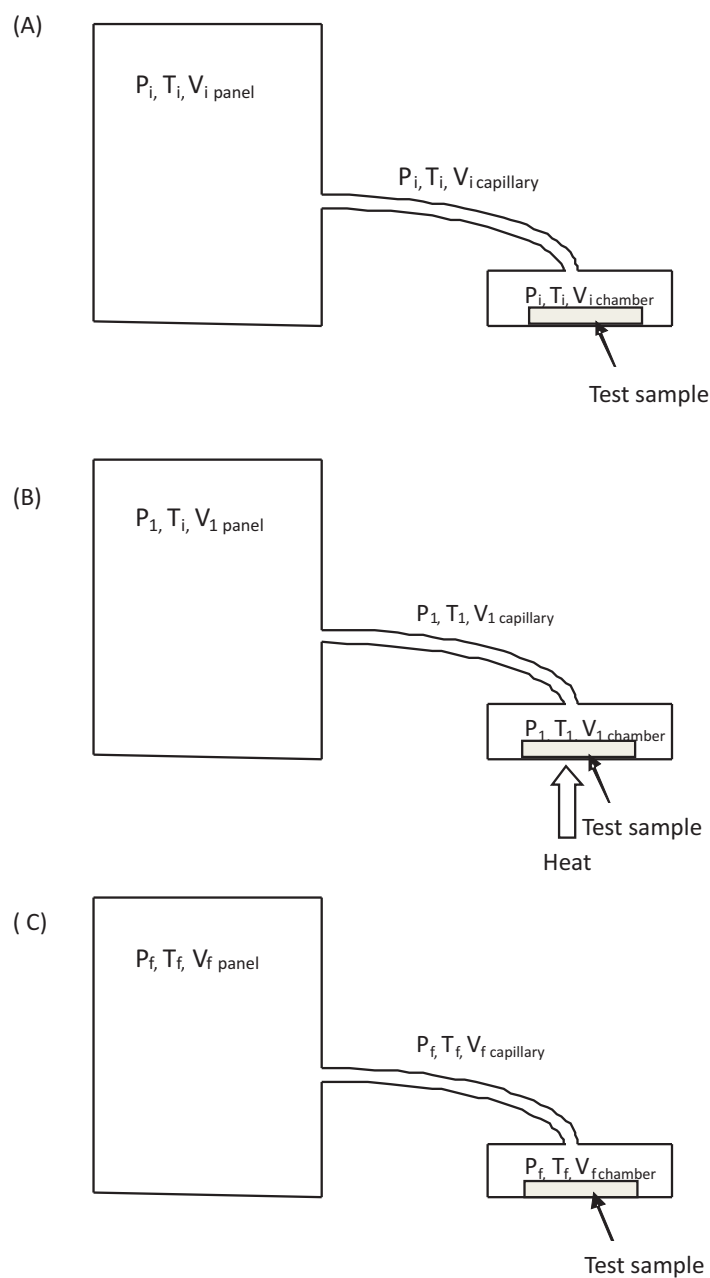


Figure 7.1: A model of the TVHS (A) before the temperature of the sample was elevated (B) before switching off the power of the heating mantle (C) at the end of the test.

Experience showed that transfer of heat from the vacuum chamber into the TVHS box is minimal. Therefore, variation of the volumes of the components inside the TVHS from the minimal heat transfer is insignificant. Therefore it can be considered,

$$V_{1panel} = V_{ipanel}$$

Fig. 7.1(c), shows the TVHS system at the end of a test. Now the TVHS system including the capillaries, the test sample, and the vacuum chamber were brought back to the room temperature. The reason for bringing these back to the room temperature is explained in Section 5.6. The Equ.7.2 applied to the conditions at the end of the test gives

$$V_{ftotalSTD} = \frac{P_f V_{ftotal} T_{STD}}{P_{STD} T_f} \quad (7.3)$$

where P_f , T_f , and V_f are final pressure, temperature and volume respectively.

Since the system is at room temperature again, the internal system volume changed from thermal expansion is considered negligible as shown in Fig. 7.1(b). Therefore

$$V_{itotal} = V_{ftotal} = V_{total}$$

Thus Equ.7.2 and Equ.7.3 can be written as

$$V_{itotalSTD} = \frac{P_i V_{total} T_{STD}}{P_{STD} T_i} \quad (7.4)$$

$$V_{ftotalSTD} = \frac{P_f V_{total} T_{STD}}{P_{STD} T_f} \quad (7.5)$$

If $V_{HydrogenSTD}$ represents the volume of hydrogen egress from the test sample at standard pressure and temperature, subtracting Equ.7.5 from Equ.7.4 gives,

$$V_{HydrogenSTD} = \frac{V_{total}T_{STD}}{P_{STD}}\left(\frac{P_f}{T_f} - \frac{P_i}{T_i}\right) \quad (7.6)$$

As explained above, P_i , T_i , P_f and, T_f were obtained during a test. V_{total} is the total volume of the system at room temperature. The method for obtaining this value is given in Chapter 6. T_{STD} and P_{STD} are standard temperature and pressure, respectively. According to IUPAC (International Union for Pure and Applied Chemistry), standard temperature and pressure values are 273.15 K (0° C) and 101.3 kPa (14.7 psi), respectively. Now, all required parameters are available to calculate the volume of hydrogen egress from the test sample at standard conditions ($V_{HydrogenSTD}$).

7.3 Units

In this thesis, hydrogen egress from a test sample is given in cubic centimeters (cm³) at standard pressure and temperature. However, the hydrogen volume can also be given in the following units:

- cubic centimeters (cm³) per 100 grams of the test sample
- milliliters (ml)
- ml/100g (milliliters per 100 grams of steel test sample)
- ppm (parts per million)

7.4 Calibration of Instruments

Measuring instruments require calibration from time to time to maintain and ensure their accuracy. In this research study, there were three pressure gauges, seven thermocouples and hydrogen containments connected to the TVHS. The seven thermocouples included six thermocouples measured temperatures at different locations in the system, and one thermocouple connected to the temperature controller. The hydrogen containments included three calibration volumes, the tubing, the connector volumes located inside the TVHS, and the free volume inside the vacuum chamber. These measuring instruments required the mentioned calibration.

7.4.1 Pressure Gauges and Thermocouples

The pressure gauges are factory calibrated in specially controlled environments. Therefore, they were not calibrated again. However, to ensure reliability, the instrument readings were compared from time to time with similar instruments. The thermocouples are generally reasonably accurate in manufacturing due to quality control, however the various thermocouples in the system were often compared to each other at room temperature.

7.4.2 Hydrogen Containments

Hydrogen volume

Equ.7.6 determines the amounts of hydrogen that egressed from a test sample ($V_{hydrogenSTD}$) at standard pressure and temperature. According to the equation, $V_{hydrogenSTD}$ is a function of the total volume of the containments where hydrogen travels and resides during a test, which is indicated by V_{total} . Thus, the value of V_{total} is required to determine $V_{hydrogenSTD}$.

V_{total} can be calculated by summing each volume that hydrogen resides during a test. For example, let's consider a test where flow control valve H and I ((Fig. 6.2) are closed, allowing hydrogen to enter (spread) only up to the first calibration volume. A list of containments along this path is given below. Fig. 6.2 can be used to identify the valves in the following list. Note: As explained in Chapter 6, valves A, B, and D are always kept closed during a test. These valves isolate the pressure gauge of the helium detection system, the vacuum pump, and the helium inlet from the rest of the system.

1. Free space inside the vacuum chamber.
2. Internal volume of the capillary tube that connects the vacuum chamber to the TVHS.
3. Internal volume of the connector that connects the capillary to the TVHS panel.
4. Internal volume of the above connector.
5. Internal volume of the capillary that connects above connector and valve F.
6. Internal volume of the valve F.
7. Internal volume of the capillary that connects valve F and the T-type connector at the joint.
8. Internal volume of the T-type connector.
9. Internal volume of the capillary that connects the above T-type connector and valve E.

-
10. Internal volume of the valve E.
 11. Internal volume of the capillary that connects the valve E and adjacent union-type connector.
 12. Internal volume of the above union-type connector.
 13. Internal volume of the capillary that connects the above union-type connector and closed valve A.
 14. Internal volume of the closed valve A.
 15. Internal volume of the capillary that connects the above union-type connector and closed valve B.
 16. Internal volume of the closed valve B.
 17. Internal volume of the capillary that connects the above union-type connector and adjacent T-type connector.
 18. Internal volume of the above T-type connector.
 19. Internal volume of the capillary that connects the above T-type connector and valve G.
 20. Internal volume of the valve G.
 21. Internal volume of the capillary that connects the valve G and the calibration volume 1
 22. Internal volume of the capillary that connects the above T-type connector and adjacent connector.

-
23. Internal volume of the above connector.
 24. Internal volume of the capillary connects that above connector and closed valve H.
 25. Internal volume of the closed valve H.
 26. Internal volume of the capillary that connects the above t-type connector and the adjacent L-type connector.
 27. Internal volume of the capillary that connects the above L-type connector and closed valve.
 28. Internal volume of the valve.
 29. Internal volume of the capillary that connects the connector between valve E and F with the t-type connector adjacent and above to it.
 30. Internal volume of the capillary that connects the adjacent and above connector and valve C.
 31. Internal volume of the valve C.
 32. Internal volume of the capillary that connects the valve C and the primary vacuum pressure gauge.
 33. Internal volume of the capillary that connects the adjacent and above connector and closed valve D.
 34. Internal volume of the closed valve D.

Thus to calculate the total volume each time, a list of containments similar to the above list for each test should be identified. A computer program was developed to make this process efficient and less complex. The computer program details are given in Section 7.5.

Volume calibration

As explained above, the volume of each section within the containment was required in calculating the total volume of the entire containment where hydrogen resided during a test. The volume of each section and component was measured before assembling the components together to construct the TVHS. Three methods, described below, were used to measure and calculate the volumes. If variations in volume were found using several methods, the average was taken as the final value of that volume. As an example, Table 7.1 provides the calculated and measured volumes of the three main components in the TVHS.

Table 7.1: Calibrated volume of three components.

Component	Manually calculated	Volume (cm ³)	
		Measured	Mean
Calibration volume 1	5.024	5.1	5.062
Calibration volume 2	5.024	5.1	5.062
Calibration volume 3	2.924	2.8	2.862
Vacuum Chamber	18.720	18.7	18.71

1. Using manufacturer specified volume information

The Swagelok[®] valves, fittings, joints and connectors have complex inner shapes. The technical drawings obtained from the manufacturer carry dimensions of most of the components and their internal volumes.

2. Manual calculation of volumes

Volumes of some of the components were calculated using their dimensions. This method is particularly used for the components that do not have complex shapes. For example, the volume of a test sample with a cylindrical shape is calculated using $\pi (d/2)^2 h$ where d and h are the diameter and thickness of the test sample, respectively. The diameter and the thickness of the test sample were measured using a vernier caliper.

3. By measuring volumes

Volumes of some components were measured by filling them with water and then measuring the volume of the water. This method was used particularly to measure the internal volume of the components that have complex internal shapes. For this method, a clean water beaker was taken, and the water was colored with food coloring. The food coloring made the water visible during the measuring process. A drop of detergent (eg. liquid soap) is also added to the water to reduce the surface tension [70]. With reduced surface tension, the water surface becomes more flat and less spherical, which simplified taking the volume measurements.

The prepared water was poured into a previously calibrated syringe marked with volume levels. Then the water was carefully injected into the internal volume of the components in small quantities using the syringe. Once the volume of the component was full of water, the reading on the syringe was taken. The internal volume of the component was given by that volume reading. This was repeated for six times, and the average of the six volume readings was taken as the final volume reading. It was important to dry the components thoroughly between each measurement because residual water could lead to inaccurate measurements. The residual water

contents could get into the system and be trapped inside once all the components are assembled tightly. It is explained in Chapter 6 that water or moisture must not be allowed into the TVHS because that could lead to inaccurate measurements.

7.5 Computer Programs

Descriptions of the three computer programs developed are given below. The programs make the calculation process faster and efficient during the tests.

7.5.1 VolCAL

A computer program to calculate the total volumes of the containments that hydrogen resides (V_{total}) during a test called VolCAL was developed. Without such a program, it would be a tedious task to manually calculate volumes for each test as explained in Section 7.4.2.

The program was based on MS Excel. Before placing a test sample inside the vacuum chamber, the diameter and the thickness of the disk shaped sample were measured. The computer program requires this information for calculating the volume of the test sample. For the test sample that was not cylindrical, the other dimensions required in calculating volume must be obtained and fed into the computer program. For example, if the test sample is cubical in shape, the length of the sides of the cube is required. The computer program also requires information of the dummy sample, if one is used for the test. More information about dummy samples is given in Chapter 5.

Once the required inputs were provided, the volume of the containments in which hydrogen resides (i.e. V_{total} in Equ. 7.6) was calculated by the program for different

options of selected volumes. During development of the program, the volumes of the each containment which was obtained through the volume calibration process (explained in Section 7.4.2), was fed into the program to make it possible to calculate the above options automatically.

7.5.2 TvhsCAL

TvhsCAL program calculated the hydrogen amounts measured using the TVHS method. This program was also based on MS Excel. When initial and final test parameters such as vacuum pressure, atmospheric pressure, and room temperatures were given as the inputs, the program calculated the amounts of hydrogen that egressed from the test sample at standard pressures and temperatures. This is indicated by $V_{hydrogenSTD}$ in Equ.7.6. The value of the V_{total} required in this program was calculated from the previously described volCAL program. The program made it easier and more efficient to determine the amounts of hydrogen that egressed from a test sample.

7.5.3 EudiCAL

EudiCAL program calculated the hydrogen amounts measured using the eudiometer method. Again, this program was based on MS Excel. The eudiometer method is described in Chapter 9. Equ.9.2 given in Chapter 9 was used in the program to calculate the amounts of hydrogen. The results are given in four units as in the program TvhsCAL.

Chapter 8

Calibration of the TVHS

8.1 Introduction

The TVHS equipment was calibrated by comparing the measurements taken by the TVHS with the same measurements taken by the mercury eudiometer. The calibration test results and the conclusions made are discussed in this chapter.

8.2 Objective

The TVHS has to be calibrated before its use. This was done by evaluating TVHS measurements with another well-known, accurate, and established hydrogen measuring technique. The mercury eudiometer was selected for this purpose. Identical test samples each charged with identical amounts of hydrogen were used. The amounts of hydrogen that egressed from each sample, at a given temperature during a fixed time interval, were measured using the TVHS and the mercury eudiometer. The objective of the calibration was to compare the measurements taken from the TVHS with the measurements taken from the mercury eudiometer.

The correlation of results obtained for the calibration test helped in gaining an understanding between the measurements taken by the TVHS and compared with those of the mercury eudiometer. This calibration was essential for obtaining an assurance on the measurements taken by the TVHS.

8.3 Method

8.3.1 Sample Preparation

The details on sample preparation are provided in Section 10.2.

8.3.2 Hydrogen Charging

Once the samples were prepared, they were exposed to a condition resulting in an identical amount of hydrogen pickup prior to the measurement tests. The acid pickling method was used to charge hydrogen into the test samples. Details on the acid pickling method are given in Section 10.3.

For each sub-test¹, two test samples were required: one sample for the TVHS test and one sample for the eudiometer. Both samples were charged together in the acid pickling bath to ensure that the two samples were charged with identical amount of hydrogen.

8.3.3 Testing

Three sets of calibration tests were carried out. These three sets were identified as Calibration Test A, Calibration Test B, and Calibration Test C. Each set of calibration tests consisted of a number of multiple tests called **sub-tests**. A summary of the calibration test matrix in the form a flow chart is provided in Fig. 8.1 to provide a better understanding. Further details of the tests are discussed below.

Calibration Test A

Calibration test A consisted of six pairs of identical sub-tests. The pairs of the sub-tests were identified as Test A1, Test A2, Test A3, Test A4, Test A5, and Test A6.

¹Term **sub-test** is defined in Section 8.3.3

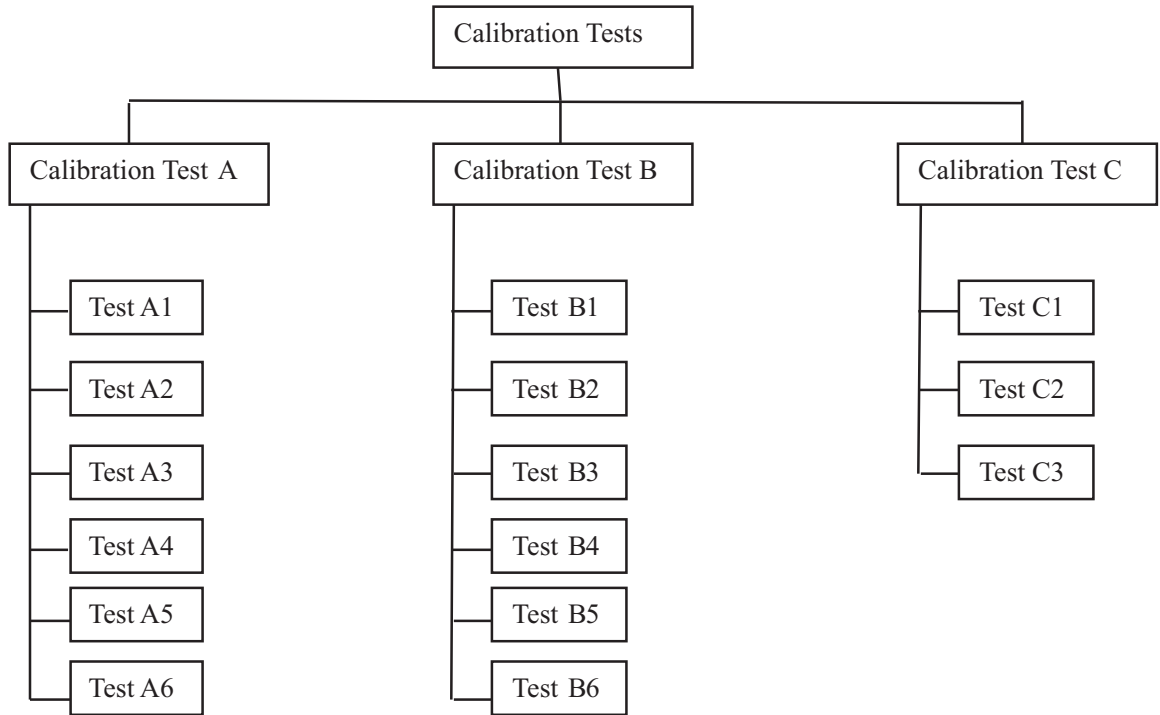


Figure 8.1: Test matrix of the calibration tests.

Each pair of the test included one test carried out using the mercury eudiometer and one test carried out using the TVHS method.

In each pair of the sub-tests, two identical 4 mm thick disk shaped test samples were used. The two test samples were charged with identical amounts of hydrogen as explained earlier. After charging, one of the two charged samples was placed inside the mercury eudiometer. The second sample was placed inside the vacuum chamber of the TVHS.

The hydrogen measurements using the eudiometer and the TVHS are carried out at 150°C (423 K). There is no particular reason for selecting 150°C as the test temperature for the calibration test. However, as explained in Chapter 8, the

maximum temperature that the eudiometer could function is 150° C due to safety reasons. Therefore, the eudiometer tests were limited to a test temperature of 150° C (423 K).

The duration of each TVHS and eudiometer test was 5000 minutes. That is approximately 83 hours or three and half days. Such a long duration was selected to provide the test sample with enough time to diffuse out as much of its hydrogen content as possible.

Calibration Test B

Like Calibration Test A, Calibration Test B also consisted of six pairs of identical sub-tests. Each pair is named Test B1, Test B2, Test B3, Test B4, Test B5, and Test B6. The only difference between Calibration Test A and Calibration Test B was the thickness of the test samples that were used in the tests. The Calibration Test B used 12 mm-thick test samples where the previous used 4 mm-thick test samples. Both the eudiometer and TVHS tests were carried out at 150° for 5000 minutes.

Calibration Test C

Similar to Calibration Test A, 4 mm-thick test samples were used in Calibration Test C. However, the tests were carried out at 50° C (323K) for 5000 minutes. In these sub-tests, only three pairs of identical tests were carried out. Each pair was named Test C1, Test C2, and Test C3.

During the improvement of the eudiometer method, which is explained in Chapter 9, the eudiometer method was used to measure hydrogen in steel test samples. Most of these measurements were carried out at 50° C (323K). These findings supported the results of the three tests. Thus, the numbers of test pairs in the Test C were

limited to three.

8.4 Results

The results of Calibration Test A, Calibration Test B, and Calibration Test C are given in Table 8.1, Table 8.2, and Table 8.3. The tables provide the sub-test number and volume of hydrogen that was collected during a test for each method. The given volumes of hydrogen have been converted to standard volumes. That means the given volumes are the collected hydrogen volumes that are converted to standard pressure and standard temperature.

Table 8.1: Calibration test A results (4 mm thick test samples, at 150° C for 5000 minutes).

Sub-test number	Standard hydrogen volumes collected from TVHS method (cm ³)	Standard hydrogen volumes collected from eudiometer method (cm ³)
Test A1	0.29	0.23
Test A2	0.24	0.18
Test A3	0.27	0.22
Test A4	0.31	0.25
Test A5	0.32	0.29
Test A6	0.35	0.31
Average ± Std.Dev.	0.30 ± 0.03	0.25 ± 0.04

Table 8.2: Calibration test B results (12 mm thick test samples, at 150° C for 5000 minutes).

Sub-test number	Standard hydrogen volumes collected from TVHS method (cm ³)	Standard hydrogen volumes collected from eudiometer method (cm ³)
Test B1	0.31	0.24
Test B2	0.32	0.27
Test B3	0.35	0.29
Test B4	0.36	0.31
Test B5	0.37	0.30
Test B6	0.39	0.31
Average ± Std.Dev.	0.33 ± 0.04	0.29 ± 0.03

Table 8.3: Calibration test C results (4 mm thick test samples, at 50° C for 5000 minutes).

Sub-test number	Standard hydrogen volumes collected from TVHS method (cm ³)	Standard hydrogen volumes collected from eudiometer method (cm ³)
Test C1	0.15	0.09
Test C2	0.12	0.11
Test C3	0.18	0.14
Average ± Std.Dev.	0.15 ± 0.03	0.11 ± 0.03

The average values of the volumes of hydrogen for each calibration test are shown in a bar chart in Fig. 8.2. The standard deviations for the average values are also shown in the graph using error bars. The standard volumes of hydrogen that were collected using the TVHS method are the gray color bars. The standard volumes of hydrogen that were collected using the eudiometer method are the bars with the textured pattern.

8.5 Discussion

8.5.1 Calibration Test A

The TVHS test results showed that the average of collected hydrogen amount during the Calibration Test A was 0.30 cm^3 with a standard deviation of ± 0.03 . The collected average amount of hydrogen from the eudiometer method for the same test was 0.25 cm^3 with a standard deviation of ± 0.04 .

8.5.2 Calibration Test B

The TVHS test results showed that the average of collected hydrogen amount for the Calibration Test B was 0.33 cm^3 with a standard deviation of 0.04. The collected average amount of hydrogen from the eudiometer method was 0.29 cm^3 with a standard deviation of 0.03.

8.5.3 Calibration Test C

For Calibration Test C, the standard amount of hydrogen collected from the TVHS method was 0.15 cm^3 with a standard deviation of 0.03. The figures for the same in the eudiometer method were 0.11 cm^3 and 0.03.

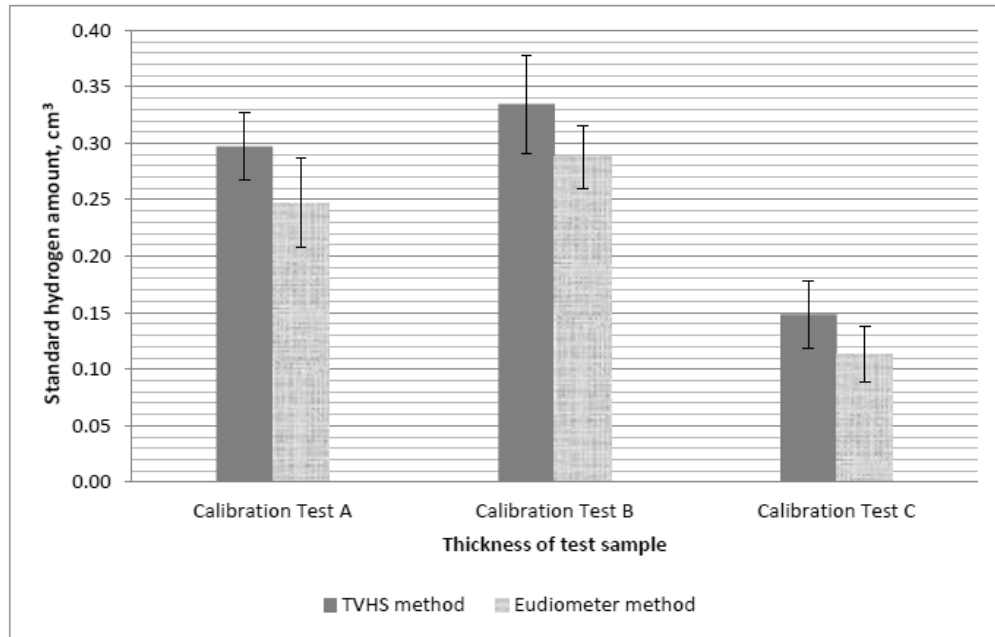


Figure 8.2: The average values of the volumes of hydrogen for each calibration test in a bar chart.

8.5.4 Unity Plot

A slight difference between the amounts of hydrogen that were collected from the eudiometer and the TVHS method was observed for all the sub-sets. A unity plot has been made to find the relationship between the amounts of hydrogen that are collected for TVHS and the eudiometer method. For the unity plot, the average values of hydrogen collected during the three calibration tests were used. The unity plot is given in Fig. 8.3.

As indicated in the figure, this is a plot of the average amounts of hydrogen from the eudiometer method against the average amounts of hydrogen from TVHS test results. According to the trending of the results,

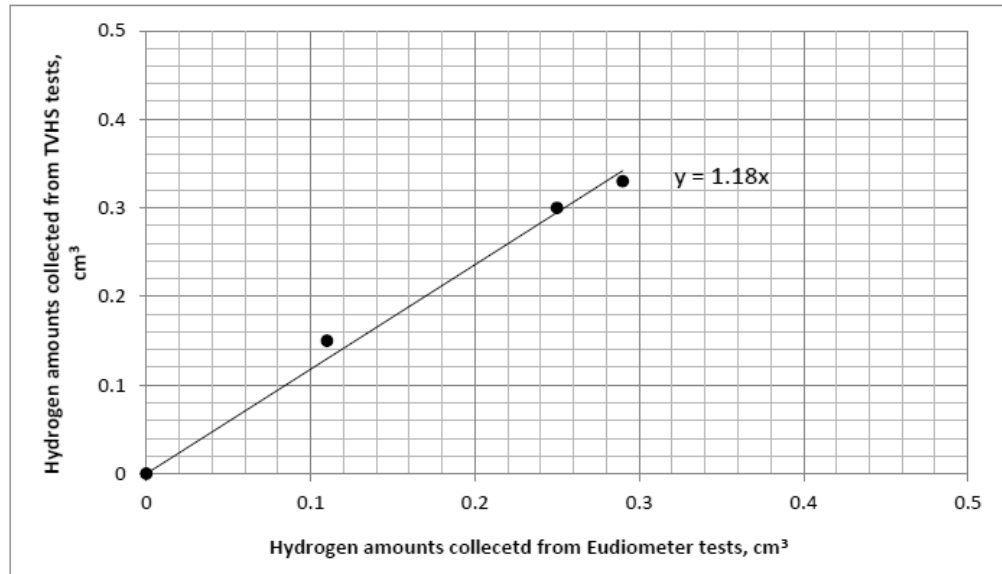


Figure 8.3: Unity plot for calibration test results.

$$H_{TVHS} = 1.18H_{Eudiometer} \quad (8.1)$$

where,

H_{TVHS} : Mean hydrogen amounts collected from the TVHS tests

$H_{Eudiometer}$: Mean hydrogen amounts collected from the eudiometer tests

Note: the average hydrogen amount is the standard hydrogen amounts that are measured in cm³.

Accordingly, when a TVHS test measured an average amount of hydrogen as 0.30 cm³, the eudiometer would measure the same amount as 0.25 cm³.

8.6 Conclusion

The TVHS can be used to measure amounts of hydrogen accurately. When the amount of hydrogen collected using the TVHS method is compared with the eudiometer method, the TVHS method registered approximately 1.18 times higher amount of hydrogen than the eudiometer method. Because this observation applied to all the sub-tests, this is considered as actual. The statistical variation of the TVHS test results is quite similar to the eudiometer test results and is not a factor in the variation between the two methods.

Chapter 9

Improvement to the Eudiometer Method

9.1 Introduction

The mercury eudiometer method also known as the mercury displacement method, is one of the most commonly used, accurate, and direct methods for measuring diffusible hydrogen contents in steels. Mercury is used as the collection medium for hydrogen because it is the only low temperature liquid metal in which hydrogen will not be dissolved or retained.

This chapter briefly describes the improvements that are implemented in the ANSI/AWS A4.3 standard standard method to improve the method's accuracy and the users' safety. More details about the improvements are available in the article titled, *Improvements in the Mercury Displacement Method for Measuring Diffusible Hydrogen Contents in Steels* [84].

In addition to the improvements, this chapter describes a quantitative analysis carried out on a surface contaminate that was collected from the mercury and that has been used in the eudiometer and the bath for a long period of time. The analysis was carried out using the Energy Dispersive Spectrometry (EDS) technique of the Phillips XL30 Scanning Election Microscope (SEM).

9.2 Standard Methods

As given in Section 2.6, there are several international standards on the mercury eudiometer method. Among these standards, the most flexible, reliable and therefore most commonly used standard is the ANSI/AWS A4.3 standard [80]. Some of the other standards include [81], [83], [82].

All these standards describe the mercury eudiometer method as a technique for determining hydrogen contents in the welded steel that hydrogen was introduced into the sample during arc welding. However, in practice, the use of mercury eudiometer method can be extended for measuring the diffusible hydrogen contents in steel samples in which hydrogen resides as a result of any number of causes.

9.3 Limitations

The mercury eudiometer method has gained its popularity mainly from the simplicity of the equipment and the ease of use. In addition, the initial setting-up cost of the equipment and operating cost are low compared to the other direct hydrogen measuring techniques.

The main limitations of this method are safety concerns arising from using mercury as the eudiometer fluid (hydrogen collection medium). Because mercury vapor is hazardous, experiments can be run only at limited elevated temperatures. This restriction makes the test duration for hydrogen collection considerably longer than for more elevated test temperature conditions: in general lower temperatures need longer times for hydrogen to diffuse out of a test sample.

9.4 Eudiometer System

The eudiometer system includes the following discrete components:

- a eudiometer tube with a capillary,
- a mercury bath,
- a heating unit, and
- a temperature measuring method.

In addition, the method needs a rough vacuum, which can be obtained by a hand vacuum pump.

9.5 Improvements to the Eudiometer Setup

A schematic of the modified eudiometer setup is given in Fig. 9.1. This modified setup incorporates a number of improvements, even though the basis of the setup follows that described in ANSI/AWS A4.3. The modifications were developed in order to improve the accuracy and the safety of the method. The modifications that were implemented on each component of the system are described as follows.

9.6 Eudiometer Tube

9.6.1 Shape

The eudiometer tube is the main component of the eudiometer system. The eudiometer tube is used to collect diffused hydrogen from the test sample, which is placed inside the tube. Three different shapes of eudiometer tubes are used commonly in

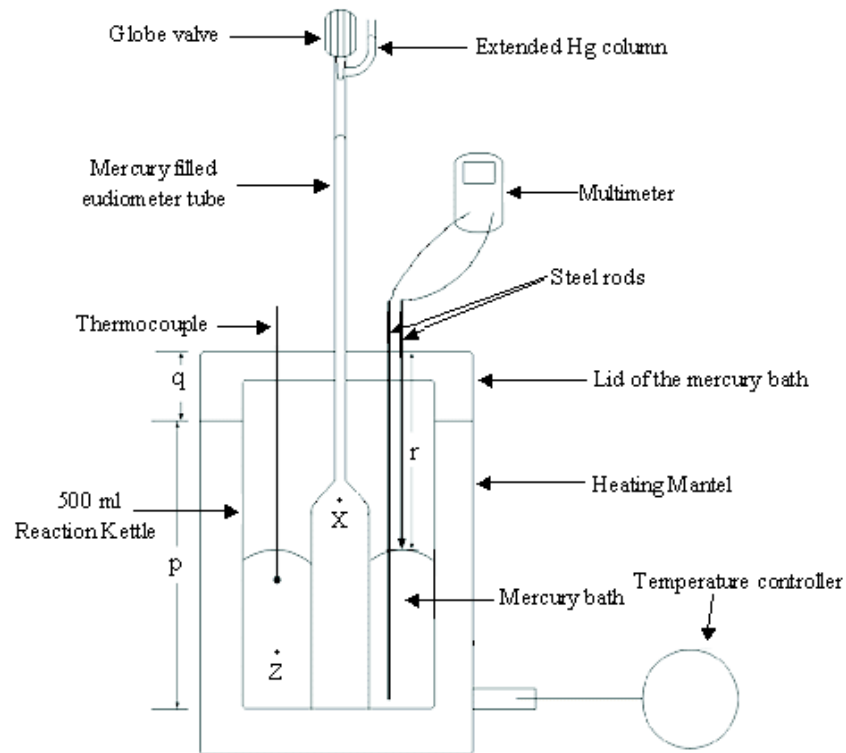


Figure 9.1: Schematic of the eudiometer test setup.

the different standards. When the performances of these shapes are considered, the shape of the eudiometer tube that is recommended in ANSI/AWS A4.3 has more advantages than the other two. Thus, the shape recommended in ANSI/AWS A4.3 was used as the basis for the improved eudiometer tube.

9.6.2 Tube Design

Initially, the lower part of the eudiometer tube was constructed with an enlarged glass- bottom bell of 45 mm in diameter to accommodate large test samples (specimens). Then, the upper part of the eudiometer tube was constructed with a calibrated capillary tube, which is 250 mm in length. Two different diameters of capil-

laries were used in the construction. The selected inner diameter of smaller capillary was 4 mm. The larger capillary with its 6 mm inner diameter was selected to measure higher levels of hydrogen without having to continually re-evacuate the capillary. In both sizes, a larger outer diameter, which gives the wall thickness of 2.75 mm, was selected to give a better degree of robustness by reducing the likelihood of breakages. This wall thickness is 37.5% larger than the wall thickness stated in ANSI/AWS A4.3

ANSI/AWS A4.3 has suggested capillary tubes with 4 mm in diameter. Even though such smaller inner diameter capillary tubes would improve accuracy from decreased volume, they cannot be used. In practice, the hydrogen cannot functionally displace the mercury and climb in the smaller inner diameter capillary without considerable mechanical help. In addition, cleaning smaller diameter tubes is difficult. Often cleaning the capillary tube is required to remove the mercury residues. The mercury residues form a thin mist on the inside wall of the glass capillary tube, making observation of the mercury level in the tube cumbersome and prone to errors.

9.6.3 Improvements for Avoiding Leaks

Leaks in the eudiometer system can cause inaccurate results. Leaks can be identified by continuing the test beyond the time required to establish the limiting state of diffusible hydrogen. A continuous decay in the vacuum from a dropping mercury level indicates a leak. However, such long observation periods make identification of leaks time consuming.

There are two locations that are likely to leak in a standard eudiometer setup: one is the possible gap between the tapered stopcock and the stopcock housing, and the other is the part of the capillary tube that rises above the stopcock. According

to experience, globe valve type stopcocks provide better leak-proof sealing than the tapered plug valve type of stopcocks that are suggested in the standard. Thus, the Teflon[®] (PTFE, Polytetrafluoroethylene) globe valve type of stopcock was used in the modified system.

In addition, a thin layer of vacuum grease was applied on the shaft and the O-rings of the globe valve to make a better contact and hence a better seal between the valve and the capillary tube wall.

If tapered plug valves were used, the possibility of leaking was minimized by introducing some mercury into the part of the capillary that rises above the valve. This was done by drawing the mercury column up through the stopcock before closing it. This same principle was applied to the globe valves. In this case, the mercury column was drawn up to a certain height in the U-shaped section of the eudiometer tube, which is indicated as *extended Hg Column* in Fig. 9.1. This method provided a direct seal on the topside of the valve therefore, in the case of the globe valve, a complete seal was obtained. However, in the case of the tapered plug valve, leakage could still occur along the side of the plug and the walls of the plug housing, which could not be eliminated.

9.6.4 Fabrication

The redesigned and improved eudiometers were fabricated in-house in the glass shop of the university. A number of identical eudiometers were fabricated to set up several eudiometer systems. Thus it was possible to carry out number of tests in parallel, without having to wait until each test was complete. The multiple test setups were also helpful when identical tests needed to be carried. A picture of the multiple

eudiometer setups is provided in Fig. 9.2.



Figure 9.2: A picture of the multiple eudiometer setups.

9.7 Test Sample Carrier

9.7.1 Need

When a test sample was placed inside the eudiometer tube, the buoyancy¹ effect caused steel test samples to float near the neck of the eudiometer tube. The following issues could occur as a result of this floating condition.

- **Difficulty in temperature control:** When the test sample floats, it is raised well above the heating source. Thus, at all times, the neck area of the eudiometer tube in which the sample is located is exposed to the room temperature

¹Density of mercury is at least one and half times higher than the density of any type of steel.

and the sample experiences lower temperatures than the temperature of an elevated mercury bath. The bath temperature is normally considered to be the test temperature. This causes an inaccurate temperature recording because at the temperature which hydrogen is collected for the sample temperature is not equal to the mercury bath temperature

- **Blockage of hydrogen bubble passage:** When a sample floats close to the neck of the eudiometer tube, it can block the path of released hydrogen bubbles into the capillary tube. Experience has shown even bouncing or tapping the eudiometer tube does not always help to clear the path and release the bubbles. Blocking the hydrogen bubbles directly affects the accuracy of the final results.

9.7.2 Design, Construction and Assembly

A special test sample carrier was designed to overcome these above-mentioned two issues. The purpose of the carrier was to force the test sample to reside in the bottom of the eudiometer tube and to maintain an orientation in which hydrogen bubbles could rise more or less unimpeded into the capillary. The carrier was constructed from glass owing to the material's inert nature. The carrier with the test sample mounting assembly is shown in Fig. 9.3 and a closer view of the assembly is given in Fig. 9.4.

Performance check

Tests were carried out to compare the amounts of hydrogen that egressed from five test sample pairs with and without the carriers. Two identically charged test samples (a pair) were used in each test: one sample with the sample carrier and the other sample without the sample carrier. The tests were carried out at 80° C for five days.



Figure 9.3: Test sample carrier.

The results of these five tests are given in Fig. 9.5. The graph clearly indicates that higher amounts of hydrogen were collected from the samples with the carrier when compared to the samples without the carrier. The average of the differences between these results was 0.05 ppm with a standard deviation of 0.01 ppm. The factor influencing the difference between these two test conditions is that of temperature difference between the test samples.



Figure 9.4: A closer view of the test sample carrier.

9.8 Mercury Bath Lid

9.8.1 Issue

Mercury does not dissolve any hydrogen. According to current research studies, mercury is the only fluid that can be used successfully as the eudiometer fluid at both room and moderately elevated temperatures. Fluids such as glycerol, paraffin, and distilled water have been used as the hydrogen collection medium in the eudiometer systems. The comparison of the performance of these fluids with mercury has shown that none of these other fluids can replace mercury and retain any degree of accuracy or reproducibility [52], [85].

The standards on the mercury eudiometer method emphasize safety precautions in handling of mercury as a result of the hazardous nature of liquid mercury and its

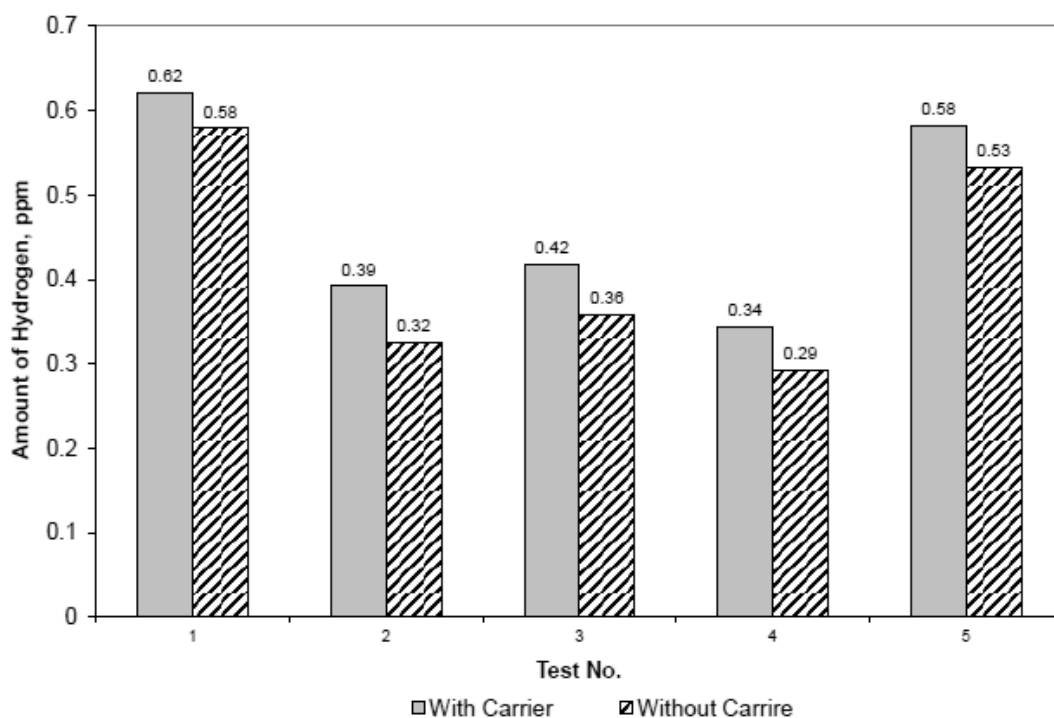


Figure 9.5: Hydrogen amounts collected from the test sample with and without the carrier.

vapors. Because mercury is a very volatile element and has a low vapor pressure, dangerous levels can readily occur in the surrounding air environment. The concentration of fumes rising from the bath surface increases with increase the of the test temperature.

9.8.2 Design, Construction and Assembly

It is important to construct a system to prevent mercury vapor entering the environment during testing. The solution was to design and construct a lid to cover the mercury bath to contain vapor during and after the tests.

The lid was constructed using Teflon[®]. Teflon[®] allowed the mercury fumes to condense and drip back into the bath without sticking to the lid's inner surface. This was important especially when opening the lid at the end of a test. It eliminated any messy spills of mercury that would occur if mercury adhered to the lid material. In addition, the Teflon was not affected by the heat of the bath.

The parts of the constructed lid and its assembly are shown in Fig. 9.6. A description on each part of the lid assembly is described below:

- **Body:** The body consisted of a large circular hole in the middle and three 2 mm-diameter through holes. One of the through holes was used as the thermocouple port. The other two holes together combined to act as mercury level measuring ports, which are described in detail later.
- **Eudiometer positioner:** This consists of two split parts, which were machined so they could be tightly fitted to the large circular hole in the middle of the lid and yet allow the capillary of the eudiometer to pass through. The capillary was able to pass through the small opening created by the two split parts. A rubber cover was easily fitted over this small opening surrounding the capillary tube to minimize the escape of the mercury fumes.
- **Clamp:** A commercially available circular steel reaction kettle clamp was used to hold the lid tightly on to the 500 ml reaction kettle containing the mercury bath.
- **Inserts:** Inserts are a type of plugs that were used to plug the ports on the body of the lid when they were not in use. These eliminate any mercury vapor that would escape through the ports.

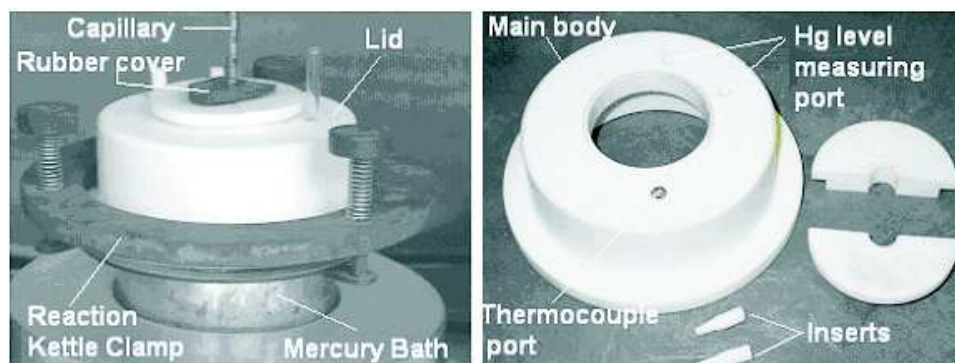


Figure 9.6: Mercury bath lid assembly and parts.

9.8.3 Advantages

As mentioned previously, the main advantage of the lids was to provide mercury vapor control, resulting in a safe working environment. Thus, the lid assembly made it possible to safely increase the test temperature to much higher levels, thereby reducing the time duration of tests. Thus, the further increase in temperature helped to collect additional progressively mobile hydrogen for test samples.

In addition, the lid system provided better insulation for the mercury bath. It resulted in preventing heat losses and efficiently stabilized the eudiometer system throughout the tests.

9.9 New mercury Level Measurement Method

In the standard eudiometer method, the mercury bath is not covered with a lid. Thus, the measurement of the mercury level, which is required in the final calculation, is carried out by simply inserting a ruler into the mercury bath. With the introduction of the lid to the bath to minimise contamination of mercury, an improved method

for measuring the mercury level was implemented.

The new method used the high electrical conductivity of mercury. To measure the mercury level, electrical continuity between two steel rods was used. During the measurement, first, one rod was immersed in the mercury bath. The free end of this rod and one end of the remaining rod with a sharp point were connected together using a multimeter set to a resistance or continuity mode. Then, the end of the sharp pointed rod was slowly inserted into the mercury bath while checking for the continuity of the circuit. When the steel point touched the surface of the mercury bath, the circuit was completed and the multimeter indicated continuity. See Fig. 9.7 for clarity. At this time, the position of the steel pointer was recorded. The depth of the mercury bath could be calculated using Equ.9.1. The depth of the mercury level in the bath is D ,

$$D = p + q - r \quad (9.1)$$

where

p : Height of the bath (excluding the thickness of the bottom)

q : Height of the Teflon lid

r : Inserted length of the steel rod

This method provided an accurate and safe method of measurement of the mercury bath depth at any temperature at any time.

9.10 Improved Test Procedure

The procedure that should be followed during the use of the mercury displacement method is explained clearly in the standards. However, additional steps that were

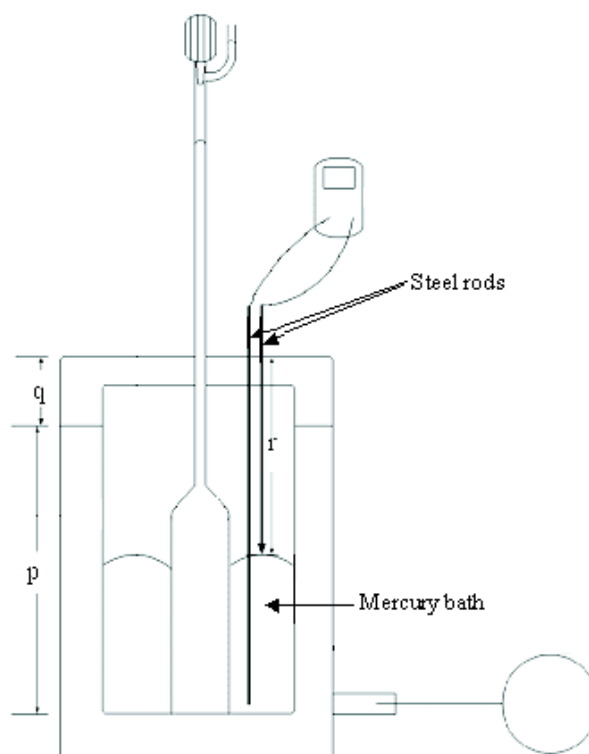


Figure 9.7: Illustration of depth measuring technique.

introduced after the improvement of the eudiometer system are explained here. Fig. 9.8 provides a photo of the improved eudiometer system.

9.10.1 System Assembly

The eudiometer system had to be assembled before starting a test. This was done by inserting the sample carrier into the eudiometer tube, then placing the test sample in the carrier, and securing the system vertically using two glass rods as shown in Fig. 9.3. next the eudiometer-test sample-carrier assembly was positioned vertically and lowered into the mercury bath. At the same time, the mercury bath lid was positioned and clamped to the reaction kettle, which contained the mercury bath,

using the circular steel reaction kettle clamps. Once this system was stable, the vacuum was drawn up slowly and carefully through the top valve of the eudiometer. A hand vacuum pump was used to draw the vacuum. When the mercury column was drawn halfway through the capillary tube of the eudiometer, the vacuum was held and the eudiometer was gently bounced against the bottom of the mercury bath to remove any entrapped air bubbles. Following this step drawing the vacuum was resumed until the mercury column reached the upper U section of the eudiometer tube. (See *extended mercury column* in Fig. 9.1 for clarity.) Finally, the valve was closed tightly to prevent any leaks. Fig. 9.8 shows the completely assembled test system. It is important that this entire action is carried out with the mercury bath at room temperature. Once the system is completely assembled, the temperature should be elevated to the required test's temperature. This procedure eliminates the rapid egress of hydrogen from the sample when immersed into hot or elevated temperature mercury during the setting up of the system.

Test duration

The test duration (or the time required to collect the total amount of diffusible hydrogen) of the mercury eudiometer method depends directly on the test temperature and varies with the chemistry of the steel. Most standards have identified the test durations as the minimum hydrogen diffusion times at the given temperature. The minimum test durations that are recommended in the standards are given in Table 9.1.

It is essential to note that the test sample dimensions and the type of test sample material play a role in the diffusion processes and therefore in the test duration. Thus, the test duration could be unique to each situation and to obtain accurate

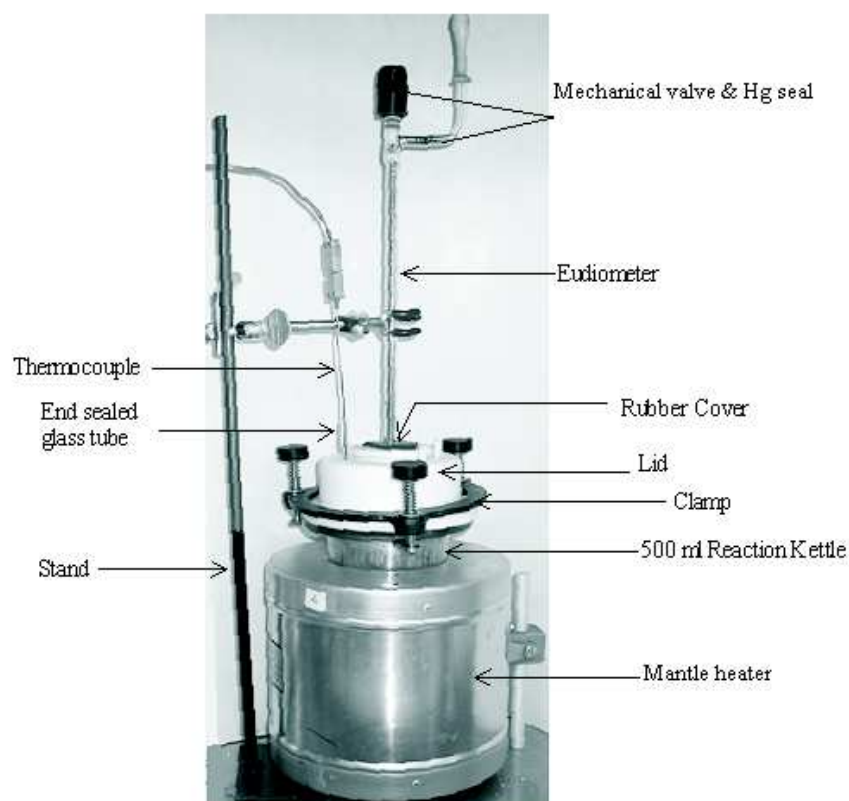


Figure 9.8: Improved eudiometer setup.

measured values of hydrogen, it is important to continue the tests for a long enough duration until no further hydrogen is found to diffuse out from the test sample.

9.10.2 Gas Column Temperature

The following equation is used to calculate the standard volume of hydrogen that egresses out from a test sample [80]:

$$V_{STP} = \frac{273.15}{273.15 + T} \frac{(P - H)V}{760} \quad (9.2)$$

where

V: measured volume of hydrogen in ml

Table 9.1: Minimum test duration at different test temperatures.

Test Temperature ° C	Minimum Duration	Standard
Room Temperature	Typically 14 days	ISO 3690 [81], AS/NZS 3752 [82]
45± 3	72 hrs	AWS A4.3 [80]
150± 3	6 hrs	AWS A4.3 [80]

T: gas column temperature in ° C

P: barometric pressure at the time of volume is measured in mmHg

H: head of mercury at the time of measurement in mm

Generally, the gas column temperature, T, is assumed to be the room temperature because of difficulties in measuring it. However, the actual measurement of the gas column temperature showed this assumption was reasonable only at a low- elevated temperature test (i.e tests that were carried out up to 45-50° C). It was observed for the tests that were carried out above 100° C. The gas column temperature was always two to four degrees higher than the room temperature.

Thus, one method to eliminate the error that occurred as a result of the observation above is adding a correction factor to the room temperature to compensate the effects of higher-elevated test temperature. This method would eliminate measuring the gas column temperature during each test, which is complex, but this method would still require the measurement of gas column temperature at least few times to derive the correction factors for each test temperature.

The other method that was successful was taking the required readings (i.e. V,T,P, and H) after the eudiometer system was brought back to room tempera-

ture. That is, in the end of a test duration, the system is allowed to cool down to room temperature before taking the readings. Then, the gas column temperature would become equal to the room temperature. This method would also eliminate possible changes to gas column pressure due to partial pressure of the mercury vapor, especially at high-elevated temperature test.

9.11 Interaction of Steel with Mercury

9.11.1 Background

When mercury was used in the eudiometer tests for an extended period without regular cleaning, a dark gray color film was seen forming on the surface of the mercury bath. The same film was also found on the inside walls of the eudiometer tube and inside the capillary tube. The mercury had to be cleaned regularly to avoid the forming film: the film made it difficult to observe the mercury level inside the capillary tube. The mercury level was required for calculating the amount of hydrogen that egressed out from a test sample. Previously, this film was considered as a form of mercury oxide.

Later, it was noticed that the amount of film-like contamination increased with the increase of the test duration and the test temperature. This observation led to a study of the interaction between steel and mercury. The main objective of the study was to find whether the dark gray film was formed as a result of a reaction between mercury and steel.

For the first step of the study, a literature review was carried out. Only a handful of studies mentioned that steel could become contaminated from mercury. The

literature review is provided in Chapter 3.

In the second step of the study, a chemical analysis on the film and a steel test sample that were in a mercury bath was carried out. The details of the analysis are given below.

9.11.2 Analysis of the Film

The details of the chemical analysis of the film found in the mercury bath and inside walls of the eudiometer tube are provided here. The analysis was carried out using the Energy Dispersive X-ray Spectrometer (EDXS) of the Phillip XL30 Scanning Election Microscope (SEM) at the Microscopy and Imaging Facility at the University of Calgary.

Before carrying out the analysis, the film was collected from the mercury bath and the inside walls of the eudiometer tube and then mounted on a base. The details on the sample collection and the method of mounting are given below.

Film collection from mercury bath

A steel sample, which was prepared as explained in Chapter 10, was charged with hydrogen and placed inside the eudiometer tube similarly to carrying out a eudiometer test. The sample was kept in the eudiometer for approximately three weeks at a temperature of 150° C. The eudiometer tube and the mercury were cleaned before the test. At the end of the test, the temperature was brought back to room temperature before collecting the film.

The film on the mercury bath was collected into a clean syringe. The collection was carried out in a careful and controlled manner to minimize the amount of mercury

drawing inside the syringe. The collected sample was then transferred to a small clean, beaker and mixed with approximately ten milliliters of distilled water. The beaker with the mixture was left to stand for few minutes. Because of the higher density of the mercury, it sank to the bottom of the beaker while the film floated on the water. The distilled water helped in separating the film from the mercury that was mixed with the film.

The film floated on the water was again collected into a new, clean syringe. Next, the wet film sample was transferred in to a clean glass dish, and the dish was left in a fume hood until it was dried. The wet film sample turned into a gray colored fine powder once it was dried,. Hereafter the film is referred as gray powder.

Film collection from eudiometer tube

As mentioned before, the gray colored film was also found sticking onto the inside wall of the eudiometer. A sample of the film was collected by rinsing the eudiometer with a small amount of distilled water until the film loosened and mixed with the water. Then, the wet sample was left inside a fume hood until the water had evaporated. Once the sample was dried, it was collected for mounting.

Sample mounting

The samples collected from the mercury bath and the eudiometers provided enough material to mount on a specimen stub or base to start the chemical analysis. A copper base was selected to mount the sample. A copper base was preferred to a carbon base because it was unlikely that the collected sample would contain copper and could possibly contain carbon. If the collected sample to be analyzed contained an element from the stub or base material, the chemical analysis would give incorrect

results by masking the elements of the base material and hence not be able to identify that element if present in the sample.

The sample was mounted on the copper base by pressing the powder sample into the tiny machined cups in the base. Once the sample was mounted, it was placed inside the vacuum chamber of the SEM to allow chemical analysis.

9.11.3 Findings on the Powder Sample

When viewing the sample with the scanning electron microscope, the mounted powder sample was black with shiny gray colored areas. It was thought that the two distinct areas were the result of having more mercury residues in one area compared to the other. It appeared that shiny gray color areas could have more mercury than the black colored area. A quantitative analysis using the EDXS was carried out on the two distinct areas as well as on an area of the copper base, well removed from the cupped location. The analyses were completed as an overall analysis on a macro area of the sample as well as spot analyses on micro areas of the sample.

The findings of the SEM analyses are given in Table 9.2. The columns of the table indicate the row numbers of the table, the location of the selected area for the analysis, the type of the analysis carried out (i.e. overall or spot), the test number, and the weight percentages of the identified elements, respectively. As indicated in the table, the identified elements were iron (Fe), carbon (C), oxygen (O), sulphur (S), mercury (Hg), and copper (Cu).

Each row of the table provides the following information.

- Rows 1 to 7 of the table provide the results of the analysis for the black areas.

Accordingly, high amounts of Hg, C, and O were identified from these areas. Minor amounts of Fe and S were also identified from the areas.

- Rows 9 to 19 of the table provide the results of the analysis for the shiny gray areas. The observations are similar to the black areas. That is, higher amounts of Hg, C, O, and smaller amounts of Fe and S are identified from the gray areas. As expected, the shiny gray areas had a higher amount of Hg than the black areas.
- Rows 22 to 27 of the table provide the analysis results for the copper base. The results indicate a high amount of Cu as expected and small amounts of C and O, which are contaminants on the copper or residual background levels as seen by the EDXS detector.

9.11.4 Conclusions on the Powder Sample

- The powder sample collected from the mercury bath and the eudiometer tube contains carbon and oxygen.
- Analysis has shown a small amount of iron in the powder sample. The amount of iron was about 2.5% of the amount of carbon in the sample.
- Analysis has shown extremely small amounts of sulphur in the powder sample. Because of the smaller quantity, it is difficult to confirm that sulphur is actually present in the sample and not measured as an error or artifact.

9.11.5 Discussion of the Powder

The chemical analysis of the powder sample showed the sample contained carbon and oxygen. The source for the oxygen could be an oxide forming from mercury

exposure to atmospheric air. The only source of carbon is from the carbon in the steel sample that was in the eudiometer. Steel contains carbon in the form of iron carbide (Fe_3C), also known as cementite. Thus mercury could have removed some carbon from the steel sample.

As a result of presence of mercury, carbon, and oxygen, the powder could be a complex of mercury-carbon-oxygen (Hg-C-O). Mercury(II) Oxalate (HgC_2O_4), which has a standard Gibbs free energy of reaction approximately - 716.3 kJ/mol² is a possible compound [86], [87] . However it is not-known that the test conditions would allow to produce a metal oxalate.

9.11.6 Analysis of a Steel Sample Immersed in Hg

A hydrogen charged steel sample that was placed in the eudiometer tube filled with mercury for about three weeks was analyzed using the SEM's EDXS technique. The objective of the study was to analyze the microstructure and chemical composition of a steel sample that was immersed in a mercury bath.

Method

Two 12 mm thick disk-shaped steel samples were prepared according to the method explained in Chapter 10. As explained, the samples were cut from a AISI 1018 steel bar and grounded using 400 grit paper. Then, the samples were charged with hydrogen using the acid pickling method. Before placing the samples in the eudiometer tube, the samples were polished and etched as required for microstructure analysis and chemical analysis using EDXS. Polishing and etching was carried out as below.

One flat surface of each ground and charged sample was further ground down

²A calculated value using entropy and enthalpy data from [86], [87]

using 600 grit paper. Then, the surfaces were polished down to one micron. Next, the polished surfaces were lightly etched using Nital³ etchant to reveal the microstructure of the steel samples.

After etching, the microstructures of the samples were observed using an optical microscope. Identical microstructures were observed in both samples. The microstructure consisted of perlite areas with a lamella pattern and ferritic areas.

After completing the microstructure analysis, one sample was placed inside the mercury eudiometer system and the temperature of the mercury was increased to 150° C. The sample was kept in the mercury-filled eudiometer for about three weeks. The other sample was kept as the base sample to compare later with the mercury immersed sample.

Then the sample which was inside the eudiometer was taken out from the mercury eudiometer system. It was well cleaned using distilled water, thoroughly dried and placed inside the SEM with the base sample to carry out the analyses.

9.11.7 Findings on Steel Sample

First the microstructures of the base sample and the mercury sample were observed from the SEM. Attention was particularly given to observe the perlite areas, which consist of ferrite and cementite lamella structure. No noticeable changes were observed between the base sample and the sample immersed in mercury (i.e the sample in the eudiometer system).

After completing the microstructure analysis, chemical analyses of the base sample and mercury immersed sample were carried out using the EDXS technique. The

³Nital is a commonly used solution for etch carbon steel samples to reveal its microstructure.

results of the analyses are given in Table 9.3. The columns of the table indicates row numbers, location of the selected area for the analysis, type of analysis carried out (i.e. overall or spot), test number, and weight percentages of the identified elements. As indicated, the identified elements were iron (Fe), carbon (C), oxygen (O), silicon (Si), Manganese (Mn), sulphur (S) and, mercury (Hg), respectively. Each row of the table provides the following information.

- Rows 1 to 5 indicate the results of the analysis on the pearlite areas of the base sample and the sample immersed in mercury. The pearlite areas of the latter have shown a 5% reduction in iron compared to the base sample that was not immersed in the bath. In addition, the pearlite areas of the sample immersed in mercury have shown higher amounts of carbon and oxygen compared to the base sample.
- Rows 7 to 11 indicate the results of the analysis on the ferrite areas of the base sample and the sample immersed in mercury. The ferrite areas of the later have also shown a 7% reduction in iron, compared to the base sample which was not immersed in the bath. In addition, the ferritic areas of the sample immersed in mercury areas showed higher amounts of carbon and oxygen compared to the base sample.

9.11.8 Conclusions for the Steel Samples

Both the pearlitic and ferritic areas of the steel sample immersed in the mercury showed higher amounts of carbon compared to the base sample. The amount of iron was less in both areas of the sample immersed in mercury, compared to the base sample.

9.11.9 Discussion for the Steel Sample

The carbon shown in the steel sample immersed in mercury could be an indication of the presence of carbon close to the surface of the sample since the electron probe in the EDX technique analyzed only to a shallow depth.

9.11.10 Overall Discussion

Section 9.11.4 concluded that the chemical analysis on the powder sample collected from the mercury bath and the eudiometer tube indicated the presence of carbon, oxygen and smaller quantity of iron were likely in the powder sample. A similar conclusion was made by analyzing the steel samples provided in Section 9.11.8 , because the chemical analysis on the steel sample showed the possibility of having a higher amount carbon compared to the base sample.

It appears that in the given test condition, the dissolution of iron is extremely low; but the test conditions seems to be favorable for dissolution of carbon . Thus the only hypothesis that could be made is hot mercury could have dissolved carbon from iron carbide (Fe_3C) in the pearlite structure, leaving the iron in the structure. The standard Gibbs free energy of reaction for Fe_3C is about 15 kJmol^{-1} [88]. The positive free energy suggests instability of the compound which could lead to easy decomposition.

If mercury could react with steels, the use of mercury in the eudiometer method could become questionable. However, this study only used hot mercury, which was at 150°C . The sample was in the eudiometer for about three weeks. According to previous experience. The film formation was also observed when the samples were in the mercury, which was at 45°C for more than a month. That suggests,

the interaction of the mercury with steel is likely time and temperature dependent. Further the film formation was not observed when steel test samples were not in presence.

As mentioned in the literature review in Chapter 3, contamination and attack of carbon steels by hot mercury which results in dissolution of iron from steel is possible. However evidence for dissolution of carbon in steel from hot mercury is not found in the available literatures. Thus, this is new knowledge and further studies are needed to conform this finding.

Table 9.2: Results of the chemical analysis on the powder sample.

Row	Location	Analysis Type	Test No.	Fe	C	O	S	Hg	Cu
1	Black area	Overall	Run1	0.31	44.91	21.19	0.89	32.72	
2	Black area	Spot	Run2-1		37.41	8.50		54.09	
3	Black area	Spot	Run2-2	0.54	35.59	11.34	0.56	52.0	
4	Black area		Average	0.43	39.30	13.68	0.73	46.27	
5	Black area	Spot without Hg	Run3-1	1.63	66.63	31.74			
6	Black area	Overall without Hg	Run3-2		68.23	31.77			
7	Black area without Hg		Average	1.63	67.43	31.75			
8									
9	Gray area	Overall	Run1	0.41	27.01	8.41	0.45	63.72	
10	Gray area	Spot	Run2-1	0.37	21.66	4.82		71.05	
11	Gray area	Spot	Run2-2	0.37	25.8	6.58	0.62	64.99	1.65
12	Gray area	Spot	Run2-3	0.42	27.75	5.26	0.50	66.06	
13	Gray area		Average	0.38	24.82	6.60	0.54	66.59	1.65
14	Gray area	Overall without Hg	Run1		61.19	38.81			
15	Gray area	Spot without Hg, Cu	Run2-1	3.01	63.21	33.77			
16	Gray area	Spot without Hg, Cu	Run2-2		63.71	36.39			
17	Gray area	Spot without Hg, Cu	Run2-3	1.31	70.49	17.05	11.05		
18	Gray area	Spot without Hg, Cu	Run2-4	1.0	66.07	18.82	14.11		
19	Gray area without Hg		Average	1.77	64.93	28.97	12.58		
20									
21									
22	Cu base	Overall	Run1		16.64	2.97			80.39
23	Cu base	Spot	Run2-1		13.48	2.31			84.2
24	Cu base	Spot	Run2-2		2.71	1.33			95.95
25	Cu base	Spot	Run2-3		2.19	1.34			96.47
26	Cu base		Average		8.76	1.99			89.25

Table 9.3: Results of the chemical analysis on the steel sample immersed in mercury.

Row	Location	Analysis Type	Test No.	Fe	C	O	Si	Mn	S	Hg
1	Pearlite base	Overall	Run1	89.84	4.24	2.99	1.51	1.51		
2	Pearlite Hg immersed	Overall	Run2-1	84.45	6.73	3.31	0.59	1.2	0.35	3.38
3	Pearlite Hg immersed	Overall	Run2-2	87.11	5.94	3.30	0.50	1.27	0.19	1.68
4	Pearlite Hg immersed	Spot	Run2-3	84.63	9.35	3.29	0.55	0.98		1.04
5	Pearlite Hg immersed		Average	85.40	7.34	3.30	0.55	1.15	0.27	2.03
6										
7	Ferrite base	Overall	Run1	97.87			0.53	1.61		
8	Ferrite Hg base	Overall	Run2-1	91.73	1.50	2.44	0	1.31	0.13	2.48
9	Ferrite Hg base	Overall	Run2-2	91.34	1.6	2.38	0.36	1.35	0.14	2.82
10	Ferrite Hg base	Spot	Run2-3	89.03	4.70	2.57	0.38	0.38	0.17	1.79
11	Ferrite Hg base		Average	90.70	2.60	2.46	0.25	1.01	0.15	2.36

Chapter 10

Test Sample Preparation

10.1 Introduction

This chapter provides information on preparing the test samples, explains the hydrogen charging method used to prepare all the test samples used in this research work.

10.2 Materials

Mild steel grade AISI 1020 was selected as the test sample material because it is one of the most commonly used and widely available type of steel for engineering applications. The chemical composition and mechanical properties of the material as per the ASTM (American Society of Testing Materials) Materials Handbook are provided in Table 10.1 , and Table 10.2 , respectively.

Table 10.1: Chemical composition of of hot rolled AISI 1020 steel bar [72].

Element	Amount %
C	0.18-0.23 max
Mn	0.30-0.60
P max	0.040 %
S max	0.050 %

Commercially available approximately 32 mm ($1 \frac{1}{8}$ inches) diameter, hot rolled steel bars were selected to prepare the test samples. All the materials required to

Table 10.2: Mechanical properties of hot rolled AISI 1020 steel bar [72].

Property	Value
Tensile strength	380 MPa
Yield strength	205 MPa
Elongation	25 %
Reduction in area	50 %
Hardness	111 HB

prepare the test samples were purchased in the initial stage of the research study. During purchasing, steps were taken to make sure that all the steel bars that were purchased belonged to the same heat (i.e. same batch) to minimize possible minor variations in the chemical composition and mechanical properties among the different heats. Thus, it was ensured that the prepared test samples had similar chemical and mechanical properties.

10.2.1 Preparation

The samples were sliced from steel bars according to the required thicknesses (i.e. 4mm or 12 mm). The slicing was carried out using a band saw to obtained disk shaped samples. The two flat surfaces of the disk shaped samples were ground down to 400 grit using Buehler's semi-automated grinder. The mill scale on the peripheral surfaces of the samples was removed by using 400 grit abrasive paper.

The samples were then baked in a furnace at 300° C for five days to remove any residual hydrogen. After baking, the surfaces of the samples were again ground, using 400 grit abrasive paper to remove any scale formed on the surfaces during baking. Finally, the samples were number-coded according to a previously selected

code to identify them during the tests. The diameter, thickness, and weight of each sample were measured.

10.3 Hydrogen Charging

10.3.1 Acid bath

The test samples were charged with hydrogen using an acid pickling method. In this method, the hydrogen charging took place at atmospheric pressure. A reliable procedure for acid pickling, which was developed by Shaw et. al was used during charging [8]. In this method, 14 wt.% HCl acid solution was used as the pickling media. The test samples were charged by immersing them in the hot acid solution, which was at 80° C. The samples were immersed for 30 minutes. The bath was slowly, but continuously agitated during that time.

The key to this charging method was the following: after charging was completed, the sample was left at room temperature for 15 minutes before it was placed in the TVHS or the eudiometer. This is to allow charged hydrogen to spread evenly inside the sample and equalize the surface hydrogen concentrations.

10.3.2 Pickling

When the steel test samples are immersed in hydrochloric acid (HCl), iron in the steel sample starts reacting with the acid. The chemical reaction are given in Section 2.1.1. It is believed that the atomic hydrogen (H) and molecular hydrogen (H_2) enter into steel.

10.3.3 Sample Holder

A special sample holder made from 316 stainless steel sheet of 1.5 mm in thickness was fabricated to hold the samples during pickling. The holder contained two holes, the size of the test sample (specimens), of tight tolerance to hold the test samples. During charging, the holder and test samples were immersed vertically into the hot acid bath. The holder helped to support the samples in such a way that the front and back surfaces were exposed to the acid as completely as possible to charge hydrogen through the two flat surfaces. Fig. 10.1 provides a schematic of the sample holder.

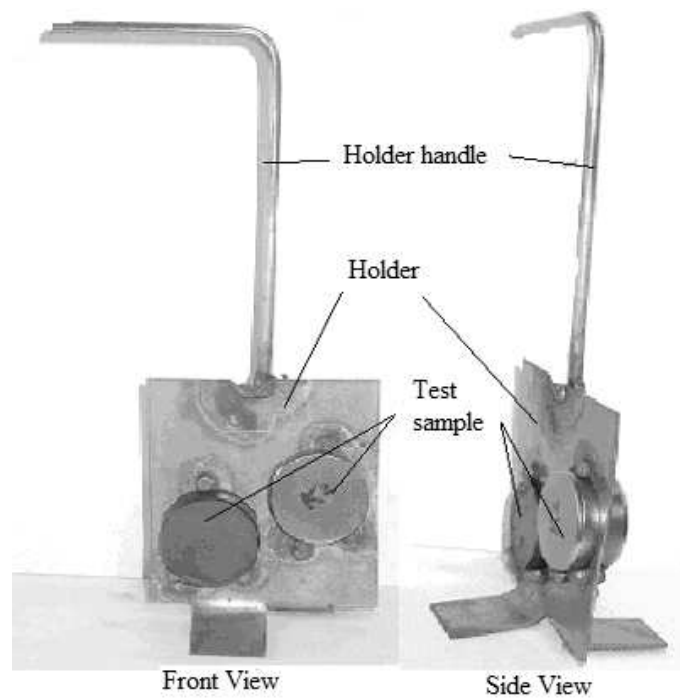


Figure 10.1: Front and side view of the holder.

10.3.4 Charging Area

Identically charged hydrogen amounts make results comparison logical and convenient. Thus during hydrogen charging, the 4 mm and 12 mm samples were desired to be charged with an identical amount of hydrogen regardless of the differences in their thicknesses. The selected charging conditions including the charging times kept identical to achieve this. However if the area that was exposed to the acid was different, the samples could have been charged with different amounts of hydrogen during pickling at a given time interval. When the surface areas were considered, the 4 mm thick sample had a smaller surface area compared to the 12 mm sample. The smaller surface area of the 4 mm sample was due to its smaller peripheral area compared to the 12 mm sample. The surface areas of front and back of both the 4 mm and 12 mm samples were identical because both sizes were cut from same steel bar.

Thus it was necessary to find a method to make the surface areas that were exposed to the hot acid bath identical for both the 4 mm and 12 mm thick samples. The method that was successful for achieving this was leaving only the front and back of the samples exposed to the acid bath by covering the peripheral areas of the samples.

Method

Accordingly a method was needed to cover the peripheral surfaces of the samples. Painting the peripheral was surfaces found to be a convenient technique. Thus a type of paint with the following properties was required:

- Able to withstand to hot hydrochloric acid

- Able to apply easily
- Able to be removed easily without leaving any residue that could decompose at elevated temperatures. (The identical surface areas were required only during the charging process. During hydrogen measurement, the samples do not need identical surface areas. Thus the paint in the peripheral surfaces could be removed when the charging process was completed. Conversely, if the paint was not removed, it could have started to decompose at elevated temperatures when measuring the hydrogen, which could result in inaccuracies in the measured hydrogen amounts. For the same reason, it was important not to leave any paint residue after removing the paint. Like the paint, the paint residue also could decompose at elevated temperatures.

After considering the different types of paint, a type of commercially available silicon sealant manufactured by GE[®] was selected for covering the peripheral surfaces of the test samples. The peripheral surfaces were covered with a thin layer of the silicon sealant using a wooden spatula. The samples were left for 24 hours for curing before being charged with hydrogen. After charging with hydrogen, before starting the hydrogen measuring tests, the covered layer of the silicon was removed by peeling it off. After peeling, the peripheral surfaces were observed using a macroscope to ensure that no residue was left behind. No residue was found at any time.

In general, during acid pickling the surfaces of a sample become a bit discolored when compared to the surfaces of a freshly ground sample. This discoloration is due to the reaction of the exposed areas of the sample with the hot acid. Conversely, the areas that are covered with silicon do not become discolored. Thus, when the silicon

coating was removed by peeling, it was possible to see a color difference between the flat surfaces and the peripheral surface; the two flat surfaces were discolored compared to the peripheral surface which was in original condition. This observation confirmed that the peripheral surfaces did not react with hot acid, so no hydrogen was charged through that surface.

Chapter 11

Results and Analysis

11.1 Introduction

The newly developed hydrogen measuring system, called TVHS (Thermal Vacuum Hydrogen System), was used in measuring hydrogen quantities in test samples made out of Grade AISI 1020 steel. The measured hydrogen amounts are used to find the following:

- the behaviour of test samples that are not charged with hydrogen (i.e. baked samples)
- the behaviour of test samples that are charged with hydrogen
- how much hydrogen would egress at different elevated temperatures
- how much hydrogen would egress at different test durations

Thus, in this chapter, the results of the tests that were carried out to find the information above and their analysis are provided.

11.2 Plotting Vacuum Decay Graphs

11.2.1 Vacuum Decay Graph

Table 6.1 shows data that were recorded during a test. The data were recorded manually because TVHS does not have an automated data acquisition system attached to it. Fig. 11.1 gives an example of a vacuum decay graph that was plotted using the

vacuum pressure decay data. All the vacuum decay graphs in this thesis have been plotted using the format explained below. The duration of the test is given on the x-axis of the graphs. The major unit of the x-axis is divided into 1440 minute-major units. This number -1440 minutes- is equal to 24 hours, which is one day (i.e. $60 \times 24 = 1440$). The y-axis of the graph indicates the vacuum pressure of the system. Thus, the graph shows how the vacuum pressure has changed over the test duration. It is important to note that the vacuum decay graphs were always plotted using the corrected vacuum pressure values unless otherwise mentioned. The reason for correcting the vacuum pressure data and the method that was used to correct that data is explained in Section 5.7.1.

Additionally, the legend of the graph provided additional information about the test. For example, the legend in the given graph reads **4-mm sample at 150° C, RUN1**, which means the curve is for the first test of an identical set of tests that was conducted at 150° C (423.15K) using a 4-mm thick test sample.

Initial and final corrected vacuum pressures were marked on the graph, these corresponding to the room temperature condition. The difference in the vacuum pressure was caused by the egress of hydrogen from the test sample.

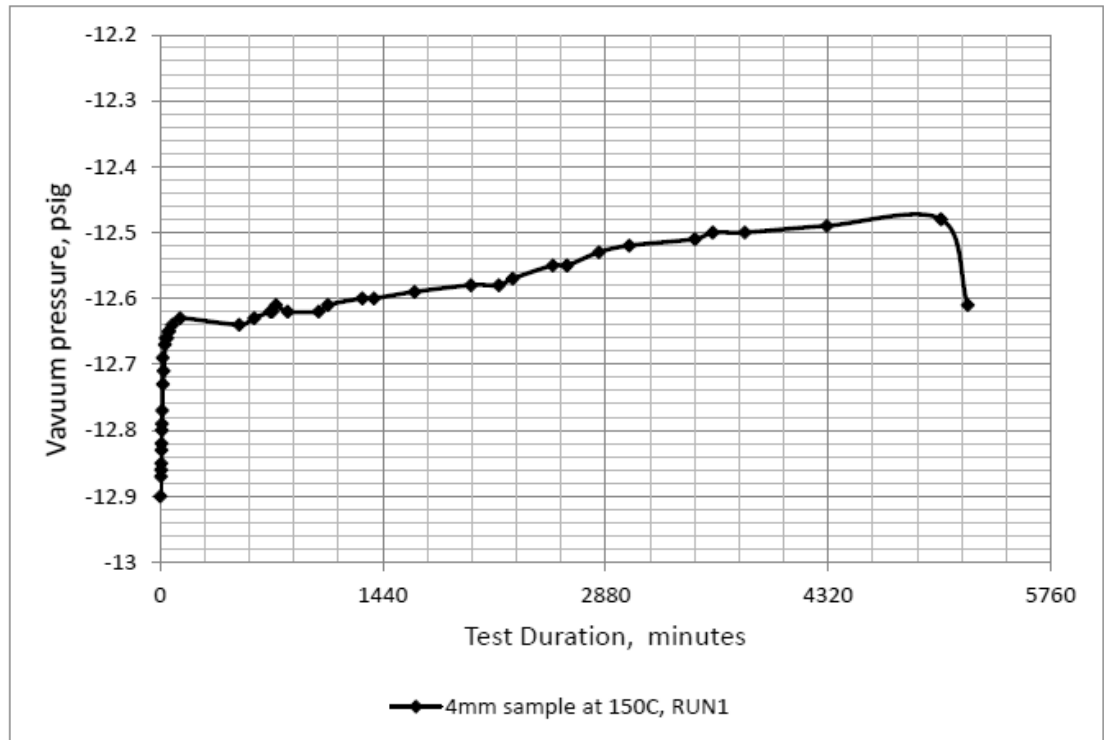


Figure 11.1: An example of a typical vacuum decay graph for hydrogen charged test sample.

11.2.2 Vacuum Decay Graph with Test Temperature

The curve, which is shown with a black line with solid black dots provided in Fig. 11.2, illustrates how the test temperature was controlled during a test. During a test, the temperature of the test sample was elevated to a predetermined level and held at that temperature during the test. In the example given, the predetermined temperature was 150° C (423.15K). The temperature values can be read from the secondary y-axis of the graph. At the end of the test, the temperature of the test sample was brought back to room temperature.

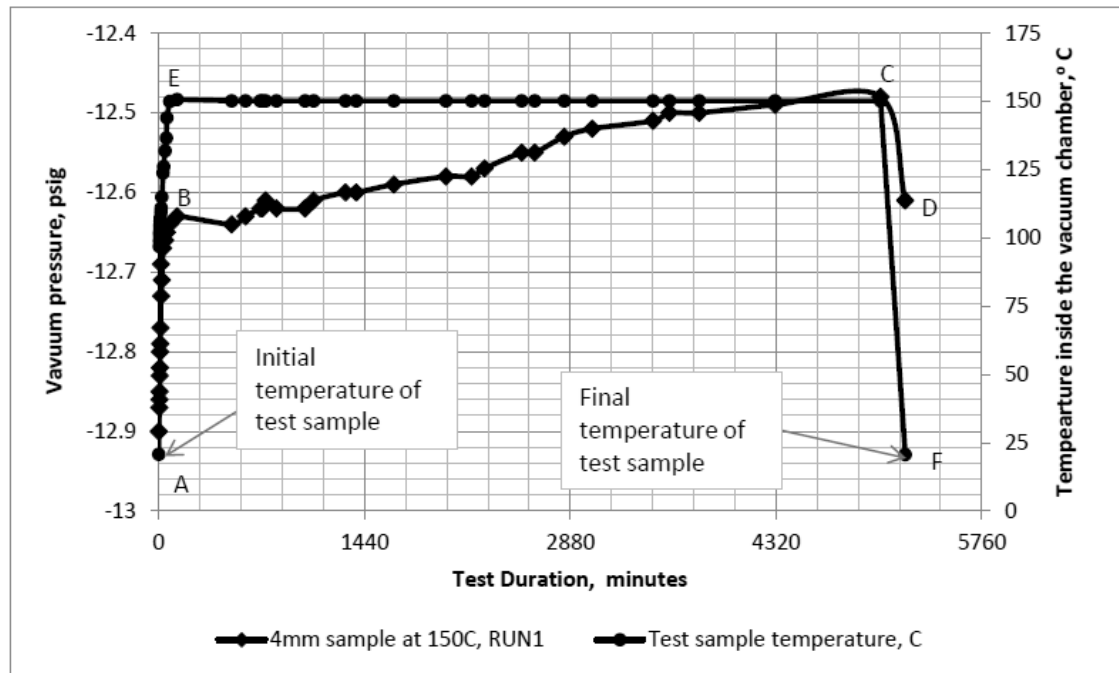


Figure 11.2: An example of a typical vacuum decay graph showing how the test temperature was controlled during a test.

As shown from the segment between A and B of the vacuum decay graph (black line with solid diamond shapes) that is given in Fig. 11.2, initially, the vacuum decay was faster. This was a result of an increase of the test temperature and accumulation of hydrogen. This can be further explained as given below:

According to Gay-Lussac's law, for a given amount of gas held at constant volume, the pressure is proportional to the absolute temperature [90]. Mathematically, this can be represented by

$$P \propto T \quad (11.1)$$

or

$$\frac{P}{T} = K \quad (11.2)$$

where P and T are pressure and temperature of the closed system, and K is a constant.

Thus, with an increase in temperature, the pressure of a closed system increases because, when the temperature of a gas increases, the kinetic energy of the particles inside the closed system increases. This means that they move faster and apply a greater force when they collide with the walls of the container. In a vacuum system, increase in pressure is indicated by a decay in the vacuum.

When the temperature reached the required test temperature, in this case 150° C (423.15K) as shown by point E of Fig. 11.2, it was stabilized at that value. With stabilization, the rate of the decay in the vacuum slowed down, which is illustrated in the B to C section of the graph. At this time, the decay in the vacuum was the result of the amounts of hydrogen egressing from the test sample. The rate of the vacuum decay slowed down further over time from the reduction in the amounts of hydrogen that egressed from the test sample.

At the end of a test, the vacuum chamber temperature was brought back to room temperature. This is indicated in point F of the temperature curve. The change in the vacuum pressure during this time is indicated in the segment between C and D of the vacuum decay graph. It is interesting to note that the segment CD indicates an increase in the vacuum pressure (not a decay in the vacuum). That is, the vacuum pressure has changed from about -12.48 psig (point C) to -12.62 psig (point D because

of the decrease in the temperature in the vacuum chamber. However, when point D of the graph is compared with point A of the graph, it indicates a vacuum drop of about 0.3 psig. This is the decay in vacuum pressure as a result of the egress of hydrogen from the test sample during the test.

11.3 Behaviour of Baked Samples

Fig. 11.3 shows the vacuum decay graph for a baked sample. The baked sample is a test sample that was baked in an oven at 400° C for 10080 minutes (7 days) to ensure that no residual hydrogen was left in the test sample.

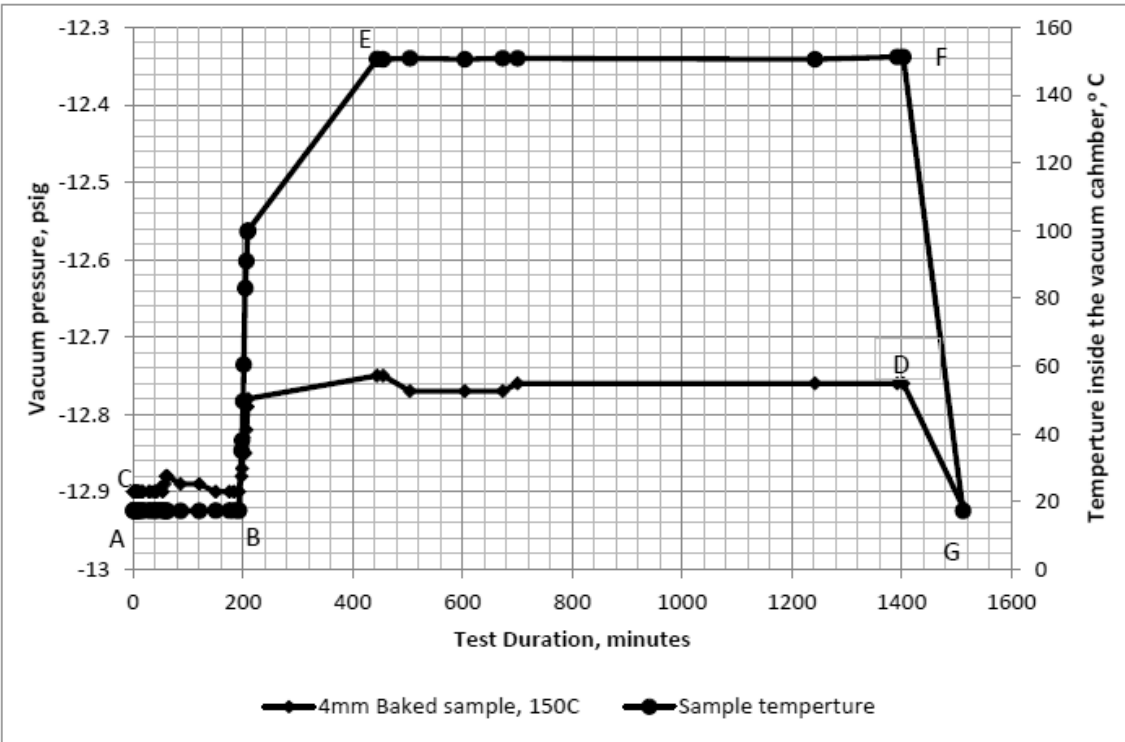


Figure 11.3: An example of a typical vacuum decay graph for a baked test sample.

11.3.1 Objective

The objective of these tests was to find out how vacuum pressure would be changed when a baked sample was placed in the vacuum chamber. Baked samples are normally thought to not contain any mobile hydrogen.

11.3.2 Results and Analysis

Tests at room temperature

A typical vacuum decay graph for a baked sample is shown in Fig. 11.3. The black solid line with dots indicates how the temperature was controlled during the test. As indicated in segment AB of the graph, during the first 200 minutes of the test, the test temperature was kept at room temperature¹. The vacuum decay curve is shown in the solid blue line with diamond shapes. As indicated from segment AB, vacuum pressure remained unchanged during this period². This can be expected from a baked test sample. Because there is no hydrogen to egress out from the test sample, the vacuum pressure should remain constant, providing there are no leaks in the system.

Tests at elevated temperature

After the sample was tested at room temperature, the temperature was elevated to 150° C (423.15 K). The sample was held at this temperature for about 1200 minutes, which is about 20 hours. At the end of the test, the temperature was brought back to room temperature.

With the increase of the test temperature, the vacuum pressure started to decay

¹The test sample temperature is given by the secondary y axis of the graph. X axis indicates the test duration.

²The vacuum pressure is given by the primary y axis of the graph.

like the test sample that was charged with hydrogen. However, the magnitude of the decay from the baked sample was less than that of the charged sample. That is, when Fig. 11.2 and Fig. 11.3 are considered, the initial vacuum decay of the hydrogen charged sample was about 0.28 psi [i.e. $-12.62 - (-12.9)$]. In comparison, the initial vacuum decay for the baked sample was about 0.14 psi [i.e. $-12.78 - (-12.92)$]. For the hydrogen-charged sample, the contributing factor for the higher vacuum decay is egress of hydrogen from the test sample. However, for the baked sample, the contributing factor for the vacuum decay was only the increase in the temperature, because there was no hydrogen to egress out of the sample.

As indicated from the segment CD of Fig. 11.3, with the elapse of time, a noticeable change in the vacuum pressure was not observed. This was obvious because there were no contributing factors (such as change in the temperature, egress of hydrogen from the test sample) for change in the vacuum pressure. When this section was compared with the segment BC of Fig. 11.2, the latter showed a gradual decay in vacuum as a result of the egress of hydrogen from the test sample.

Back to room temperature

The point G of Fig. 11.3 indicates the vacuum pressure after the test sample was brought back to room temperature. As the test conditions at the end of the test were identical to the conditions at the beginning of the test, the vacuum pressure has also reached the original level. If this is compared with point D of the Fig. 11.2, the point has not reached to the original vacuum pressure. As explained in Chapter 5, this is because of accumulation of hydrogen, but in the baked sample, there was no hydrogen to accumulate. The calculated hydrogen amounts of the baked samples showed the mean hydrogen amount is 0.004 cm^3 at the standard pressure

and temperature, which is a much smaller quantity.

Volume expansion and contraction

The changes in the test temperature caused volume expansion and contraction in the vacuum chamber. This could also be a contributing factor for the changing vacuum pressure. However, as explained in Chapter 5, the whole TVHS system was brought back to room temperature to avoid any effects from the changing temperature.

11.4 Behaviour of Hydrogen Charged Samples

11.4.1 Objective

The objectives of the tests were to establish the behaviour of the hydrogen charged test sample and use the TVHS to determine the amounts of hydrogen in a steel test sample.

11.4.2 Results of 4 mm Test Samples

The vacuum decay graphs for the five tests for the 4-mm thick test sample is given in Fig. 11.4. The test duration of each test was approximately 5000 minutes (~ 3.5 days).

The amounts of hydrogen collected during each test are given in Table 11.1. The hydrogen amounts are given as standard volumes in cubic centimeter. According to the results, an average amount of 0.30 cm^3 of hydrogen was collected from the 4-mm thick test sample in the given test conditions (i.e. at 150°C for a duration of approximately 5000 minutes).

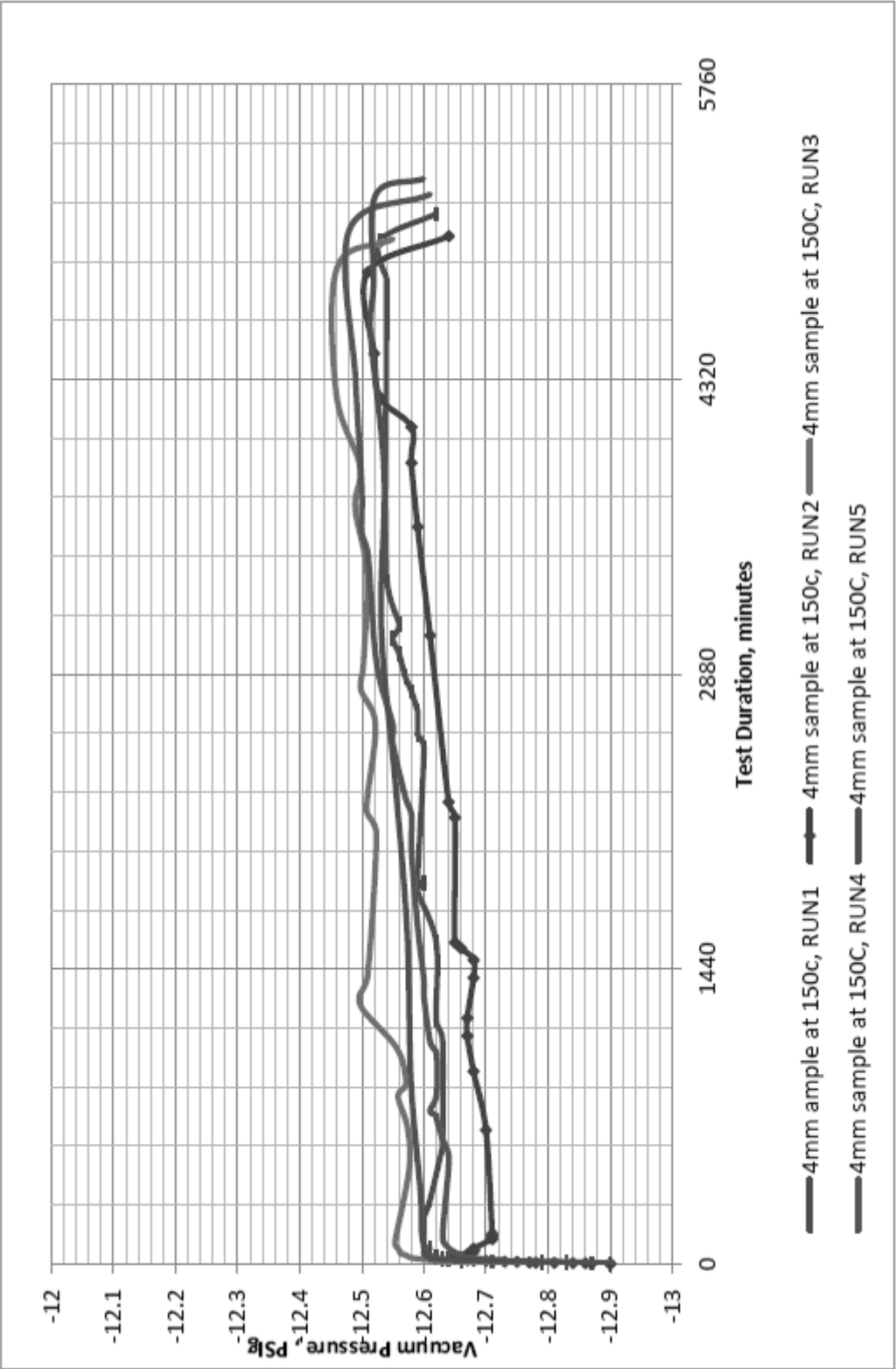


Figure 11.4: Vacuum decay graphs for hydrogen charged 4 mm thick sample.

Table 11.1: Amounts of hydrogen that egressed out from the 4 mm thick test samples, during tests at 150° C for a duration of 5000 minutes

Sub-test number	Standard hydrogen volumes collected from TVHS method (cm ³)
Run 1	0.35
Run 2	0.24
Run 3	0.27
Run 4	0.32
Run 5	0.31
Mean $\pm$ Std.dev.	0.30 $\pm$ 0.04

11.4.3 Results of 12 mm Test Sample

The vacuum decay graphs for the five tests for the 12 mm thick test sample are given in Fig. 11.5. The duration of each test was approximately 5000 minutes ($\sim$ 3.5 days). The amounts of hydrogen collected during each test are given in Table 11.2. According to the results, an average amount of 0.34 cm³ of hydrogen was collected from the 12 mm thick test sample in the given test conditions (i.e., at 150° C for a duration of approximately 5000 minutes)

11.4.4 Analysis

An average volume of 0.30 cm³ of hydrogen egressed from the 4 mm disk-shaped test samples. An average volume of 0.34 cm³ of hydrogen egressed from the 12-mm disk-shaped test samples.

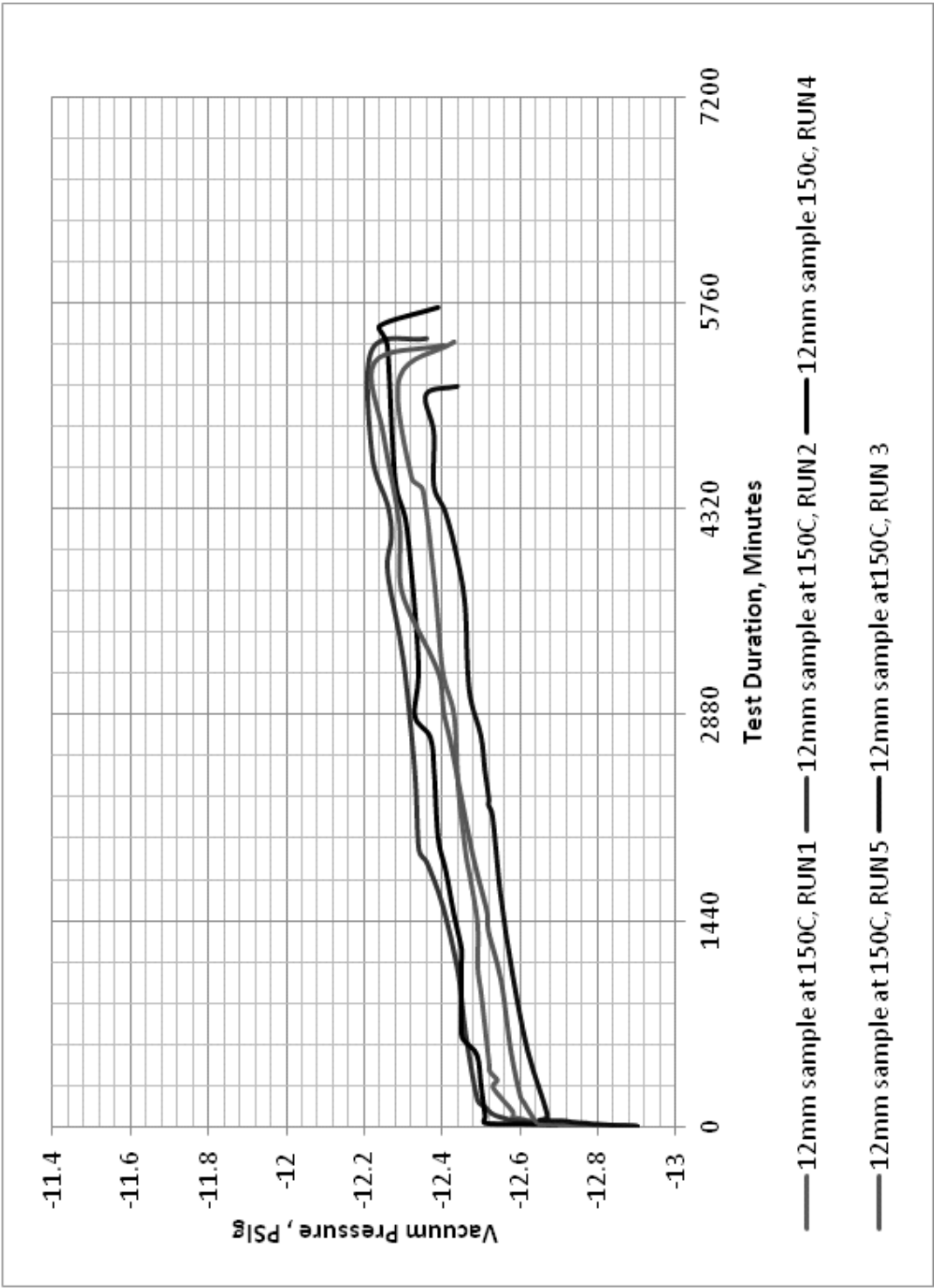


Figure 11.5: Vacuum decay graphs for hydrogen charged 12 mm thick sample.

Table 11.2: Amounts of hydrogen that egressed out from the 12-mm thick test samples, during tests at 150° C for a duration of 5000 minutes

Sub-test number	Standard hydrogen volumes collected from TVHS method (cm ³)
Run 1	0.37
Run 2	0.30
Run 3	0.36
Run 4	0.39
Run 5	0.30
Mean $\pm$ Std.dev.	0.34 $\pm$ 0.04

11.5 Hydrogen Measurement at Different Temperatures

11.5.1 Objective

The objectives of these tests were to determine hydrogen amounts in steel test samples that were at different temperatures using the TVHS. The 4-mm thick samples were tested at 50° C, 150° C, 250° C, and 350° C and 12-mm samples were tested at 150° C, 250° C, and 350° C. For each selected temperature, at least five identical tests were carried out. The duration of each test was about 2900 minutes, which is approximately 2 days.

11.5.2 Test Results for 4-mm Test Samples

Tests at 50° C

The vacuum decay graphs for the first three tests for the 4-mm thick test samples at 50° C are given in Fig. 11.6. The average amount of hydrogen collected during the five tests along with the standard deviation is given in Table 11.3. An average standard amount of 0.09 cm³ of hydrogen was collected at 50° C for a period of approximately 2900 minutes.

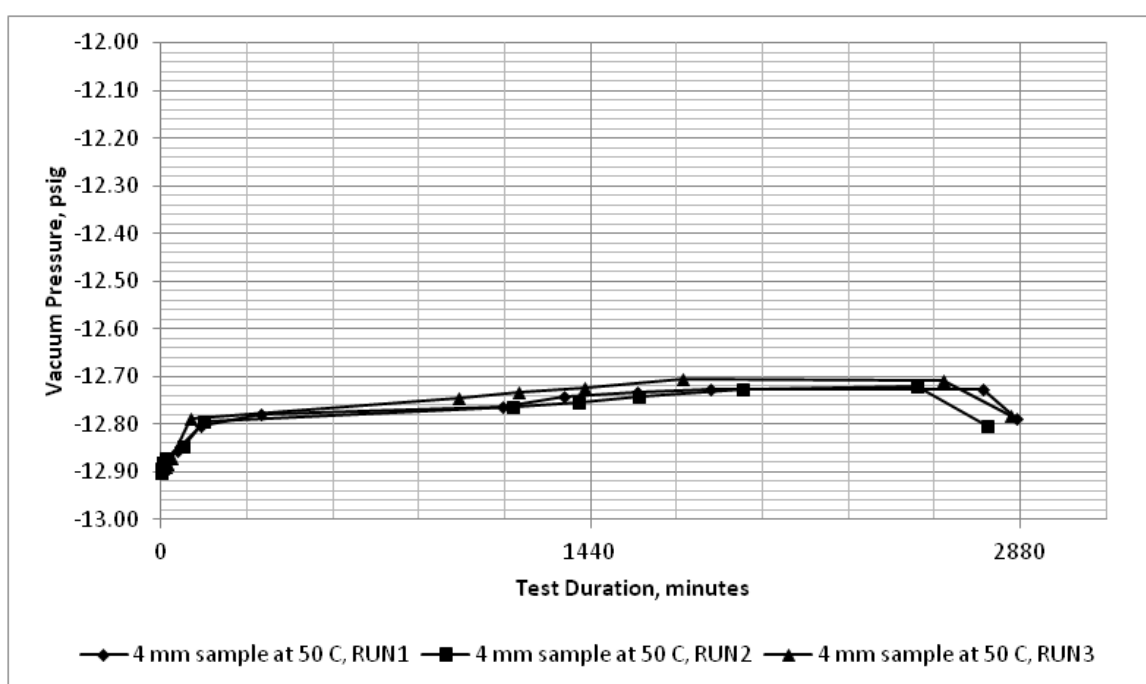


Figure 11.6: Vacuum decay graphs for hydrogen charged 4 mm thick sample at 50° C tests.

Table 11.3: Amounts of hydrogen that egressed out from the 4 mm thick test samples, during tests at 50° C for a duration of 2900 minutes

4-mm test sample at 50° C	Hydrogen volume at STP, cm ³
Run 1	0.09
Run 2	0.10
Run 3	0.10
Run 4	0.08
Run 5	0.10
Mean $\pm$ Std.dev.	0.09 $\pm$ 0.01

Tests at 150° C

Fig. 11.7 gives the vacuum decay graphs for the first three tests that were carried out at 150° C. Table 11.4 gives the average amount of hydrogen collected during five tests. An average standard amount of 0.25 cm³ of hydrogen was collected at 150° C for a period of approximately 2900 minutes.

Table 11.4: Amounts of hydrogen that egressed out from the 4 mm thick test samples, during tests at 150° C for a duration of 2900 minutes

4-mm test sample at 150° C	Hydrogen volume at STP, cm ³
Run 1	0.32
Run 2	0.24
Run 3	0.20
Run 4	0.24
Run 5	0.28
Mean $\pm$ Std.dev.	0.25 $\pm$ 0.05

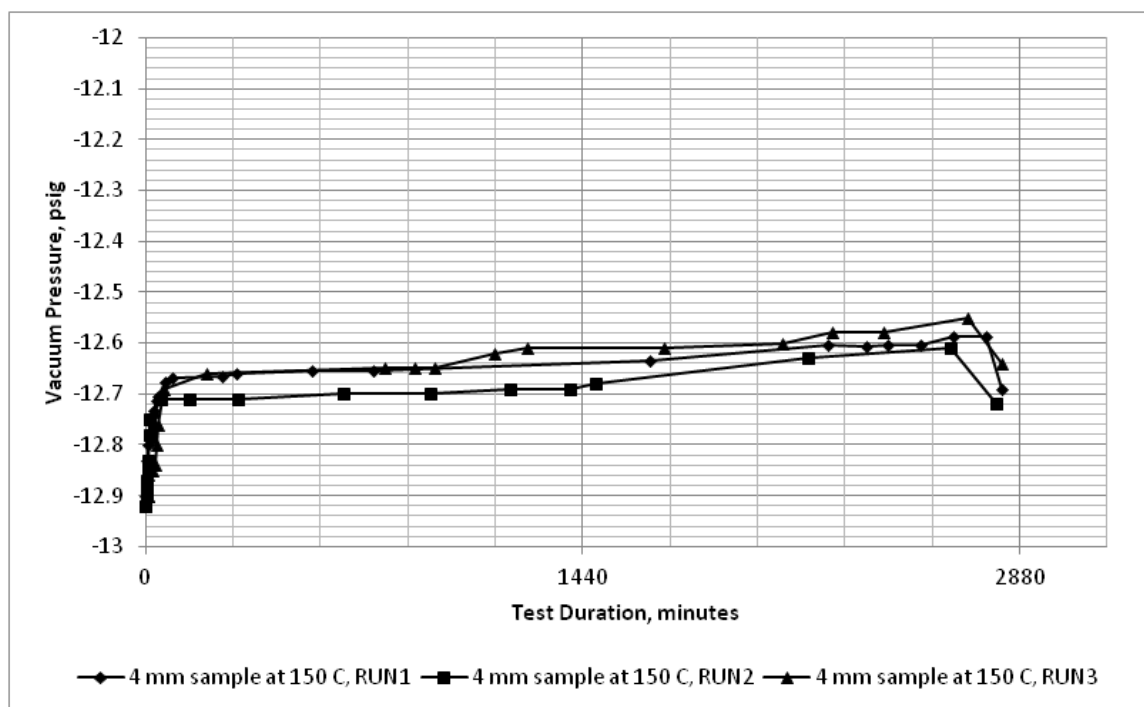


Figure 11.7: Vacuum decay graphs for hydrogen charged 4-mm thick sample at 150° C, 2900 minutes tests.

Tests at 250° C

The vacuum decay graphs for the first three tests for the 4 mm thick test samples at 250° C are given in Fig. 11.8. Table 11.5 provide the average amount of hydrogen collected during five tests. An average standard amount of 0.35 cm³ of hydrogen was collected at 250° C for a period of approximately 2900 minutes.

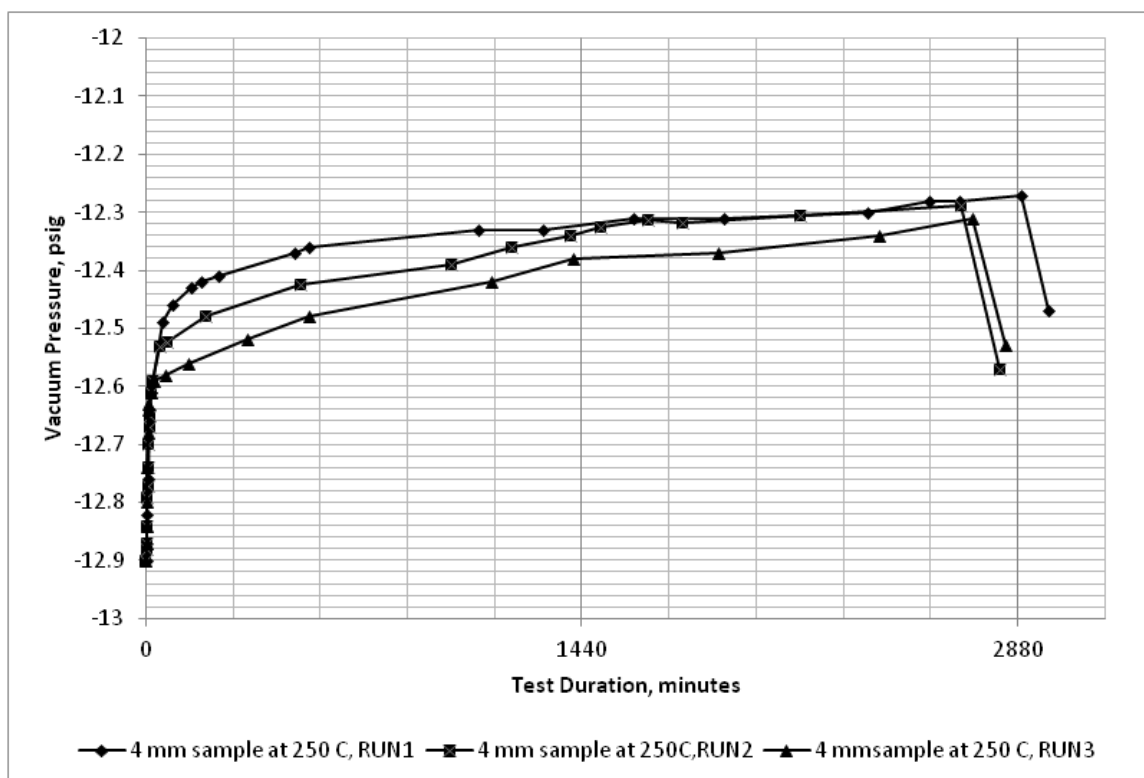


Figure 11.8: Vacuum decay graphs for hydrogen charged 4-mm thick sample at 250° C, 2900 minutes tests.

Table 11.5: Amounts of hydrogen that egressed out from the 4-mm thick test samples, during tests at 250° C for a duration of 2900 minutes

4-mm test sample at 250° C	Hydrogen volume at STP, cm ³
Run 1	0.34
Run 2	0.40
Run 3	0.31
Run 4	0.38
Run 5	0.31
Mean ± Std.dev.	0.35±0.04

Tests at 350° C

Fig. 11.9 gives the vacuum decay graphs for the first three tests that were carried out at 350° C. Table 11.6 gives the amounts of hydrogen collected during five test. An average standard amount of 0.95 cm³ of hydrogen was collected at 350° C for a period of approximately 2900 minutes.

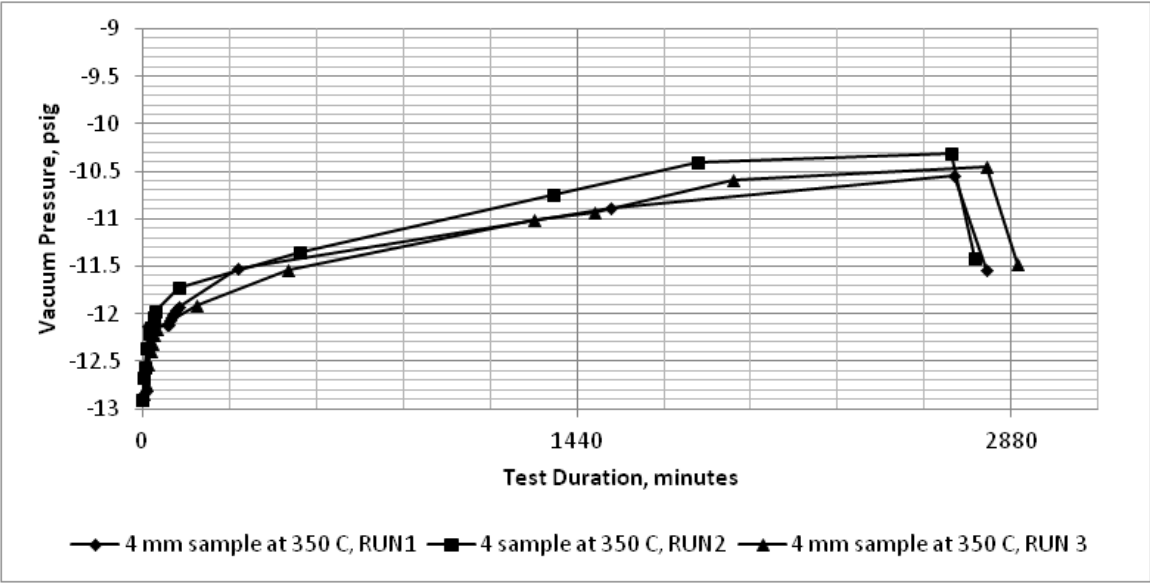


Figure 11.9: Vacuum decay graphs for hydrogen charged 4-mm thick sample at 350° C, 2900 minutes tests.

Table 11.6: Amounts of hydrogen that egressed out from the 4 mm thick test samples, during tests at 350° C for a duration of 2900 minutes

4-mm test sample at 350° C	Hydrogen volume at STP, cm ³
Run 1	0.99
Run 2	0.94
Run 3	0.92
Run 4	0.97
Run 5	0.93
Mean $\pm$ Std.dev.	0.95 $\pm$ 0.03

11.5.3 Test Results for 12 mm Test Samples

Tests at 150° C

The vacuum decay graphs for the first three tests for the 12 mm thick test samples at 250° C are given in Fig. 11.10. Table 11.7 shows the average amount of hydrogen collected during five tests. An average standard amount of 0.28 cm³ of hydrogen was collected at 150° C for a period of approximately 2900 minutes.

Table 11.7: Amounts of hydrogen that egressed out from the 12 mm thick test samples, during tests at 150° C for a duration of 2900 minutes

12-mm test sample at 150° C	Hydrogen volume at STP, cm ³
Run 1	0.26
Run 2	0.34
Run 3	0.23
Run 4	0.28
Run 5	0.26
Mean $\pm$ Std.dev.	0.28 $\pm$ 0.04

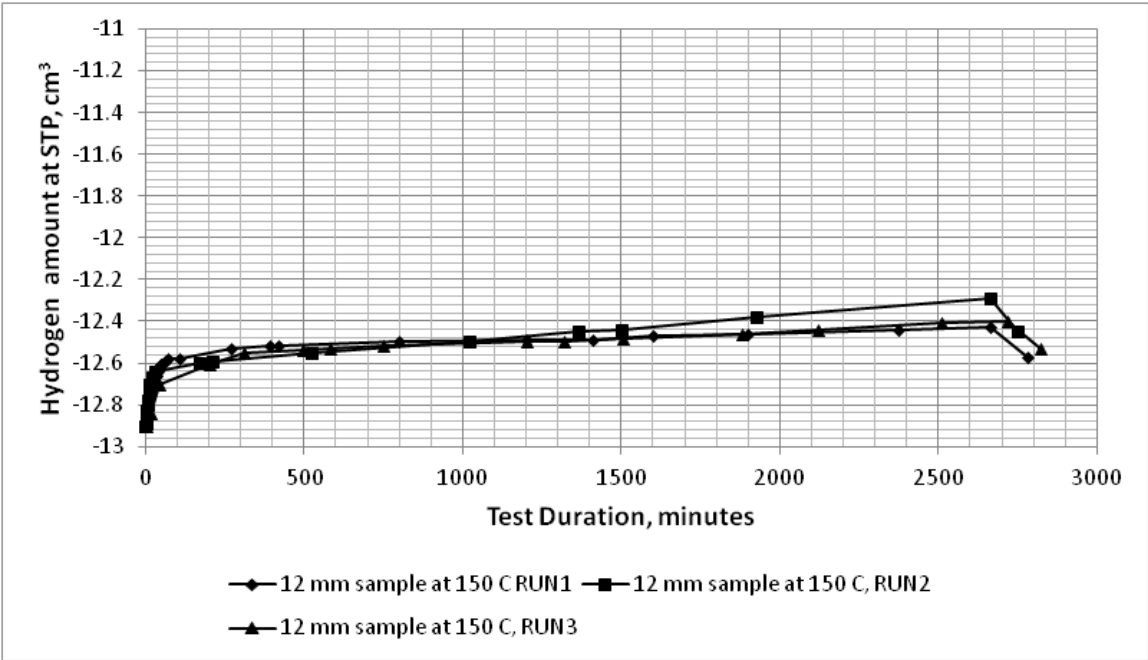


Figure 11.10: Vacuum decay graphs for hydrogen charged 12 mm thick sample at 150° C, 2900 minutes tests.

Tests at 250° C

The vacuum decay graphs for the first three tests for the 12 mm thick test samples at 250° C are given in Fig. 11.11. Table 11.8 provide the average amount of hydrogen collected during five tests. An average standard amount of 0.48 cm³ of hydrogen was collected at 250° C for a period of approximately 2900 minutes.

Tests at 350° C

Fig. 11.12 gives the vacuum decay graphs for the first three tests that were carried out at 350° C, and Table 11.9 provides the average amount of hydrogen collected during five tests. An average standard amount of 1.06 cm³ of hydrogen was collected at 350° C for a period of approximately 2900 minutes.

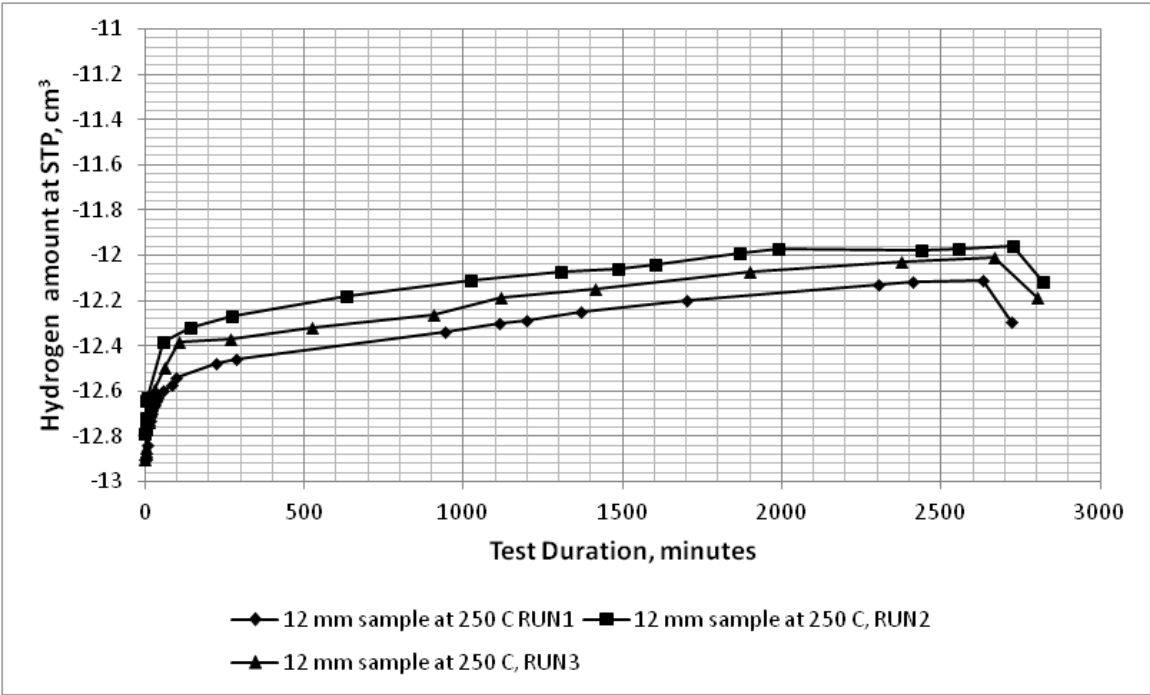


Figure 11.11: Vacuum decay graphs for hydrogen charged 12-mm thick sample at 250° C, 2900 minutes tests.

Table 11.8: Amounts of hydrogen that egressed out from the 12-mm thick test samples, during tests at 350° C for a duration of 2900 minutes

12 mm test sample at 250° C	Hydrogen volume at STP, cm ³
Run 1	0.44
Run 2	0.56
Run 3	0.53
Run 4	0.47
Run 5	0.45
Mean ± Std.dev.	0.48±0.04

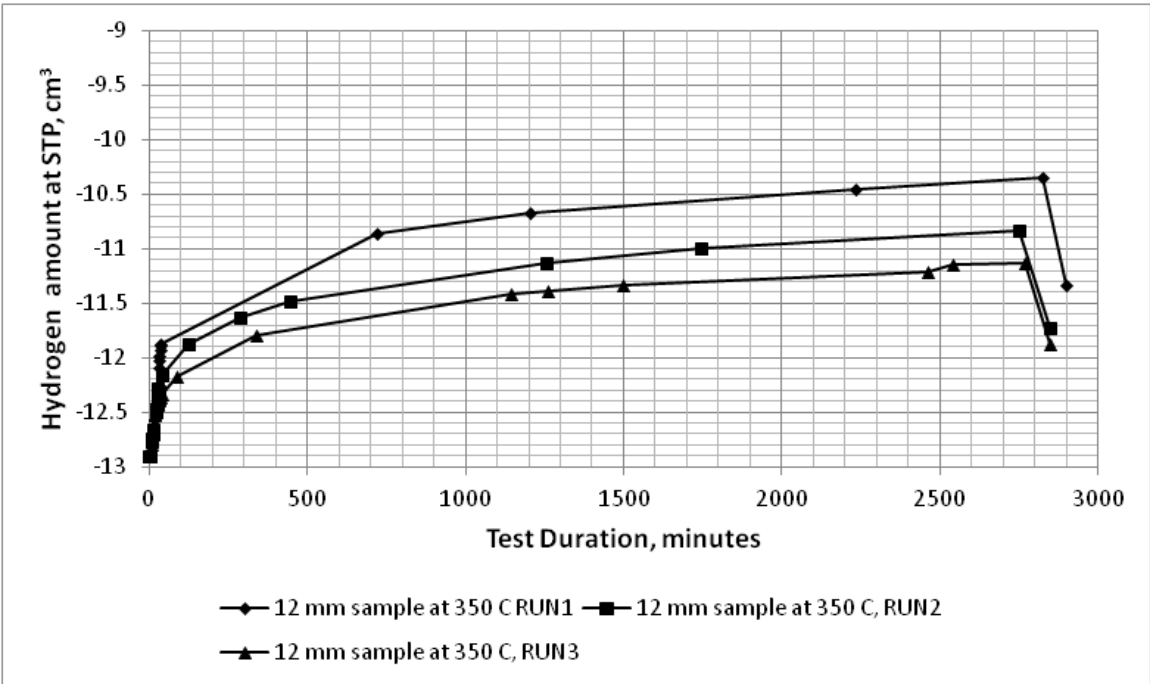


Figure 11.12: Vacuum decay graphs for hydrogen charged 12-mm thick sample at 350° C, 2900 minutes tests.

Table 11.9: Amounts of hydrogen that egressed out from the 12-mm thick test samples, during tests at 350° C for a duration of 2900 minutes

12-mm test sample at 350° C	Hydrogen volume at STP, cm ³
Run 1	1.10
Run 2	1.05
Run 3	1.04
Run 4	1.06
Run 5	1.03
Mean ± Std.dev.	1.06±0.03

11.5.4 Analysis

Fig. 11.13 compares the hydrogen amounts collected from the 4-mm and 12-mm test samples at different elevated temperatures. The error bars provide the standard deviation for the average hydrogen amounts.

According to the figure, the curves for the 4-mm and 12-mm thick samples followed a similar pattern. As explained in Chapter 10, both the 4-mm and 12-mm thick samples were charged with what was originally thought to be the same amount of hydrogen. However, the average amount of hydrogen for the 12-mm thick samples showed a slightly higher amount of hydrogen than the 4-mm thick samples.

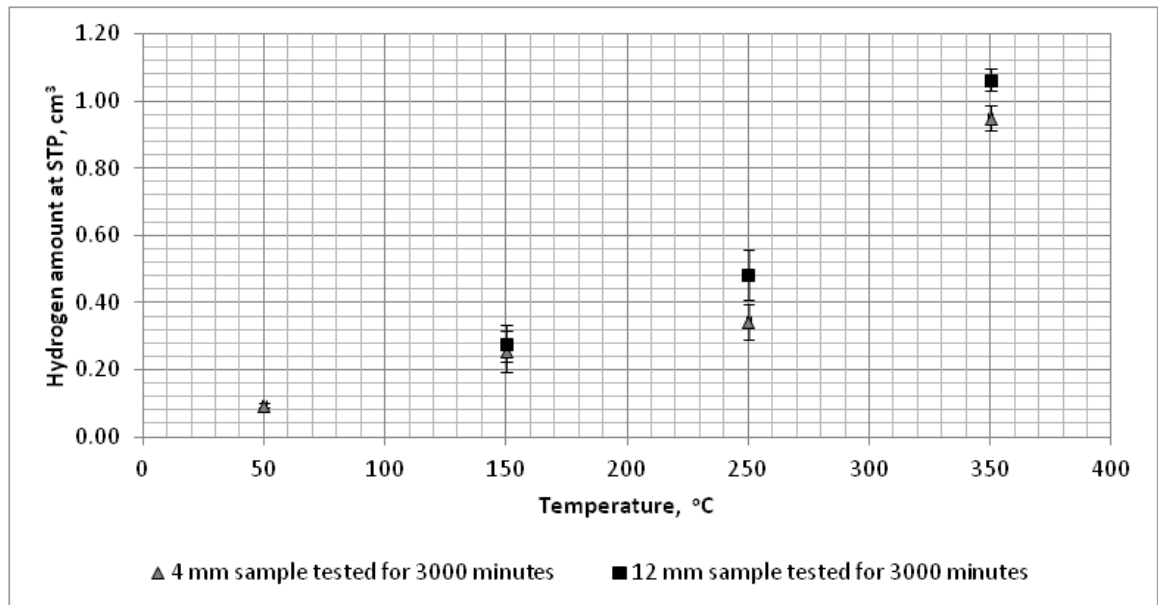


Figure 11.13: Comparison of hydrogen amounts collected from the 4-mm and 12-mm test samples at different elevated temperatures.

Fig. 11.14 compares the hydrogen amounts collected from the 4-mm and 12-mm test samples as a percentage of the hydrogen amount collected at 350° C for each

thickness. For example, at 50° C, the percentage of hydrogen amount = (amount collected at 50° C/amount collected at 350° C) x 100 = (0.09/0.95) x 100 = 10%. Accordingly, when the amount of hydrogen that egressed at 50°, 150°, 250°, and 350° C are compared, it is apparent that a significant amount of hydrogen had egressed at 350° C. Because of this significant change in the amounts, the test samples that were used at 350° C were reheated to the same temperature to learn their behaviour. More details of these test results are given in Chapter 12.

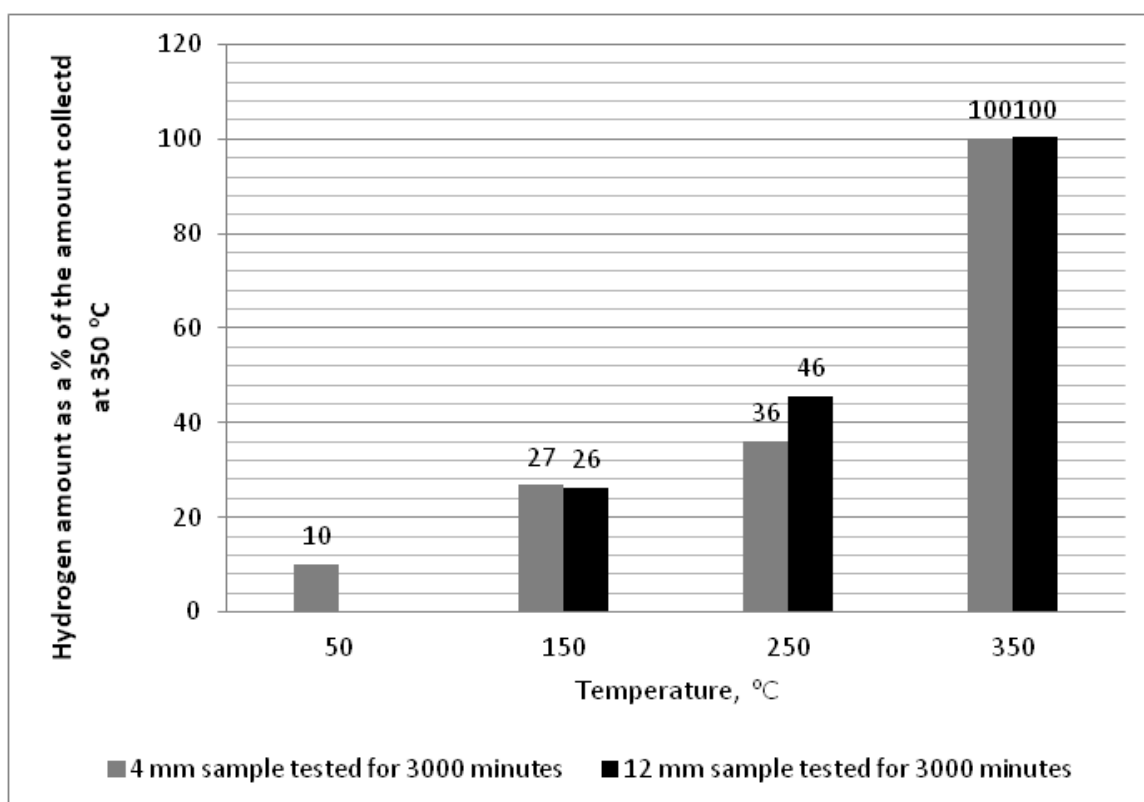


Figure 11.14: Bar chart to compare hydrogen amounts collected from the 4-mm and 12-mm test samples.

11.6 Hydrogen Measurement at Different Test Durations

11.6.1 Objective

The objective of these tests was to discover how hydrogen collection times affect the amounts of hydrogen that egress from a test sample when it is kept at constant temperatures. The selected temperatures were 150° C and 350° C. The selected tests' durations were approximately 1000 minutes, 3000 minutes, 5000 minutes, and 8000 minutes.

11.6.2 Test Results for 150° C Tests

A typical vacuum decay graph plotted for a test that was carried out for a test duration of approximately eight thousand minutes is given in Fig. 11.15.

4-mm thick test samples

Fig. 11.16 shows the amounts of hydrogen collected over varying time durations. In the figure, the y-axis shows the amounts of hydrogen at a standard temperature and pressure. The hydrogen amounts are given in cubic centimeters. Each data point represents the average amount of hydrogen that was collected from at least three identical test runs. Thus, the error bar indicates the standard deviation of the average hydrogen amounts.

Table 11.10 was prepared using the results obtained from the graph in Fig. 11.16. The table provides the amounts of hydrogen collected in half a day (720 minutes), one day (1440 minutes), two days (2880 minutes), three days (4320 minutes), four days (5760 minutes), and five days (7200 minutes). The table also indicates the hydrogen amounts as a percentage of the amount of hydrogen collected in five days.

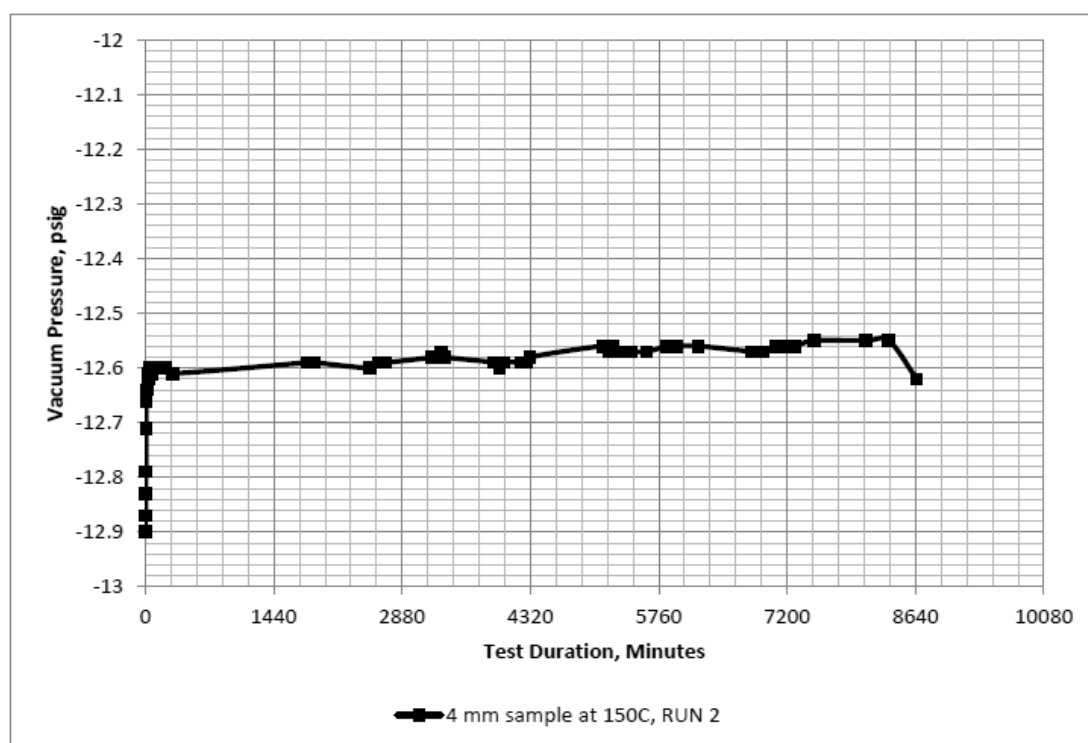


Figure 11.15: A typical vacuum decay graphs for hydrogen charged 4 mm thick sample at 150° C, long duration tests.

After five days, no noticeable increase in hydrogen amounts was noticed during the tests.

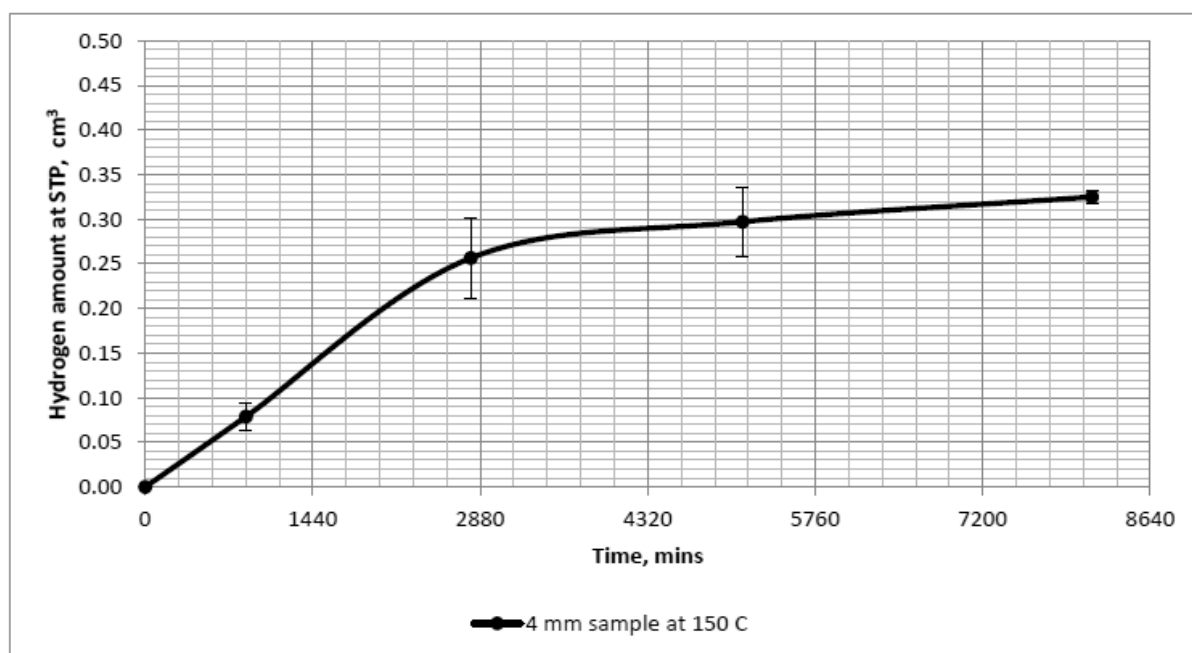


Figure 11.16: Amounts of hydrogen collected from 4-mm thick sample over the time durations during tests at 150° C.

Table 11.10: Amounts of hydrogen collected from the 4-mm thick test samples over the time, during tests at 150° C

Time Days (minutes)	Average amount of hydrogen at STP in cm ³	% of hydrogen (taken 0.31 cm ³ as 100%)
$\frac{1}{2}$ day (720)	0.06	19%
1 day (1440)	0.14	45%
2 days(2880)	0.26	84%
3 days(4320)	0.29	94%
4 days(5760)	0.30	97%
5 days(7200)	0.31	100%

12-mm thick test samples

Like Fig. 11.16, Fig. 11.17 shows the amounts of hydrogen collected in different time durations using a hydrogen-charged 12-mm thick test sample.

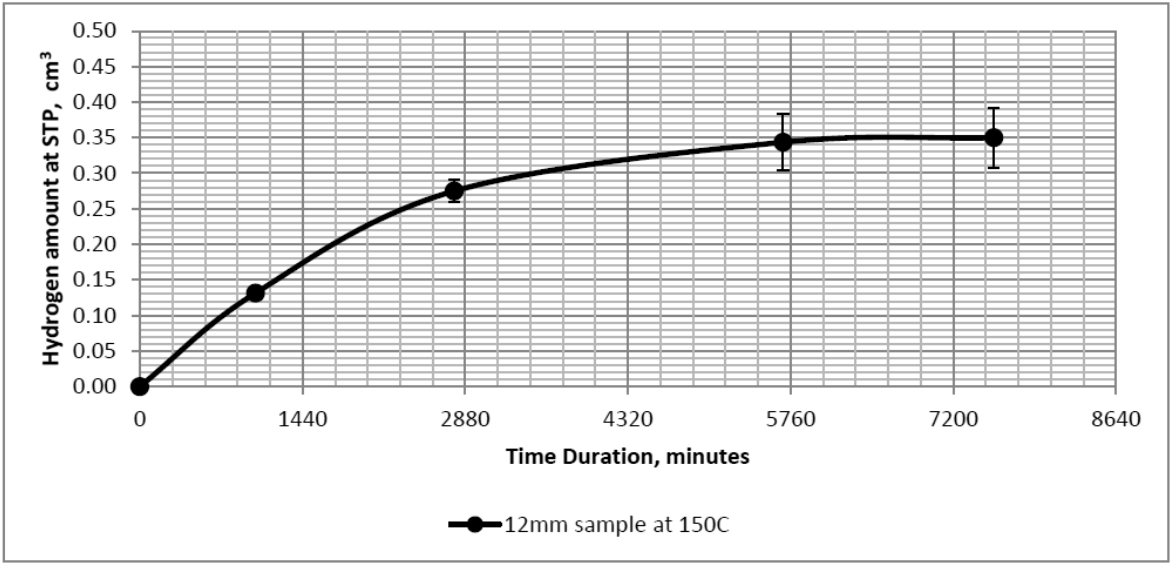


Figure 11.17: Amounts of hydrogen collected from 12-mm thick sample over the time durations during tests at 150° C.

Like Table 11.10, Table 11.11 was prepared using the results obtained from the graph in Fig. 11.17. The table also indicates the hydrogen amounts as a percentage of the amount of hydrogen collected in five and half days. After five days, no noticeable increase in hydrogen amounts was noticed during the tests.

Table 11.11: Amounts of hydrogen collected from the 12-mm thick test samples over the time, during tests at 150° C

Time Days (minutes)	Average amount of hydrogen at STP in cm³	% of hydrogen (taken 0.35 cm³ as 100%)
$\frac{1}{2}$ day (720)	0.13	37%
1 day (1440)	0.18	51%
2 days(2880)	0.28	80%
3 days(4320)	0.32	91%
4 days(5760)	0.34	97%
5 days(7200)	0.35	100%

11.6.3 Analysis

Comparison of results for 4-mm and 12-mm samples

Fig. 11.18 compares the test results of the 12-mm thick sample with the 4-mm thick test sample. The two curves follow a similar pattern, showing a slightly higher amount of hydrogen for the 12-mm thick test sample.

Fig. 11.19 is a graphical comparison between the percentages of average hydrogen amounts provided in Table 11.10 and Table 11.11. The average hydrogen amount collected at 7200 minutes was 100% in these plots. This assumption can be considered reasonable because, the collected average hydrogen amounts for both the 4 mm and 12 mm samples had started to level off after the fourth day (5760 minutes).

According to Fig. 11.19, at the end of the first day (1440 minutes), only about fifty percent of hydrogen had been collected during the tests. It took about four days (4320 minutes) to collect about ninety percent of the hydrogen.

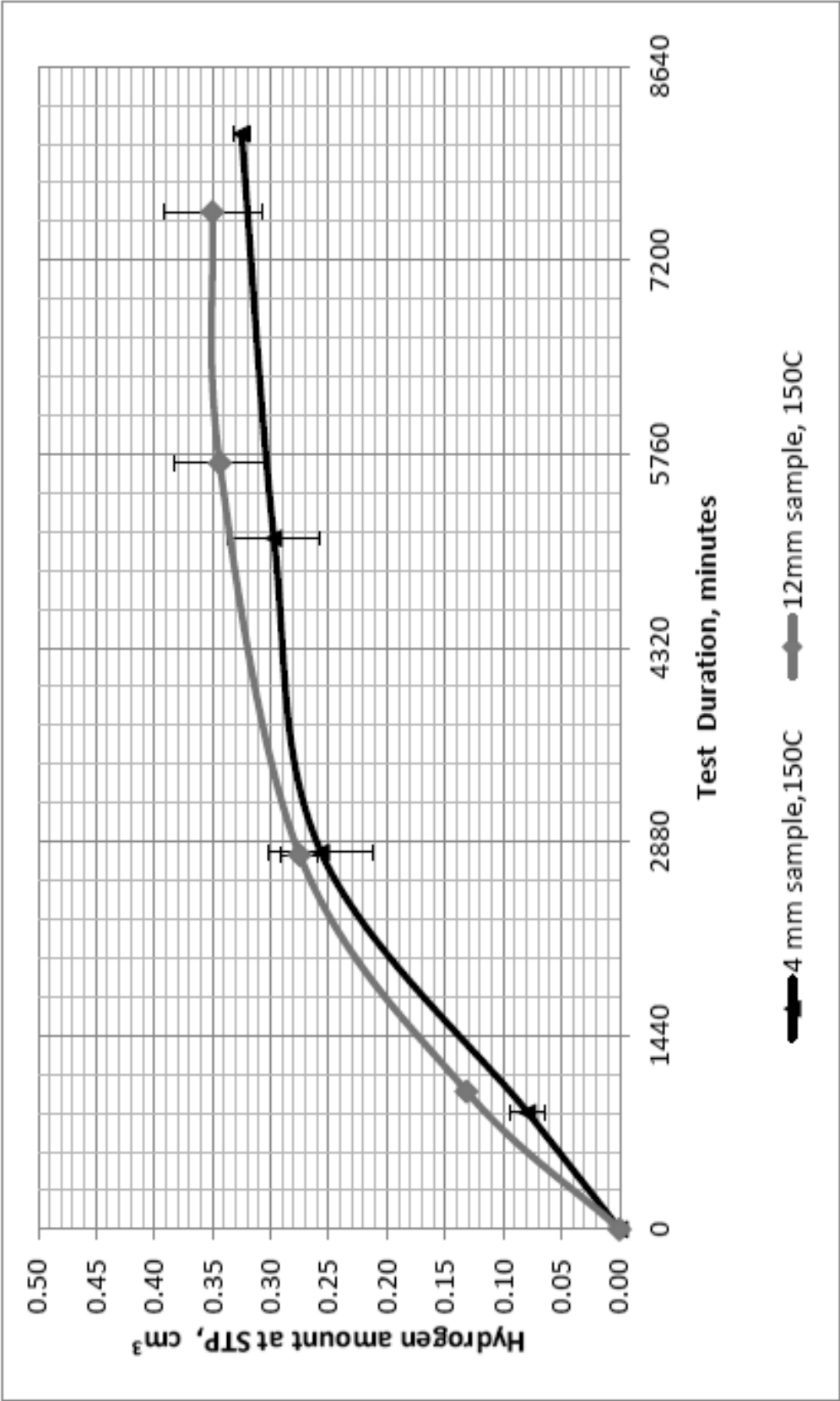


Figure 11.18: Comparison of amounts of hydrogen collected from 4-mm and 12-mm thick sample over the time durations during tests at 150° C.

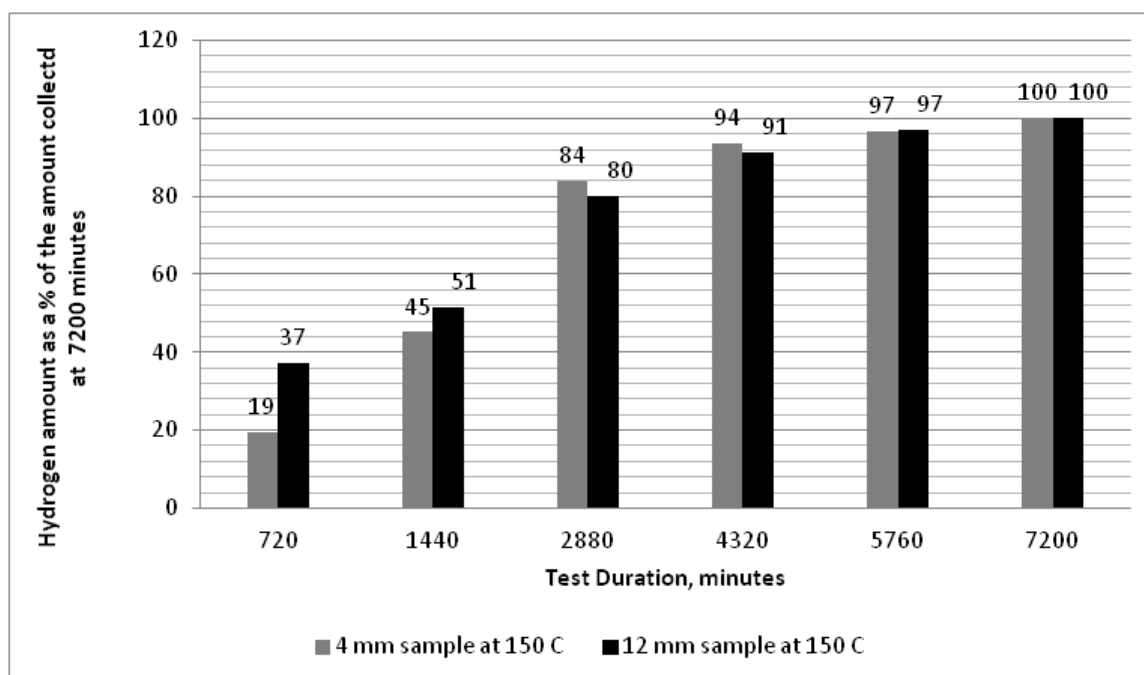


Figure 11.19: Bar chart to compare the percentages of average hydrogen amounts provided in Table 11.10 and Table 11.11.

Comparison of TVHS results with Eudiometer results

Fig. 11.20 compares the average hydrogen amounts measured using the TVHS method (shown in Fig. 11.16 above) with the average measured hydrogen amounts using the eudiometer method for identical tests. The figure shows that the TVHS method has collected a slightly higher amount of hydrogen when the test duration is more than 2880 minutes (two days). However, initially, the eudiometer method collected a higher amount of hydrogen than that collected using the TVHS method. Similar results were observed during the calibration tests. More details on that can be found in Chapter 8.

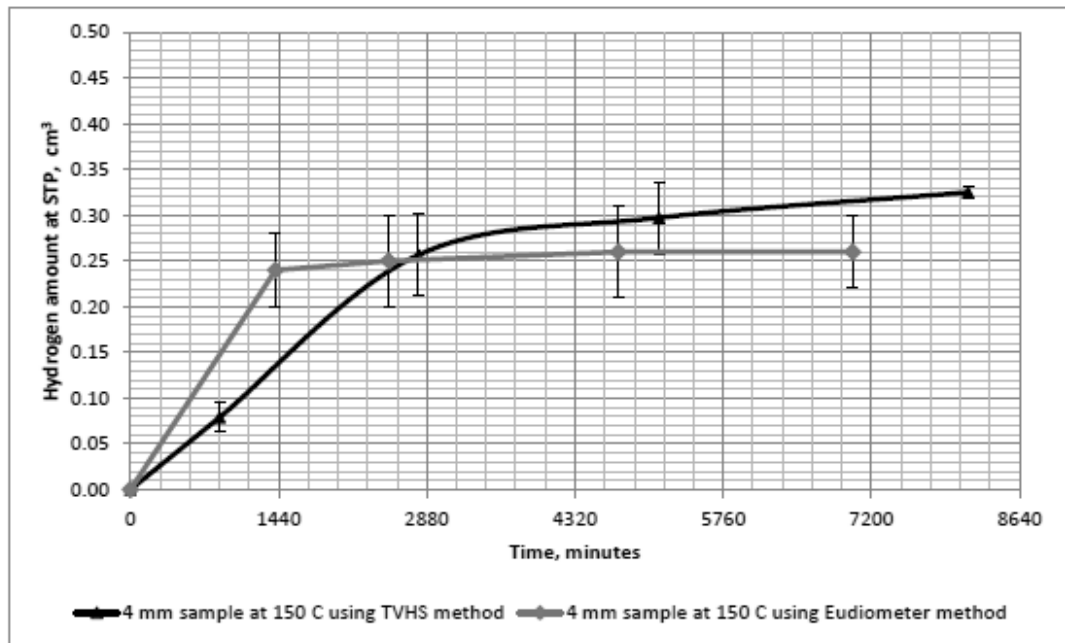


Figure 11.20: A comparison of hydrogen amounts collected using the TVHS and the improved eudiometer method.

11.6.4 Test Results for 350° C Tests

A typical vacuum decay graph plotted for a test that was carried out for test duration of approximately eight thousand minutes is given in Fig. 11.21. During the test, the temperature of the 12-mm test sample was maintained at 350° C.

4 mm thick test samples

Like Fig. 11.16, Fig. 11.22 shows the amounts of hydrogen collected in different time durations. Table 11.12 was prepared using the results obtained from the graph in Fig. 11.22. The table provides the amounts of hydrogen collected in half a day (720 minutes), one day (1440 minutes), two days (2880 minutes), three days (4320 minutes), four days (5760 minutes), and five days (7200 minutes). The table also

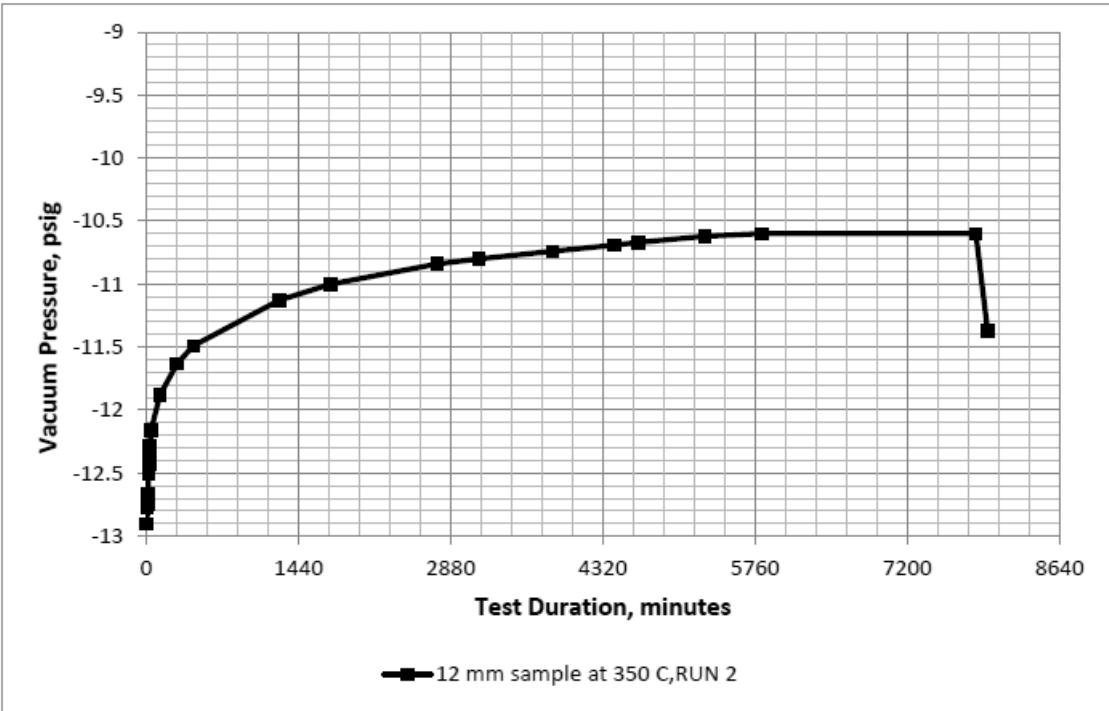


Figure 11.21: A typical vacuum decay graphs for hydrogen charged 12 mm thick sample at 350° C, long duration tests.

indicates the hydrogen amounts as a percentage of the amount of hydrogen collected in five days. After five days, no noticeable increase in hydrogen amounts was noticed during the tests.

12 mm thick test samples

Like Fig. 11.22, Fig. 11.23 shows the amounts of hydrogen collected within different time durations using a hydrogen-charged, 12 mm thick test sample. Table 11.13 was prepared using the results obtained from the graph in Fig. 11.23.

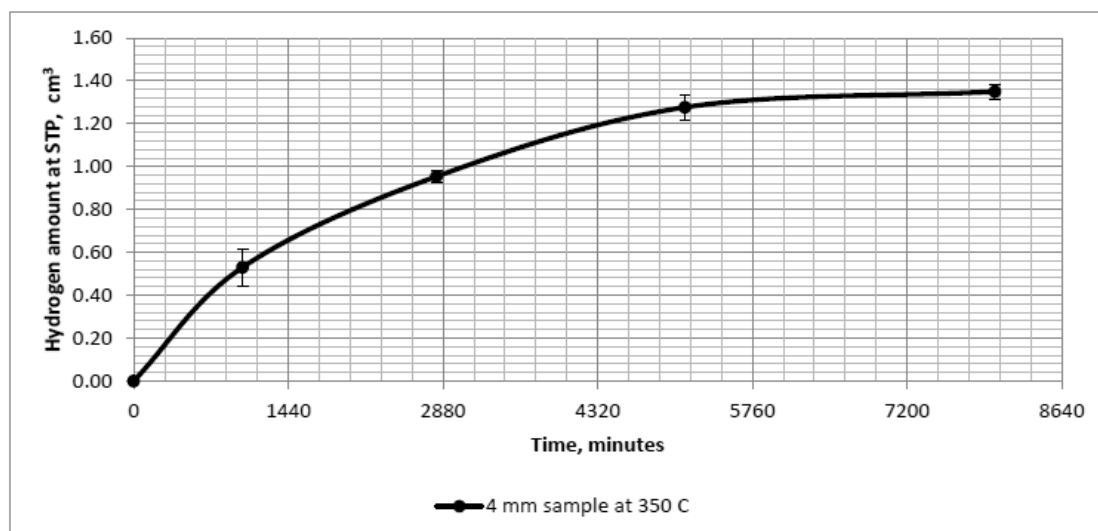


Figure 11.22: Amounts of hydrogen collected from 4-mm thick sample over the time durations during tests at 350° C.

Table 11.12: Amounts of hydrogen collected from the 4 mm thick test samples over the time, during tests at 350° C

Time Days (minutes)	Average amount of hydrogen at STP in cm ³	% of hydrogen (taken 1.32 cm ³ as 100%)
$\frac{1}{2}$ day (720)	0.44	33%
1 day (1440)	0.64	48%
2 days(2880)	0.96	73%
3 days(4320)	1.20	91%
4 days(5760)	1.32	100%
5 days(7200)	1.32	100%

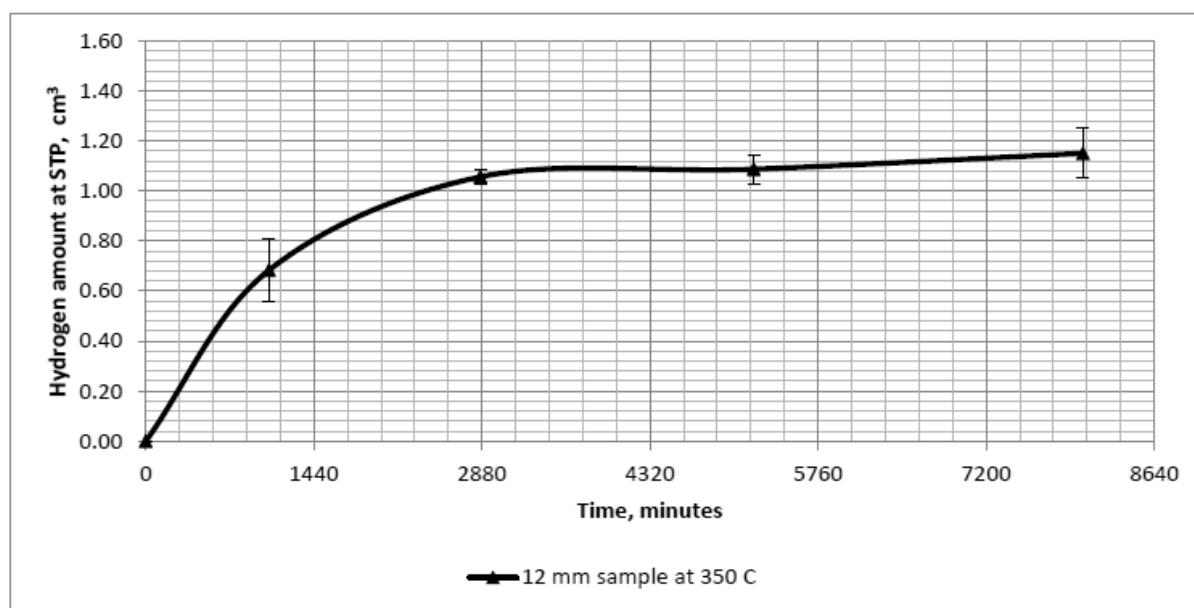


Figure 11.23: Amounts of hydrogen collected from 12 mm thick sample over the time durations during tests at 350° C.

Table 11.13: Amounts of hydrogen collected from the 12 mm thick test samples over the time, during tests at 350° C

Time Days (minutes)	Average amount of hydrogen at STP in cm ³	% of hydrogen (taken 1.12 cm ³ as 100%)
$\frac{1}{2}$ day (720)	0.60	54%
1 day (1440)	0.80	71%
2 days(2880)	1.08	96%
3 days(4320)	1.08	96%
4 days(5760)	1.12	100%
5 days(7200)	1.12	100%

11.6.5 Analysis

Fig. 11.24 compares the test results of the 12 mm thick sample with the 4 mm thick test sample.

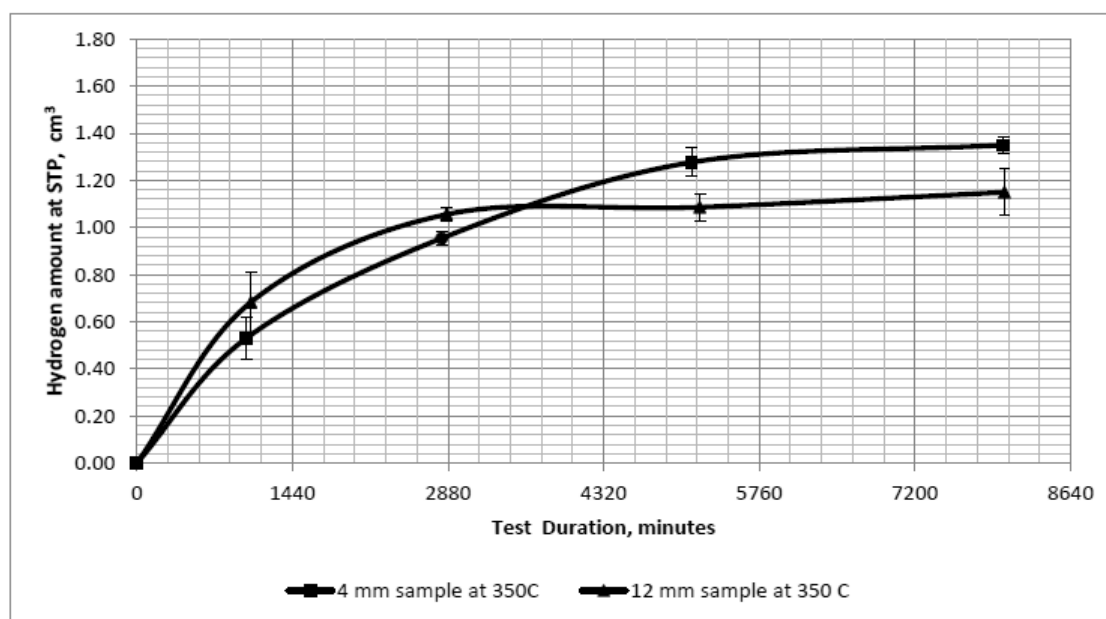


Figure 11.24: Comparison of amounts of hydrogen collected from 4 mm and 12 mm thick sample over the time durations during tests at 350° C.

Fig. 11.25 provides a graphical comparison between the percentages of average hydrogen amounts provided in Table 11.12 and Table 11.13. The average hydrogen amount collected at 7200 minutes was 100% in these plots. According to the results, it took about four days (4320 minutes) to collect about ninety percent of the hydrogen.

From the figure it is also apparent that the long test durations (more than three days) resulted in collecting more hydrogen from 4 mm thick sample compared to 12

mm thick sample, which would not normally be expected. All the previous results showed the average amount of hydrogen for the 12 mm thick sample were higher than the amounts collected from the 4 mm samples.

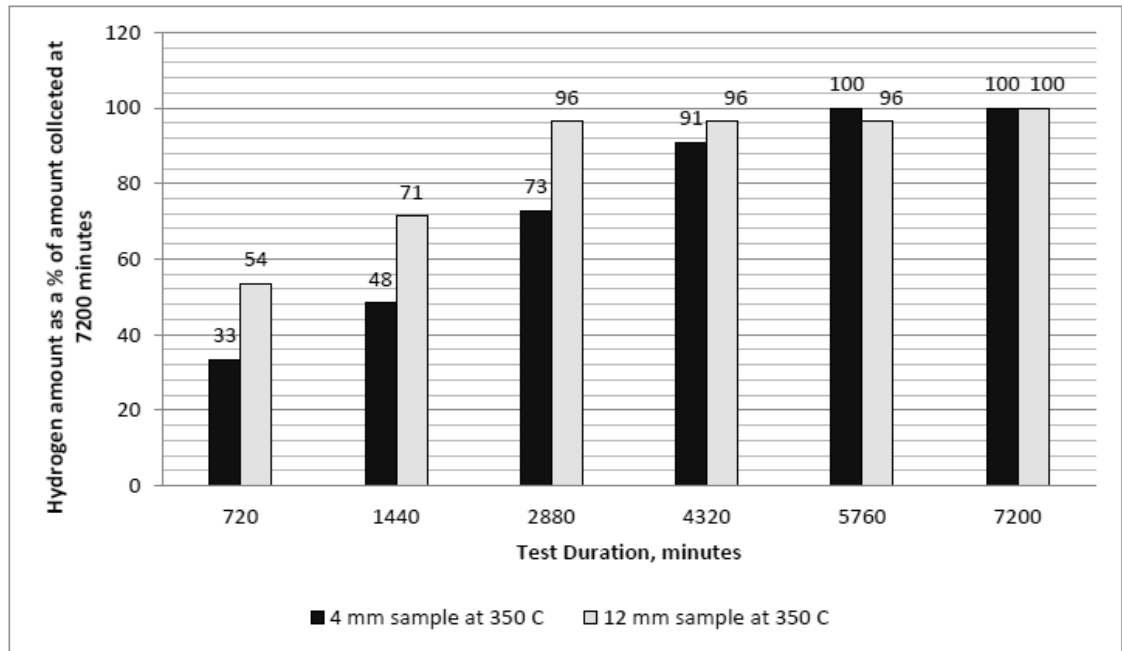


Figure 11.25: Bar chart to compare the amounts of hydrogen collected from 4 mm and 12 mm thick sample over the time durations during tests at 350° C.

11.7 Combination of Temperature and Time results

This section provides the analysis that was completed to find how the test temperature and test duration affected the amount of hydrogen collected during the tests. To do the analysis, the test results provided in above sections were used.

Fig. 12.13 shows how the hydrogen amounts are changed with the test duration when the 4 mm thick test sample's temperature is increased. For example, the black

color line with the diamond shapes indicates how much hydrogen egressed from 4 mm thick test sample at different temperatures when the test was carried out for 720 minutes (1/2 day). Similarly, each curve shows the egressed hydrogen amounts for the test durations of 1440 minutes (a day), 2880 minutes (two days), 4320 minutes (three days), 5760 minutes (four days), and 7200 minutes (five days). According to the figure, with the increase of time and temperature, the hydrogen amounts that egressed increased. A significant change in the hydrogen amounts is indicated when the temperature is increased from 250° C to 350° C. Conversely, the increase in the amount of hydrogen collected was reduced with the longer test durations. For example, the amount of hydrogen collected for 5760 minutes (black color line with gray dots) is almost similar to the amount of hydrogen collected for 7200 minutes (gray color line with stars). Similar observations were noticed for the tests that used 12 mm thick samples.

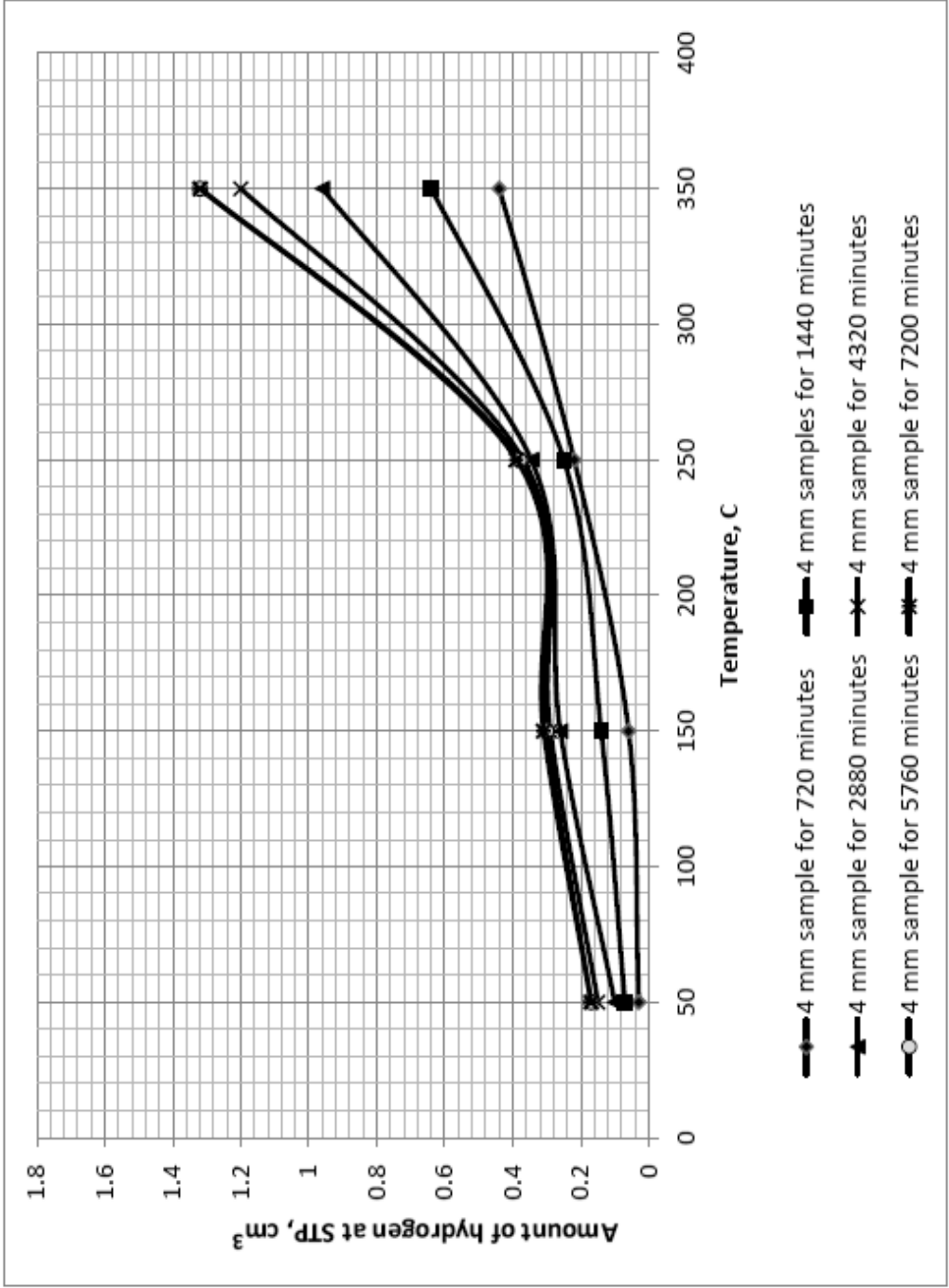


Figure 11.26: Change in hydrogen amounts with time and temperature for 4 mm thick test sample.

Chapter 12

Discussion

12.1 Eudiometer Method

Chapter 9 describes the improvements that were implemented in the standard eudiometer method. As described in the chapter, the improvements included modifying and adding new parts to the eudiometer system (apparatus) as well as modifying the hydrogen measuring procedure. These improvements increased the accuracy and efficiency of the eudiometer method and improved the users' safety.

The chapter also describes a quantitative analysis carried out on a powder sample that had accumulated in the eudiometer system in which a steel test sample was immersed for a long period of time. The temperature of the mercury in the eudiometer system was maintained at 150° C. As described, a microstructure and quantitative analyses were also performed on the steel sample. The findings of the analysis show it is possible to dissolve carbon from a steel sample when the sample is immersed in mercury at low-elevated temperatures for an extended period of time. That means mercury at low-elevated temperatures could have promoted the dissolution process. As described in Chapter 3, there are no findings in the literature similar to those of this study. However, mercury-contaminated steel pressure vessels and piping in gas processing facilities have been reported, and research studies describe how decontamination of mercury from the steel surfaces has been done. There are reports also on dissolution of iron by boiling mercury (that is the mercury at higher than 500° C). Findings of this thesis work also showed the powder sample could contain small

amount of iron. However the amount of iron was about 2.5% of the amount of carbon detected in the sample. However none of studies found in literature have identified the possibility of hot mercury to dissolve carbon from steel. Thus, the findings of this research work contribute new knowledge, and further studies are needed to confirm this finding.

As explained in Chapter 3, the positive free energy of the cementite (Fe_3C) suggests instability of the cementite in steel which could lead to easy decomposition and dissolve carbon from the pearlite structure [88][89]. In addition, as described in there, the chemical analysis of the powder sample showed the sample contained mercury (Hg), carbon (C) and oxygen (O). These observations are in favour for decomposition of unstable cementite and formation of a new stable compound with mercury. Mercury(II) Oxalate (HgC_2O_4), which has a standard Gibbs free energy of reaction of approximately $-716.3 \text{ kJmol}^{-1}$ is a possible compound of Hg-C-O. However it is not-known that the test conditions would allow to produce a metal oxalate.

If mercury reacts with steels, as suggested by the findings, the use of mercury in contact with steel would become a questionable practice for equipment that is exposed to mercury for a long time, especially if low-elevated temperatures were involved. Mercury and mercury compounds are found in all geological hydrocarbons, including coal, natural gas, gas condensates, and crude oils [58]. As a result, mercury can be distributed through hydrocarbon production, processing, and transport systems where equipment and piping are made out of steels. For use in the mercury eudiometer, the contamination means frequent cleaning.

12.2 TVHS Method

The main task of the research work was the design and construction of a new hydrogen measuring device called the Temperature Vacuum Hydrogen System (TVHS) and to explore some higher temperature measurements of hydrogen in steel using this new device. Despite the careful attention and time spent focusing on the details during the design and construction stages, several problems occurred during the initial test trial stage. These problems included leaking from joints, difficulties in stabilizing the test temperature, various problems related to gaskets, problems caused by variation of temperature in some parts of the system, and an apparent random drift in pressure gauge readings. Among them the latter two were the most challenging to solve as a direct solution was not apparent at that time.

As described in Section 5.6, the variation in the temperature in some sections of the TVHS system as a result of dissipated heat from the components, and volume expansion of the sections as a result of the heat and elevated test temperatures made the initial calculation of hydrogen amounts complex. It was found if the system was brought back to the initial room temperature at the end of a test, correcting the volumes for different temperatures was not required during the calculations. Thus, the expansion of the volume of each individual section from elevated temperatures can be disregarded and finally result in more accurate measurement. As a comparison, the relative percentage difference¹ between the measured hydrogen amounts after the system brought back to the initial room temperature and without applying this method was calculated. It was approximately within 13%, based on the tests carried out at 150°C.

¹Based on the formula: relative percentage difference between a and b = $(a-b)/(a+b)/2 \times 100$

As described in Section 5.7.1, initial test results using the TVHS concluded that the primary vacuum gauge readings were extremely sensitive to the changes in the room temperature as well as the atmospheric pressure. Thus, it was required to find a solution to eliminate the effects of the room temperature and atmospheric pressure on the primary vacuum gauge before continuing the hydrogen measuring tests. After considering the possible solutions, the solution that was implemented was to use a separate (secondary) vacuum pressure gauge to observe the effects of the atmospheric pressure and temperature on the gauge. Once this information was known, it was possible to correct the primary vacuum pressure readings that were obtained in the hydrogen measuring tests. This resulted in simply taking the difference between the readings of the two gauges.

12.2.1 System Specifications

Following table provides the specification of the TVHS which represent the current status of the equipment.

Table 12.1: System specifications of the TVHS.

Parameter	Range
Maximum size of a test simple	Disk shape sample with 36 mm in diameter and 30 mm in thickness
Maximum operating temperature	400° C
Accuracy*	0.8% of V_{STD}
Min.to Max volumes could be measured	~ 0.001 to 63 cm^3 (0.004 to 230 <i>ppm</i>) at STP

Accuracy*

As stated in Table 12.1, the accuracy of the TVHS is 0.8% of V_{STD} . The accuracy was calculated using the propagation of error method which based on a chain rule in calculus [112]. The propagation of error (also known as propagation of uncertainty) is the effects on a function by a variable's error or uncertainty [113]. For example when the variables are the values of experimental measurements, they have uncertainties because of limitations in the measurement (e.g. instrument precision). The derived equation is given in 12.1.

$$U(V_{STD}) = \sqrt{U(P_m)^2 \frac{V_m^2 k^2}{T_m^2} + U(V_m)^2 \frac{P_m^2 k^2}{T_m^2} + U(T_m)^2 \frac{P_m^2 k^2 V_m^2}{T_m^4}} \quad (12.1)$$

Where,

$U(V_{STD})$ is the error (or uncertainty) of the measured hydrogen amounts at the standard temperature and pressure,

P_m , V_m and T_m are the measured values of pressure, volume and temperature,

$U(\text{Variable})$ is the uncertainty associated with the each measured variables,

k is a constant which can be calculate using $\frac{T_{STD}}{P_{STD}}$.

12.2.2 System Essentials

During the design stage of the TVHS, the following have been identified as essential requirements for new hydrogen measuring equipment because the currently available hydrogen measuring equipment is limited for most or all of these essential requirements.

- Able to measure amounts of various types of hydrogen amounts (i.e. easily mobile and progressively mobile) accurately and efficiently. Easily convertible to a unit that could measure total hydrogen

- Able to provide direct measurement
- Adaptable to measure very small to very large volumes of hydrogen accurately
- Able to handle test samples (specimens) with different shapes and different sizes
- Safe to use
- Economical and simple to construct
- Contains its own leak detection system
- Suitable for industrial use

The following section discusses where the TVHS stands when the above-mentioned essentials are considered.

- **Measuring all types of hydrogen:**

Easily mobile and progressively mobile

The TVHS is currently capable of measuring easily mobile hydrogen and progressively mobile hydrogen up to a temperature of 400° C. The limitation in the operating temperature is a result of the deteriorating sealing ability of the deoxidized copper gasket that is used in the vacuum chamber assembly. As explained in Section 5.4, tests were carried out to find the maximum temperature that deoxidized copper gasket can withstand without losing its sealing ability. The tests were similar to a vacuum decay leak test. The test results showed that the copper gaskets started to leak in the tests carried out at 450° C. No leaks were noticed at 400° C, which was

the previous test temperature. Thus, 400° C is considered the maximum operating temperature of the TVHS.

Literature suggests 260° C as the maximum operation temperature for the gaskets made out of copper [92]. The softening curve for deoxidized copper provided in [93] suggests a sudden degradation in the hardness of the material (i.e. softening of copper) when the temperature was increased to more than about 250° C. When compared to the suggested values in the literature, the deoxidized copper gaskets used in the vacuum chamber assembly reached a higher operating temperature. In the assembly, two vee apexes and eight steel bolts were used to secure the lid to the vacuum chamber, sandwiching the gasket between them (see Fig. 4.3). These special design features and the compressive forces resulted by the vacuum atmosphere could have helped to elevate the operating temperature that would otherwise start leaking at around 250° C. The paper in [93] also mentioned the possibility of improving the sealing capacity by improving the design of a joint.

The operating temperature of the TVHS can be increased if the copper gaskets are replaced by a gasket material that can withstand an elevated temperature. Also, it is essential that material has extremely low permeability to hydrogen compared to deoxidized copper. As explained in Section 5.4, grade 304L stainless steel is a good candidate for gasket material. Literature suggests 760° C as the maximum operating temperature for the gaskets made out of 304 L [92]. Even though the permeability to hydrogen of austenitic type stainless steels is not superior to deoxidized copper, they are superior to most of the other gasket materials [94]. As described in Section 5.4, the development of double annealing of 304 L material resulted in soft usable gasket material for use from 400° C to at least 530 ° C (~ 800 K).

Total hydrogen

The TVHS was designed so the vacuum chamber and heating mantel were located externally to the rest of the system (i.e. the TVHS panel). This location made it easier to convert the system to a unit that measured the total hydrogen. The total hydrogen in a sample is normally measured by fusing the sample, and it requires a high temperature vacuum furnace. Thus, the TVHS can be converted to a total hydrogen measuring unit simply by replacing the vacuum chamber and the heating mantel by a suitable, high temperature vacuum furnace. Also, additional methods would be required to isolate other gases that may evolve during fusing steel.

- **Measuring hydrogen amounts directly:**

As explained in Chapter 7, unlike most of the hydrogen measuring systems available, the TVHS uses the universal gas law to determine hydrogen amounts using basic parameters such as pressure, volume, and temperature. Thus, the method does not use any other assumptions in determining the hydrogen amounts, which is a key factor for accuracy in the measurements.

- **Measuring different volumes of hydrogen:**

The TVHS has the flexibility to measure different amounts of hydrogen by selecting the required calibration volumes as described in Chapter 4. Opening and closing each valve in the system make it possible to increase and decrease the total volume of the TVHS system. Thus, when measuring a higher volume of hydrogen, the total volume of the TVHS can be increased by engaging extra calibration volumes. Conversely, when measuring smaller volumes, the extra volumes can be disengaged from the system. The ability to select volumes was established to increase the measuring sensitivity of the system over a wide range of hydrogen concentrations.

- **Measuring hydrogen in samples with different shapes and sizes:**

The spacious internal area of the vacuum chamber of the TVHS helped to accommodate test samples with different shapes and sizes. This capacity was especially helpful in measuring hydrogen amounts in a cutoff sample from a large component to determine the amount of hydrogen in the large component. Larger size cutoff test samples provide a much more accurate result compared to smaller size samples because larger size samples represent a higher percent of the volume of the component to be checked.

As mentioned, the vacuum chamber can accommodate regularly and irregularly shaped samples. It is convenient when specially shaped samples are not needed to be fabricated before doing the measurements. More importantly, when the cutoff samples are needed for failure analysis or quality assurance purposes, the longer sample preparation time affects the accuracy of the results. This is because longer sample preparation time results in more hydrogen egressing from a sample before the measurement is taken. In addition, the system can be used with other specially sized and shaped vacuum chambers, hence allowing a high degree of flexibility when measuring hydrogen in various sizes and configurations of components.

- **Users' safety:**

Unlike the eudiometer method, the TVHS is a safe method for users because the method uses no hazardous substances such as mercury. According to current knowledge, mercury is the only liquid medium at room temperature that can be used to collect hydrogen because it does not allow any hydrogen to dissolve within it. During recent years, regulations related to the handling of mercury have become more

stringent to protect users' safety. Thus, regardless of the benefit of using mercury as the hydrogen collection medium, mercury is being used less often.

Therefore, it is important to find alternative methods to measure hydrogen amounts accurately because most of the advances in using hydrogen depend on answering the questions related to hydrogen amounts. In such situations, TVHS can be selected as a safe method to replace the unsafe mercury eudiometer method.

- **Cost analysis:**

The TVHS uses the pressure drop method to calculate the amount of hydrogen egressing from a test sample. Thus, the method requires an accurate, sensitive, and reliable pressure gauge to measure the pressure drop. Use of a pressure gauge has made the TVHS system a much more economical method compared to using alternative methods such as a gas chromatograph in the system. The use of a pressure gauge is also simple and direct compared to the expensive alternative methods available. The material costs including the cost of electronic gauges for construction of the TVHS were approximately five thousand five hundred Canadian dollars in 2012 terms.

- **Leak detection:**

Leaks are one of the main causes of inaccurate results when measuring gas quantities. Thus, the TVHS's helium gas leak detection system helped to identify any leaks in the system. A discussion on the leak detection system is provided in Chapter 4.

- **Industrial use:**

The TVHS was designed and constructed while keeping in mind the possibility of using the basics of the method in industry. The current findings of this research work show that the method can be used as a quality assurance method in the manufacturing industry. Some of the manufacturing processes, such as manufacturing of automobiles, require the measurement of hydrogen in the manufactured parts before they are assembled. Thus, most of the time, manufacturers want to know whether the parts have reached the threshold levels of hydrogen, rather than measuring the exact amount of hydrogen in each part. The TVHS method is a good candidate to use in such applications. According to the outcome of this thesis work, the TVHS can be used to compare the hydrogen amounts as well as to measure the exact amounts of hydrogen.

- **System Accuracy**

As explained in Chapter 7, the TVHS method uses volume, pressure, and temperature readings to determine hydrogen amounts. Thus, the accuracy of the determined values depends largely on the accuracy of the physical measurements. According to [95], three basic error sources in physical measurements directly affect the accuracy. They are damaged or improperly installed instruments, instruments that are not calibrated properly, and operator/observer errors during recording readings. During this research study, several steps were taken to prevent the sources of error. These steps included regularly checking the instruments for their functionality, thorough research before purchasing instruments, calibrating the measuring instruments, and using a single observer (rather than several observers) to take the readings. More details on some of these steps are provided in Section 7.4.

12.3 Outcome of Calibration Tests

The calibration tests showed that when the amount of hydrogen collected using the TVHS method is compared with the eudiometer method, the TVHS method registered a slightly higher amount of hydrogen. This was true for all 15 of the sub-calibration tests and number of initial trial-tests. During the research work in the initial trial tests, about three dozen similar calibration tests were carried out, even though only 15 calibration tests are mentioned in this thesis. In all those tests, a similar observation was noticed. The average relative percentage difference of the amount of hydrogen collected during the calibration tests was 20.6%

As described in Chapter 8, a unity plot was made to find the relationship between the amounts of hydrogen that were collected using the two methods. Accordingly the Equ.8.1 provides the relationship which is:

$$H_{TVHS} = 1.18 H_{Eudiometer}$$

where,

H_{TVHS} : Mean hydrogen amounts collected from the TVHS tests

$H_{Eudiometer}$: Mean hydrogen amounts collected from the eudiometer tests

Similar observations to the above were also found in literature. For example, [96] compares the hydrogen amounts that egressed from welded test samples in mercury and vacuum. As shown in Table 12.2, higher amounts of hydrogen were collected from the samples in the vacuum in the majority of the tests, compared to the samples in mercury.

Table 2.5 of Chapter 2 shows similar test results that were gathered from another source. Accordingly, the amount of hydrogen extracted from the hot extraction

Table 12.2: Comparison of the hydrogen amounts that egressed from welded test samples in mercury and vacuum [96].

Test	Test Duration (Days)	Diffusible hydrogen amounts egressed under mercury <i>ml/100g</i>	Diffusible hydrogen amounts egressed under vacuum <i>ml/100g</i>
1	8	18.0	18.5
2	8	18.3	18.0
3	13	12.4	14.65
4	14	5.1	4.85
5	20	4.6	6.9

method is higher than the amounts collected from the standard eudiometer method. Thus Eqn. 2.16 provides the relationships between hydrogen amounts collected using hot extraction and eudiometer methods and it is:

$$H_{HotExtraction} = 1.18 H_{Eudiometer}$$

.

Interestingly the equation is same as the Equ.8.1 which was obtained from this research work.

It is also important to note that if the test temperatures are too high the comparisons are not valid because of the high volatility of mercury in the eudiometer method could cause inaccurate results.

12.3.1 Possible Reasons for Differences in Amounts for Two Methods

No possible reasons for differences in measured hydrogen amounts for two methods were given in the literature. Thus to find the reason for the observations above, the

test parameters that governed the collected amount of hydrogen were considered. When any sub-calibration test was considered, the following parameters were identical for both the TVHS test and the eudiometer test, so it is unlikely that these would affect the differences in amounts:

- material type
- test sample size
- method of hydrogen charging, thus the amount of hydrogen
- tests duration (i.e. hydrogen collection times)
- test temperature

For example, when the *sub-test Test A-1* calibration test was considered, both the TVHS and the eudiometer tests used identical test samples that were charged with identical amounts of hydrogen. The tests were carried out at 150° C (423 K) for 5000 minutes in both methods.

However, the environments of the test samples were considered (that is the medium in which the test samples were immersed and the pressures); they were different for each method. During the TVHS test, the test samples were in a vacuum atmosphere that had an average vacuum of approximately -12.8 psig (-88.9 kPag). The hydrogen that egressed from the test samples was collected in the containments, which were also at a similar vacuum. During the eudiometer tests, the test samples were inside a mercury bath, thus the samples were at pressure of approximately 14.5 psi (99.9 kPag), which was higher than the atmospheric pressure. In this method, the hydrogen that egressed out of the test samples rose and collected on the top of

the eudiometer tube that contained a vacuum of approximately -7 psig (-48.3 kPag), which is not as strong as the vacuum in the TVHS. Thus, the environments that the test samples were experiencing and the vacuum pressure of the hydrogen collection area were different.

Difference in mediums

It has been widely accepted that mercury does not have any effect on the collection amounts of hydrogen, for mercury does not dissolve any hydrogen contained in it. However, it is not known whether a steel/mercury interface or steel/vacuum interface is more favourable when hydrogen egresses from steels. Evidence in literature shows that the medium in which samples are immersed can affect the amounts of hydrogen that egress. Smialowski, M. [97] stated about early work done on hydrogen in steels that “some information exists concerning the influence of environment on the rate of hydrogen removal from iron and steels. Some workers found the evolution rate of hydrogen dependent upon the composition of the bath in which samples were dipped.” Hudson, M. [98] reported that hydrogen does not escape from steel samples when immersed in pure dioxane, an organic compound. A study on analysing the amount of hydrogen in steels stored in different inhibitors is provided in [99]. The study concluded that formation of a surface layer on steel as a result of interacting with the medium could affect the amount of hydrogen that egressed.

Ohno et al. [100] studied the behaviour of hydrogen bubbles in different mediums with respect to rising rate and buoyancy of hydrogen bubbles. Glycerin, water, alcohols, and mercury were used as the collection mediums to collect hydrogen that was diffused from welded steel test samples. The findings are given in Fig. 12.1 as a relation between the rising rate and the radius of gas bubbles in the selected

collecting mediums. Accordingly, the bubble rising rate in glycerin was the slowest when compared to the rates of the other collecting mediums. According to the authors, the rising rate of gas bubble in a medium is mainly related to the viscosity of the medium and the size of gas bubble, therefore the rising rate of the gas bubbles in mercury was about 10^4 times greater than that in glycerin.

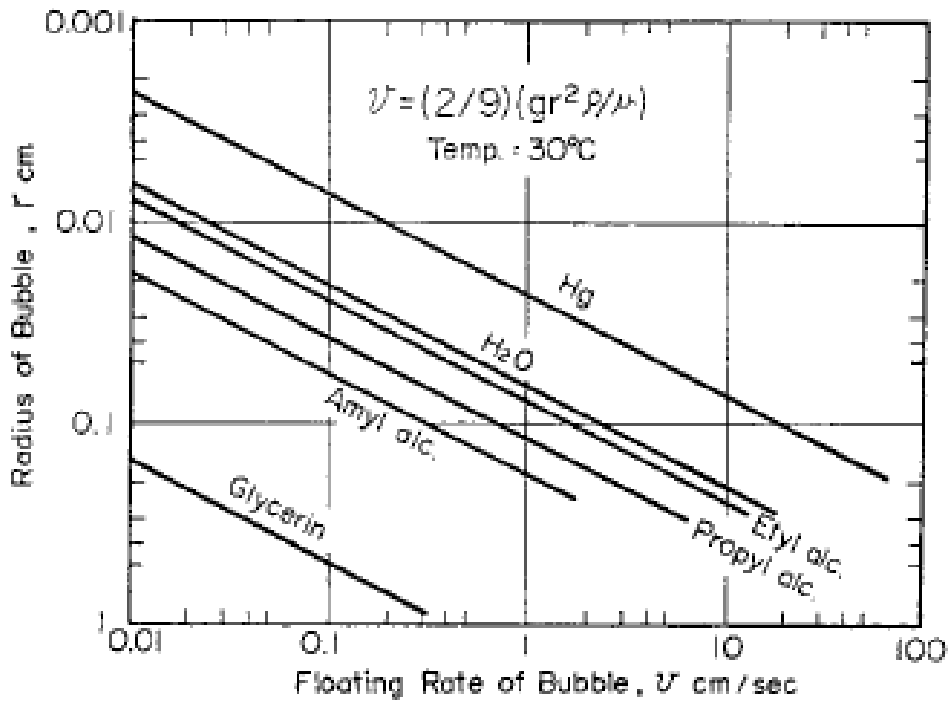


Figure 12.1: Relation between the rising rate and the radius of gas bubbles in the selected collecting mediums [100].

How an immerse medium could affect the egressed hydrogen volumes is a complex question to answer because many variables, such as surface tension, possible film formation, and properties of the medium, would come into play in this answer. Instinct would say a steel/vacuum interface would be more favourable than a steel/mercury

interface due to the fewer surface forces that are exerted from a vacuum; thus, the hydrogen in the steel samples that were in the TVHS system could have come out more efficiently than those in the eudiometer system. However, this idea requires further research.

Difference in pressure

In addition to the difference in the mediums, the test samples also experienced two different pressure levels in the two methods. As explained above, during tests, the test sample inside the eudiometer tube experienced a slightly higher pressure than atmospheric pressure. Conversely, the test sample inside the TVHS experienced a vacuum pressure that was lower than the atmospheric pressure. Thus, it could be the difference in the pressure that the test sample experienced that caused the difference in the amounts of hydrogen collected. The higher pressure gradient that was provided by the TVHS could have resulted in more hydrogen egressing from the test samples.

Scialdone, J. et.al. [101] provides findings of outgassing rates and diffusion coefficients formed by gases having molecular masses of $M=18$ and $M=100$ diffusing in air at different pressures. Tests were carried out at room temperature (20°C , 293K). The test results are provided in Table 12.3.

According to the results, with the increase of the external pressure (i.e. when the pressure is reaching closer to atmospheric pressure), both the outgassing rate and diffusion coefficient decreased. That means, at higher pressures, less gas has come out compared to that of lower pressures. Even though the test conditions above are not identical to the conditions in the calibration test of this research work, it suggests the outgassing rate and diffusion coefficients are strongly affected by external pressure;

Table 12.3: Outgassing rates and diffusion coefficients at different pressures [101].

External Pressure <i>torr(P_{SI})</i>	M=18 Outgassing rates <i>(g/cm²/s)</i>	M=18 Diff.coeff. <i>(cm²/s)</i>	M=100 Outgassing rates <i>((g/cm²/s)</i>	M=100 Diff.coeff. <i>(cm²/s)</i>
E-01(0.0019)	4.8E-2	1824	1.5E-10	805.2
E-00(0.019)	4.8E-3	182.4	2.5E-11	80.52
E+01(0.19)	4.8E-4	18.24	8E-12	8.052
E+02(1.9)	4.8E-5	1.824	2E-12	.805
760(14.69)	9.6E-6	0.24	5E-13	0.106

thus, the amount of gas that comes out of a material is inversely proportional to the external pressure.

12.3.2 Possible Reasons for Differences in Amount for Different Thicknesses:

The calibration tests were carried out using 4 mm and 12 mm thick test samples that were charged with hydrogen in identical conditions. Therefore, it was expected that identical amounts of hydrogen would result during measurements. However, for majority of tests a difference in amounts between the two thicknesses was observed. That is, the 12 mm thick sample showed a higher amount of hydrogen than that in the 4 mm thick sample. This difference could be the result of having a slightly greater hydrogen diffusion into the thicker sample during charging due to the higher concentration gradient in the thicker sample. That is, the concentration in the centre of the sample was lower and rose somewhat more slowly for the thicker sample. Thus, during the tests, a slightly higher amount of hydrogen could have egressed from the thicker sample.

12.4 TVHS Tests Outcome: Comparison of the Hydrogen Amounts with the Amounts given in Literature

Table 12.4 compares the calculated percent coefficient of variation ($C_v\%$) values of the measured hydrogen amounts using the TVHS method with the amounts measured using other methods which were given in literature. The $C_v\%$ provides the percentage variation in mean values and it is useful when comparing two or more sets of data that measured in different units of measurements. In general, if a $C_v\%$ is small it indicates that the group is less variable and it is more uniform. The first column of the table describes the method. The second column provide the ranges of the measured hydrogen amounts in given units. The last column provides the calculated $C_v\%$ values for the measured hydrogen amounts. The test results were based on steel samples, unless otherwise mentioned.

The $C_v\%$ value for TVHS compares well with the other given values, but it appears higher compared to the most of the other values. However when comparing, it is important to note that the $C_v\%$ value for the TVHS was based on measurement of smaller quantities of hydrogen, compared to the measured quantities using the other methods (see range in the second column of Table 12.4). In general, measurement of small quantities of any substance is practically challenging and thus the results could affect on $C_v\%$. If the $C_v\%$ for the TVHS is calculated based on the test results range from 1 to 1.5 cm³ (1 to 2 ppm), which is a higher range, it is 2.3%. The new value is lesser than the $C_v\%$ values of most of the methods.

Note: In Table 12.4, ¹ Material used was titanium (Ti) ² Material used was copper (Cu)

Table 12.4: Comparison of hydrogen amounts using $C_v\%$.

Method	Range	$C_v\%$
TVHS method	0.1-1.5 ml (0.15-2.15 ml/100g, 0.1-2.0 ppm)	9.3
Eudiometer method [52]	5.0-10.0 ml/100g	7.4
Hot extraction method [51]	0.7-1.8 ppm	4.0
Hot extraction method ¹ [35]	27.0-35.0 ppm	7.4
Tin fusion method [51]	0.7-1.8 ppm	11.2
Tin fusion method ² [55]	6.7-7.7 ppm	1.2
Inert fusion method using Eltra2000 OHN [54]	0.8-1.7 $\mu\text{g/g}$	6.8
Inert fusion method using Leco TCH600[54]	0.8-1.7 $\mu\text{g/g}$	8.3

12.5 TVHS Tests Outcome: Hydrogen Amounts at Different Temperatures

12.5.1 Key Finding

Chapter 11 provides the hydrogen amounts collected at different temperatures using the TVHS method. The test temperatures were 50°C , 150°C , 250°C , and 350°C . Fig. 12.2 is plotted using the data in Chapter 11 to compare the average hydrogen amounts collected over the time of the test temperatures. According to Fig. 12.2, about ten percent more hydrogen was collected at 150°C compared to the amount collected at 50°C , and about fifteen percent more hydrogen was collected at 250°C . However, according to the test results, about eighty five percent more hydrogen was collected at 350°C compared to the amount collected at 50°C . Thus, the amount of hydrogen collected at 350°C was significantly higher compared to the amounts collected at lower temperatures.

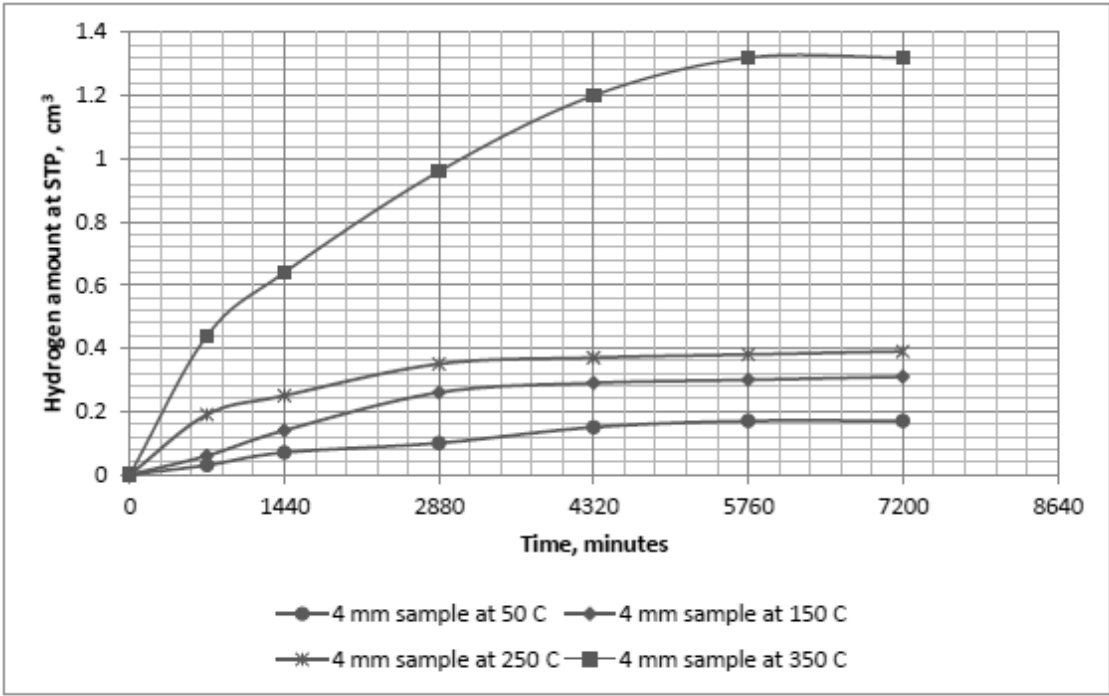


Figure 12.2: Comparison of the average hydrogen amounts collected at different test temperatures as a function of time .

A similar observation was noted in [33]. The hydrogen contents of low-alloyed steel samples that were charged with hydrogen using electroplating were measured at various constant temperatures using a gas chromatography system connected to a furnace. The test results are provided in Fig. 12.3, and the results provided in the graph are summarized in Table 12.5.

From looking at Table 12.5, it is clear that both 300° C and 350° C have resulted in higher amounts of hydrogen egressing compared to other test temperatures. Thus, about ninety percent more hydrogen was collected at 350° C compared to the amount that was collected at 150° C. The value obtained from the TVHS system was about

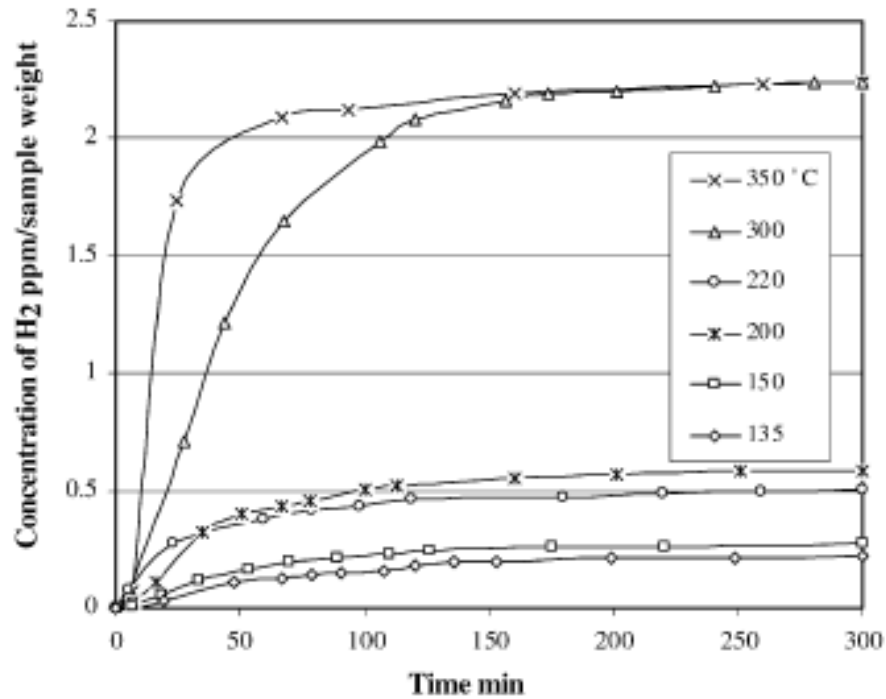


Figure 12.3: Evolution of hydrogen at 135, 150, 200, 220, 300, 350° C as a function of time [33].

seventy five percent compared to the amount that was collected at 150° C.

12.5.2 Additional Confirmations

Because the tests that were carried out showed unusually high amounts of hydrogen egressing at 350° C, it was decided to do additional tests to confirm the test results. For these tests, the same samples that were tested at 350° C (until the collected hydrogen amounts reached a steady state) were reheated to 350° C. No significant change in the vacuum drop was expected during the reheating tests because these samples had already released hydrogen amounts at 350° C until the levels reached a steady state.

Table 12.5: Results obtained from Fig. 12.3 [33].

Test Temperature $^{\circ}\text{C}$	Approximate amount of hydrogen <i>ppm/sample weight</i> (obtained from Figure 1)	Amount collected as a percentage of amounts collected at 350°C (obtained from Figure 1)
135	0.24	11%
150	0.25	11%
200	0.60	27%
220	0.50	22%
300	2.25	100%
350	2.25	100%

Fig. 12.4 provides a typical vacuum decay graph obtained by using the TVHS method that compares the hydrogen charged test sample heated to 350°C and the same sample reheated to 350°C after completing the initial test. In detail, the black color line with triangles represents a typical vacuum decay graph for a test that was carried out at 350°C using a 12 mm thick hydrogen-charged test sample. After the test was completed (in about five and half days), the sample was again heated to 350°C , and the vacuum decay was observed. No changes to the test parameters or the THVS were done during the reheating test, except the test was terminated in about three and half days because there was no obvious change in the vacuum pressure.

According to the graph (gray color line with squares), it is clear no significant change in the vacuum pressure occurred during the reheating test amount, which was expected. The results of these tests confirmed that the higher amount of hydrogen that egressed at 350°C was actual, and it was not caused by any other condition of

the TVHS.

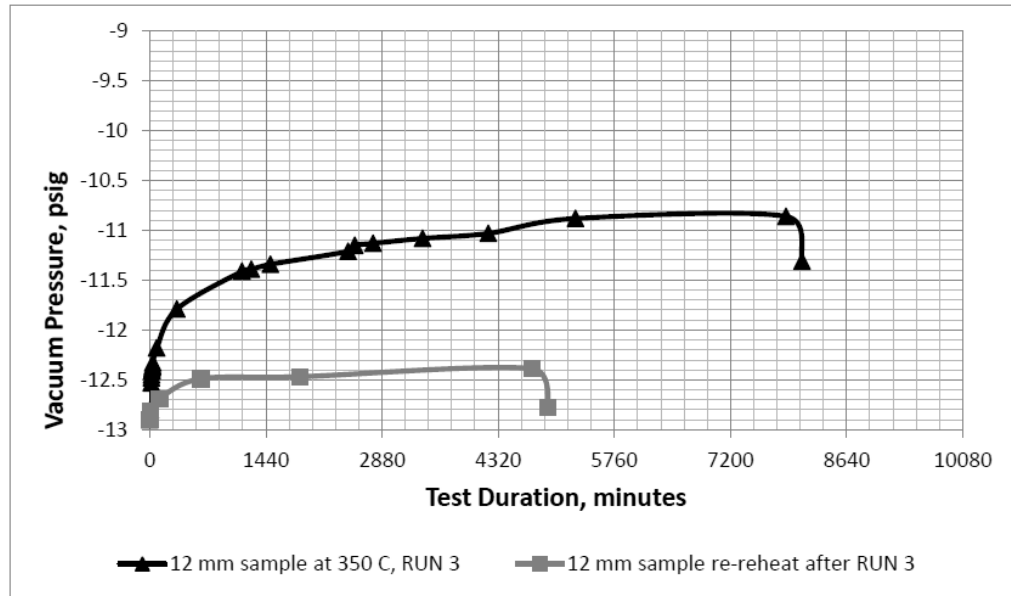


Figure 12.4: A typical vacuum decay graph compares the hydrogen charged test sample heated to 350° C and reheated to 350° C after completing the initial test.

12.5.3 Possible Reasons for Significant Hydrogen Amounts at 350° C

The possible reasons for egressing significantly higher amounts of hydrogen can be explained using the principles behind the trapping sites of hydrogen in steels. Generally, the absorbed (charged) hydrogen is not homogeneously distributed inside steels. It can be found either in the lattice, or segregated to atomic and microstructural imperfections, such as vacancies, solute atoms, dislocations, grain boundaries, voids and second phase particles. In these localized regions, the mean residence time of a hydrogen atom is considerably longer than in a normal interstitial lattice site [30]. The ability of a trap site to hold a hydrogen atom is associated with the activation en-

ergy for hydrogen release [102], [103],[104]. It is believed that the hydrogen captured in such locations (also called as deeper traps) is immobilized at lower temperatures because of insufficient activation energy and that hydrogen would be released upon heating the sample. This suggests, for the steels samples used in this research work, the greater part of charged hydrogen would have been trapped in deeper traps in which the elevation of temperature to less than 350° C was not adequate for releasing the hydrogen. According to Glikman, L. A. et.al., when mild steels were charged with hydrogen using acid pickling method, hydrogen preferentially accumulated at grain boundaries [105].

This phenomenon could be applicable to the lower temperature too, but shallower traps would not show a significant difference in the amounts of hydrogen released. For example, consider the following test that was carried out using the TVHS method. Fig. 12.5 gives the vacuum decay graph for a test that was carried out for about twenty-eight days (39725 hours) using the TVHS. The 4 mm thick test sample was used in the test. During the test, the test sample temperature was elevated to 50°, and the vacuum decay was monitored for about 25 days. Such an extended duration at that temperature should normally give enough time for the majority of hydrogen to egress. After 25 days, the sample was heated to 150° C and kept at that temperature for about two and half days. At the end of that period, the sample was brought back to room temperature, and the amount of hydrogen collected was determined.

As shown in Fig. 12.5, the increase in temperature caused an increase in the vacuum pressure which is an indication of egress of additional hydrogen amounts. As given in Table 12.6, the collected standard amount of hydrogen at 50° C after

25 days was 0.20 cm^3 , and once the temperature was increased to 150° , a 0.08 cm^3 (i.e. $0.28-0.20=0.08$) an extra amount of hydrogen had egressed: this would be the amount of hydrogen that was trapped in a slightly deeper trap where 50° C was not adequate to release it.

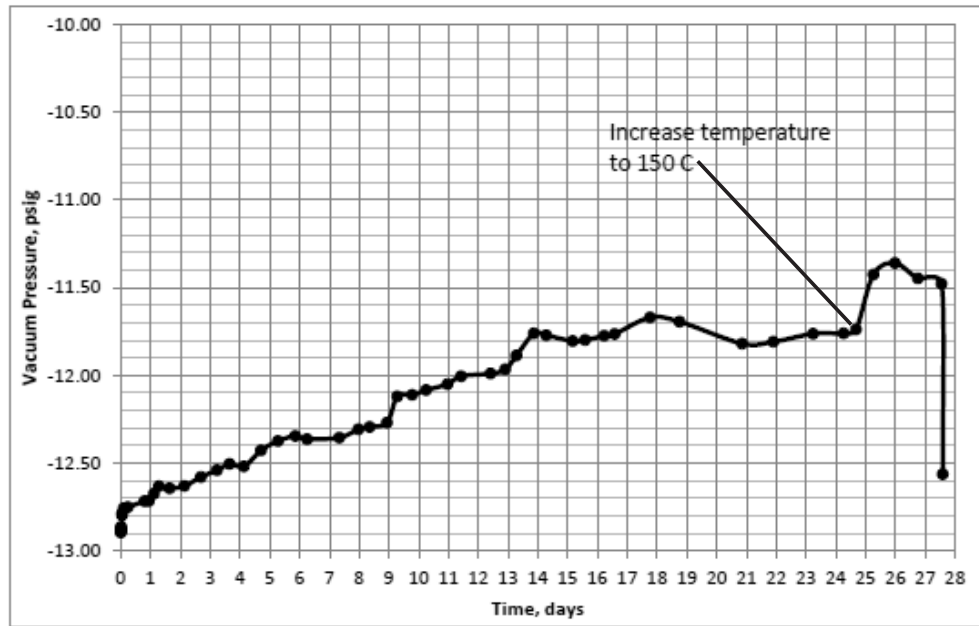


Figure 12.5: A vacuum decay graph for a test sample at 50° C and then increased to 150° C .

12.5.4 Evidence from Literature

The following sections discuss the transient temperature/ hydrogen amount data that were gathered from the literature.

Following Fig. 12.6, provides the measured hydrogen amounts liberated when a hydrogen charged steel sample was heated continuously from 25° C to 1000° C [1].

Table 12.6: The collected hydrogen amounts at 50°C after 25 days and once the temperature was increased to 150°.

Test Details	Volumes of hydrogen at STP in cm^3
4-mm sample at 50° C for 35560 hours	0.20
4-mm sample first at 50° C and then 150° C. Total test duration is 39725 hours	0.28

A gas chromatograph was used in the measurement. Before the tests, the sample was charged with hydrogen and heated to 25° C to remove the hydrogen that was trapped at the ambient temperature. As illustrated in the figure, larger amounts of hydrogen were released at temperatures around 80 to 110° C and 370 to 420° C. No significant amount of hydrogen was released between 420 to 1000° C even though one would expect peaks where steel goes through a phase transformation. This finding suggests the type of the steel tested required heating up to 420° C to release the hydrogen from the traps where most of the hydrogen is captured.

Ishizaki, T. et.al [106] state similar findings to those above. During their research work, the hydrogen evolution from charged steel samples was examined by heating them continuously in a vacuum quartz tube attached to a quadruple mass spectrometer system. The results are provided in Fig. 12.7. The first significant peak was noticed from 673 to 873 K (400-600° C). This could be the indication that hydrogen in the deeper traps has been released. Two other insignificant peaks were also noticed around 973 K (700° C) and 1173K (900° C). These could be related to the change in hydrogen evolution when steel was transforming the phases.

Wang, M., et.al.[110] analyse the hydrogen desorption (release) curves for charged

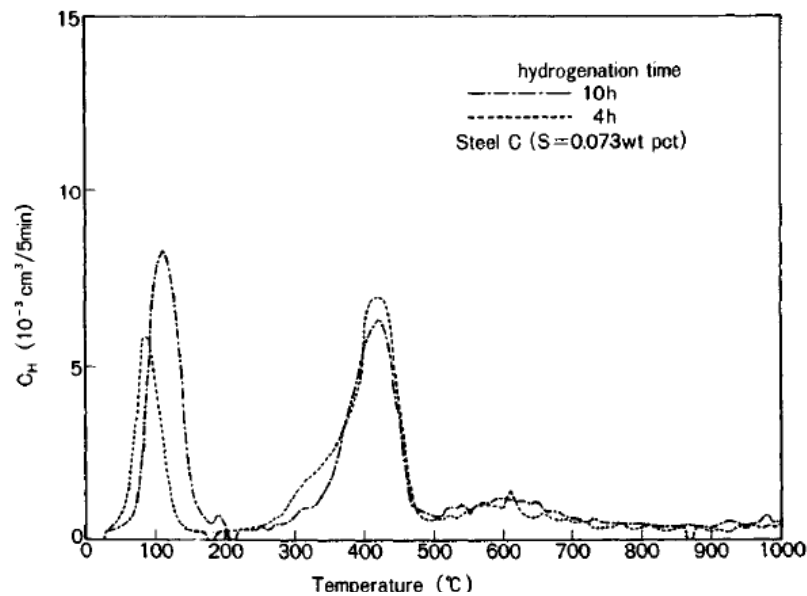


Figure 12.6: Liberation of hydrogen at high temperatures [1].

and uncharged test samples, According to the reference Fig. 12.8 provides a typical hydrogen desorption curve of the selected steel which is quenched and tempered AISI 4135. At a heating rate of 100 K/h, the uncharged test sample has shown one small hydrogen release peak at 407° C (680 K). The calculated hydrogen content corresponding to this peak was 0.06 wppm. Compared with the uncharged sample, hydrogen charged samples showed additional hydrogen desorption peak at a lower temperature of around 177° C (450 K) and the hydrogen content corresponding to this peak depended on the charging conditions. The calculated activation energies of hydrogen release corresponding to the lower and higher temperature peaks were 14.9 and 68.4 kJ/mol, respectively. According to authors, from the activation energies and peak temperatures, the lower temperature peak probably corresponds to the hydrogen in lattice and trapped by reversible trapping sites such as dislocations and

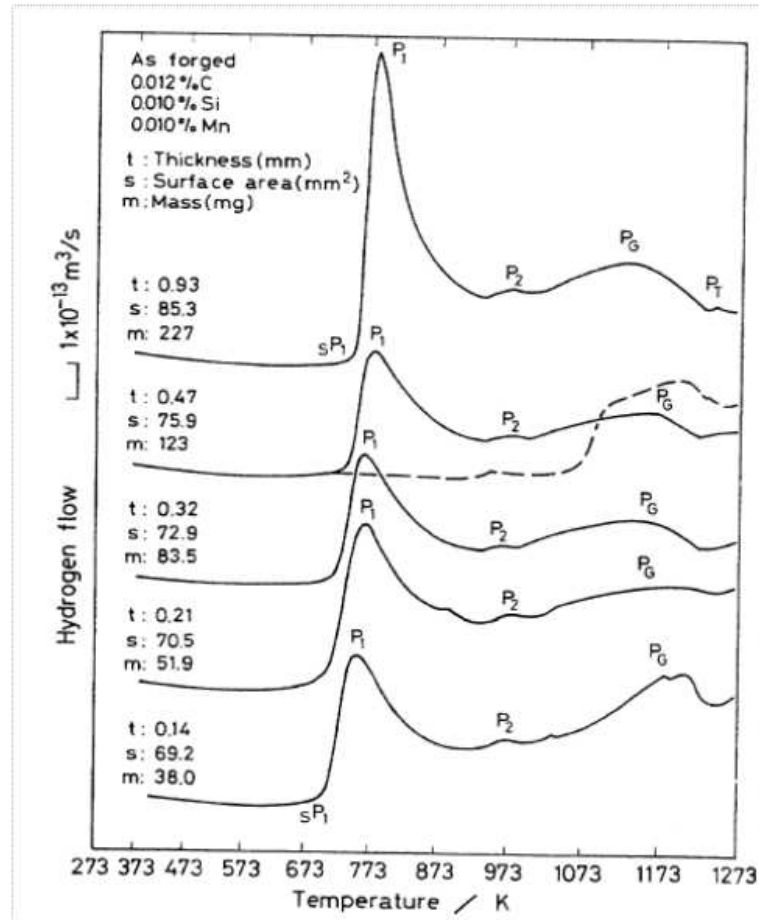


Figure 12.7: Hydrogen evolution from charged steel samples [106].

grain boundaries, while the higher temperature peak presumably corresponds to the hydrogen trapped by irreversible trapping sites such as the interfaces between ferrite and cementite.

Similar evidence can be found in [107], [108], and [109] which used the thermal desorption method with continuous heating to analyze steels with various trapping sites.

Smialowski, M. [97] provided optimum temperature ranges for hydrogen removal

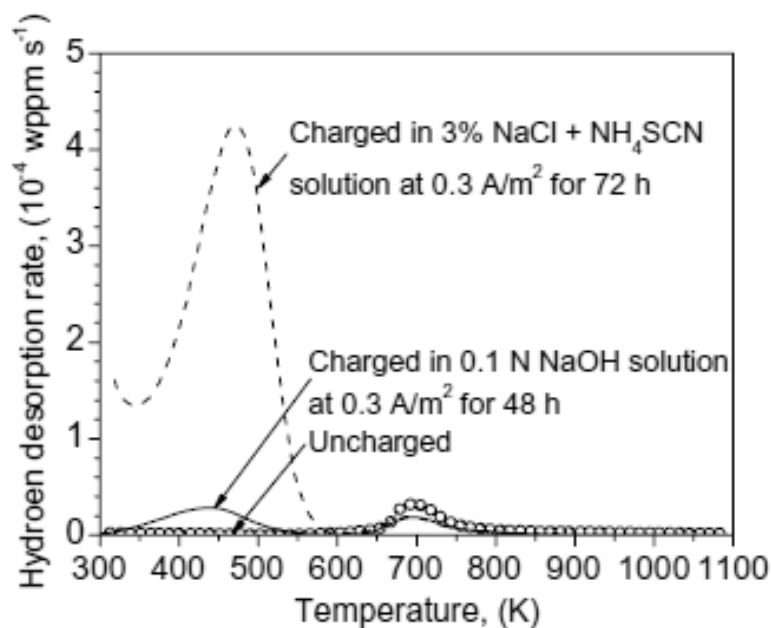


Figure 12.8: Hydrogen evolution from charged and uncharged steel samples [110].

from different types of steels using the early work on hydrogen in steels. See Table 12.7. Hydrogen has entered into these steels during the steel making process. It appears that the given hydrogen amounts are the maximum hydrogen amounts collected at the test temperature; thus, the method has not used the continuous heating method.

In summary, the literature suggests steel samples show a noticeable peak related to the amount of hydrogen that egressed mostly between the temperatures 250° C and 600° C. The TVHS test results also show a significantly higher amount of hydrogen egressed at 350° C when compared to the amounts collected at 50, 150°, 250°, and 350° C. However, in the TVHS method, at each temperature, hydrogen amounts were collected until they become stabilized rather than using continuous

Table 12.7: The temperature ranges that collected the highest amount of hydrogen for low carbon steels [97].

Carbon % in steel	Temperature, ° C
0.15	200 to 650
0.19	200 to 400, 725
0.27	250 to 400
0.29	250 to 500, 600

heating. Regardless of the differences in the hydrogen measuring techniques (steady versus transient), the temperature of 350° C obtained from the TVHS method is well within the temperature range given in the literature. Further the continuous heating methods given in the literature will result in a time lag in hydrogen egress, resulting in a higher indicated temperature than what is found in this study when using a steady state method.

12.5.5 Importance of Finding

This is an important phenomenon that could have great practical importance when it is necessary to choose the correct temperature for removing hydrogen from components (i.e. baking temperature). It is always critical to find the optimum temperature-time relations for pre-heating and post-heating applications to control the damage that occurs from hydrogen. Thus, it is worthwhile to carry out further research on this. It is apparent that the temperature or temperature range at which the majority of hydrogen amounts egress could be affected by the test parameters, such as the test method and the test sample materials.

12.6 TVHS test outcome: Hydrogen Amounts at Different Test Durations

12.6.1 Key Findings

Section 11.6 provides the hydrogen amounts collected at different time durations. Fig. 12.2 is plotted using these data to compare the average hydrogen amounts collected over 720 minutes (1/2 day), 1440 minutes (1 day), 2880 minutes (2 days), 4320 minutes (3 days), 5760 minutes (4 days), and 7200 minutes (five days) . Thus, the figure shows how hydrogen amounts are approaching a steady state with time for each of the test temperatures. In general, the following are apparent from the figure.

For all four selected test temperatures (i.e. 50, 150, 250, and 350° C),

- At the end of the first day (1440 minutes), only about fifty percent (50%) of V_{max} is collected. V_{max} is the amount of hydrogen collected at the end of the fifth day.
- It took about three days (4320 minutes) to collect about ninety percent (90%) of V_{max} .

From these observations, the following can be concluded:

- Even though higher test temperatures have resulted in egressing higher amounts of hydrogen, these test temperatures have not resulted in stabilizing the hydrogen amounts in a reduction of testing time.

- The time durations for hydrogen amounts to come to a steady state that were observed in this research study are much longer than the time durations that are provided in some of the standard methods and literature.

12.6.2 Possible Reasons for Taking a Longer Time to Stabilize Hydrogen Amounts at Higher Temperatures

In general, based upon diffusion mechanisms it would be expected that the hydrogen amounts would start reaching a steady state (V_{max}) much faster at higher test temperatures as shown in Fig. 12.3 and Fig. 12.11 which were obtained from the literature. However, according to the TVHS results given in Fig. 12.2, it took a much longer time to stabilize the hydrogen amounts at 350° C. To stabilize the hydrogen amounts faster, the hydrogen amounts should egress from the material at a higher rate, and that rate should be gradually slowed down as shown in a typical hydrogen evolution graph similar to Fig. 12.3 which is obtained from [33]. However, the curve for 350° C in Fig. 12.2 shows that initially for a shorter period of time, hydrogen egressed from test sample at a higher rate (which is indicated by the higher gradient) and later on the rate slowed down. Fig. 12.9 is prepared using Fig. 12.2 showing the gradients in dotted lines to make the observation clearer.

According to Fig. 12.9, the initial hydrogen egression rate later declined faster where it would normally gradually decline. From the figure, basically two different gradients are apparent, especially for the 350° C, 250° C, and 50° C test results. This suggests a change in the hydrogen egression rate during the test duration. It is also apparent if the initial rate was maintained for 350° C curve, the amounts would have stabilised in about 2000 minutes, which is much sooner than 5760 minutes. In fact, it would be sooner compared to the timing for 50 and 150° C.

Similar findings are obvious from the test results of 12 mm thick samples, which are given in Fig. 12.10. Even though the curve for 350° C started stabilizing a bit sooner than the curves for the lower temperatures, two different gradients are still apparent. However, before exploring this further, it would be sensible to repeat the tests more times by collecting hydrogen at smaller time intervals than the intervals used in the tests.

The average hydrogen egression rate for each temperature can be calculated by dividing the V_{max} values for the temperature by 7200 minutes. Thus, the average hydrogen egression rate at 50, 150, 250, and 350° C for 4 mm samples are given in Table 12.8. From the table, it is clear that the average rate of hydrogen egression was higher at higher temperatures as would be expected, even though the steady state was not reached sooner.

Table 12.8: The average rate of hydrogen egression with respect to temperature.

Temperature, °C	average hydrogen egression rate, cm ³ per minutes
50	2.4E-5
150	4.3E-5
250	5.4E-5
350	1.8E-4

12.6.3 Possible Mechanisms

The test results suggests two mechanisms are occurring. First, some amount of hydrogen comes out at a higher rate at the elevated temperatures. These could be the easily-mobile hydrogen amounts in the sample. Second, elevated temperatures results

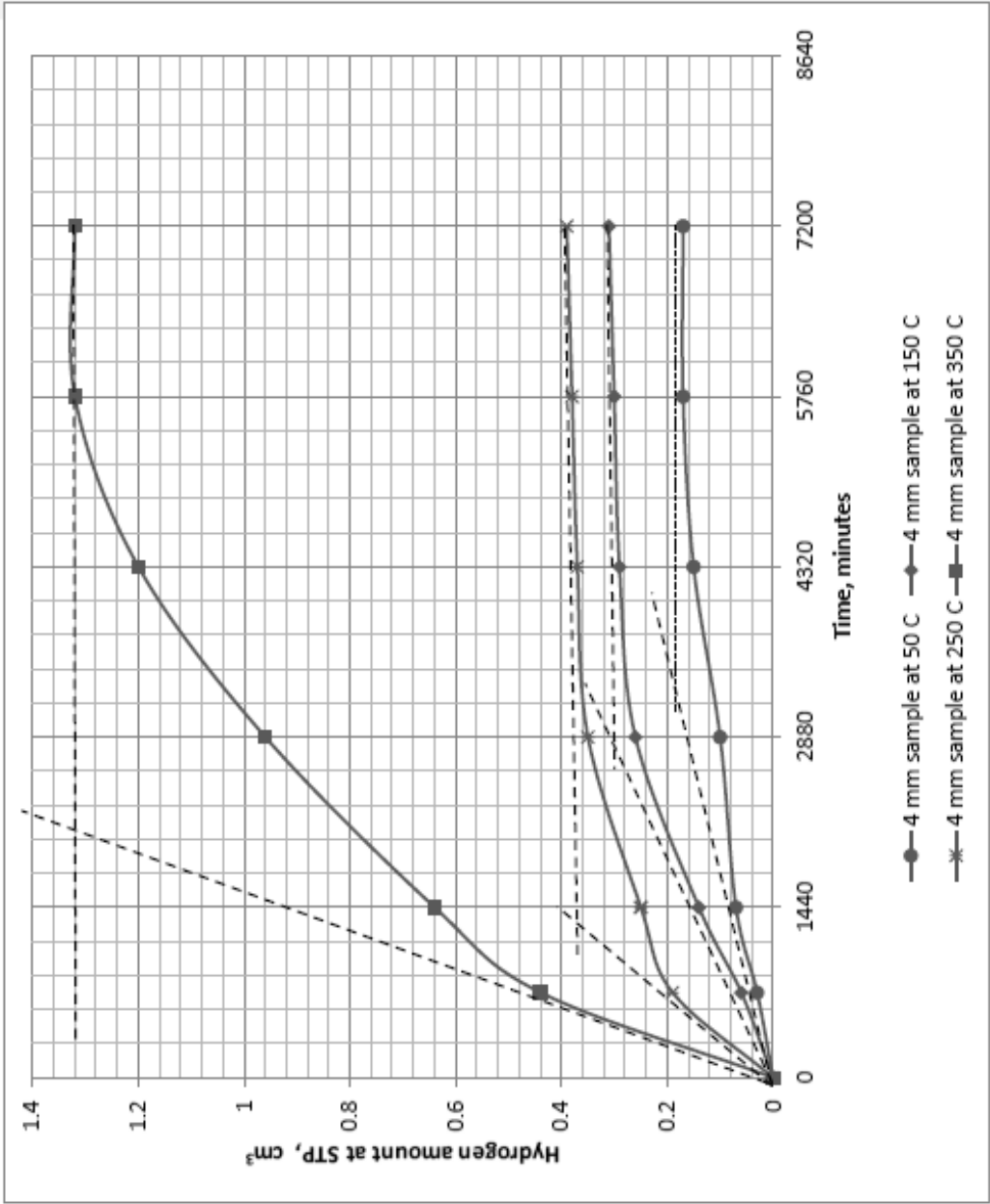


Figure 12.9: Hydrogen egression rates for 4 mm sample.

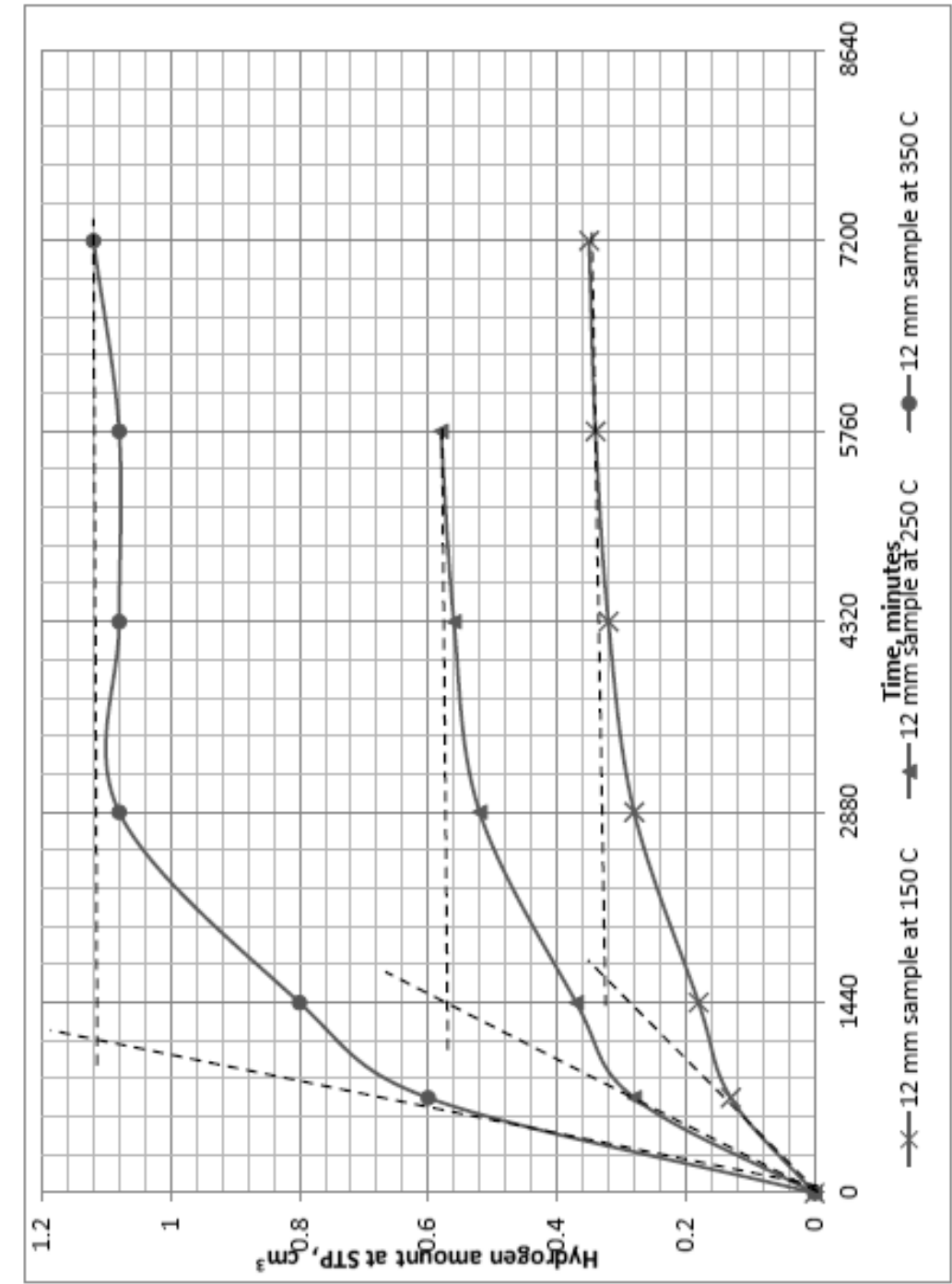


Figure 12.10: Hydrogen egression rates for 12 mm sample.

in further amount of hydrogen (possibly the progressively-mobile hydrogen contents) to comes out at a slower rate. Thus the overall test duration is not shortened.

12.6.4 Comparison of Duration to Stabilize the Hydrogen Amounts with Literature Findings

Lets consider following few examples from the literature and one example from previous research work.

Fig. 12.3 [33] shows the concentration of hydrogen with respect to time for the amounts of hydrogen that egress up to 350°C . A tubular furnace attached to a gas chromatograph was used for the measurements. The disk shaped (6 mm diameter, 15 mm thick) test samples were made out of steel with 0.34% C. As shown in the graph, only 300 minutes was required when the hydrogen amounts seem to have been stabilized for all the temperatures. Fig. 12.11 [51] shows the partial pressure of hydrogen with respect to time for 650, and 950 to 1000°C , where the time scale has reached up to only 30 minutes. Here, hydrogen has been collected using the hot extraction method and measured using a pressure gauge. Cylindrically shaped (approximately 0.6 mm diameter and 2.4 mm thick, 3 g in weight) test samples were made out of 0.3% C; low alloy steel was used in the tests.

Fig. 12.12 compares the evolution of hydrogen at room temperature as a function of time for three types of steels. According to the figure, hydrogen amounts were not stabilised for two types of steel even after 1440 hours (~ 60 days).

When the examples above are considered, in general they show that, with the increases of temperature, the time taken for hydrogen to egress has been reduced as

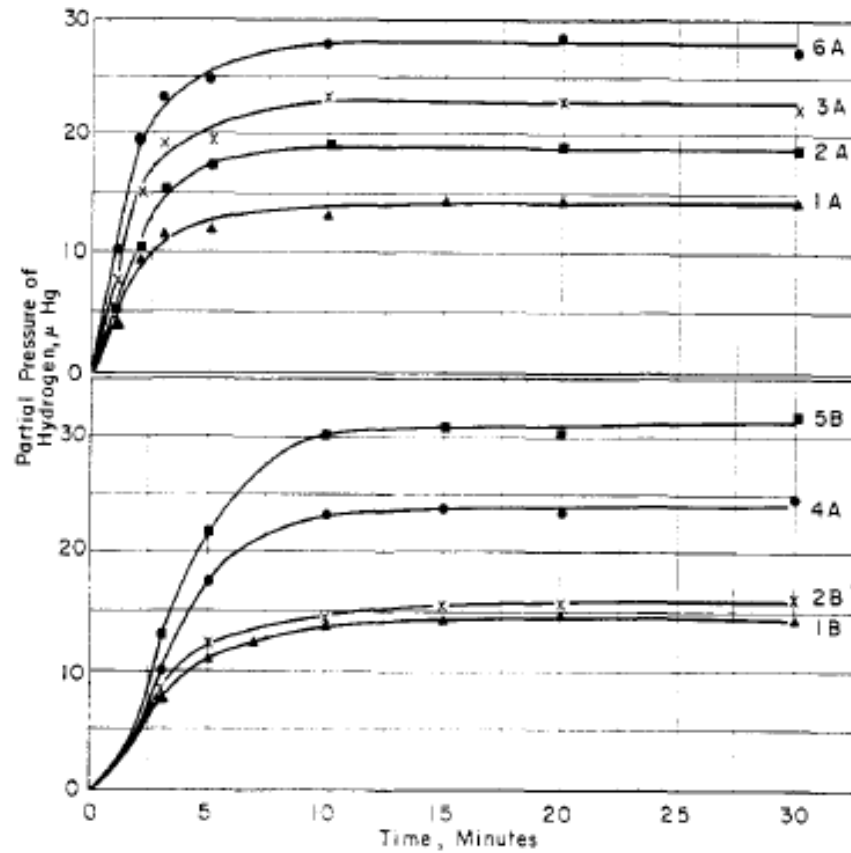


Figure 12.11: Evolution of hydrogen at 650, and 950 to 1000° C as a function of time [51].

suggested by the diffusion theories. However, it is extremely difficult to compare and come to a conclusion on a time scale (i.e. seconds, minutes, or days) that it would take at each temperature to collect the maximum amount of hydrogen because of the vast differences between the recorded measuring methods, test sample sizes, shapes, surface conditions, and their material type. Also it is doubtful whether the samples were given adequate time until the hydrogen amounts reached to a steady states.

In addition, a theoretical model to predict the time taken for hydrogen amounts

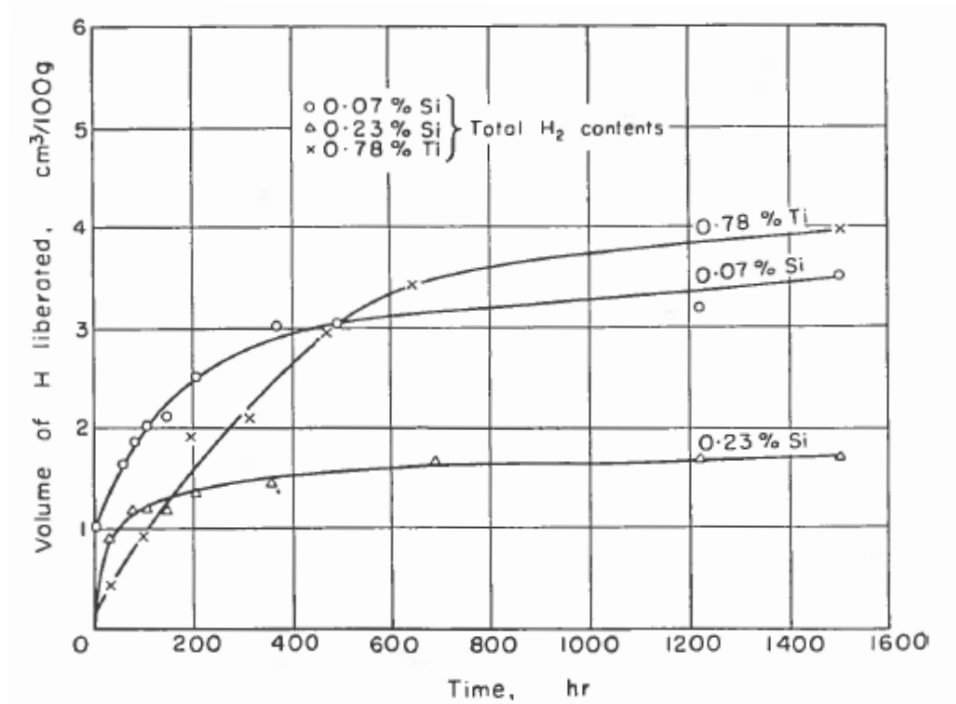


Figure 12.12: Evolution of hydrogen at room temperature as a function of time for three steel types [97].

to egress has become worthless because the diffusion information for hydrogen in iron and steel is controversial and covers a wide range of values. For example, one of the main issues that has to be resolved in such a model is what diffusion coefficient should be used for steel. Many researchers have concluded there is a significant range for the value of the diffusion coefficient for typical carbon steels [111]. According to a review of diffusion coefficient (D) values of iron and steels reported over the last sixty years, D at 150°C could vary from $1.2\text{E-}8$ to $4\text{E-}6$ [8]. The use of such a wide range of D values could cause the predicted time for egress of hydrogen from a thin steel sample to vary from a few minutes to few days.

Thus in summary, it is difficult to compare the durations to stabilize the hydrogen

amounts using the currently available information related to hydrogen.

12.7 TVHS Test Outcome: Correlation of Hydrogen Amounts

The following section describes two methods for correlating the hydrogen amounts that have egressed at different test temperatures for TVHS tests. These methods use the combined effect of the test temperature and test duration on the hydrogen amounts collected for predictions.

12.7.1 Method 1

Fig. 12.13 shows rate of hydrogen egression (i.e. how much hydrogen was egressed over a 2880 minutes period) for 4 mm thick at different test temperatures. Data from Section 11.6 are used to plot this graph.

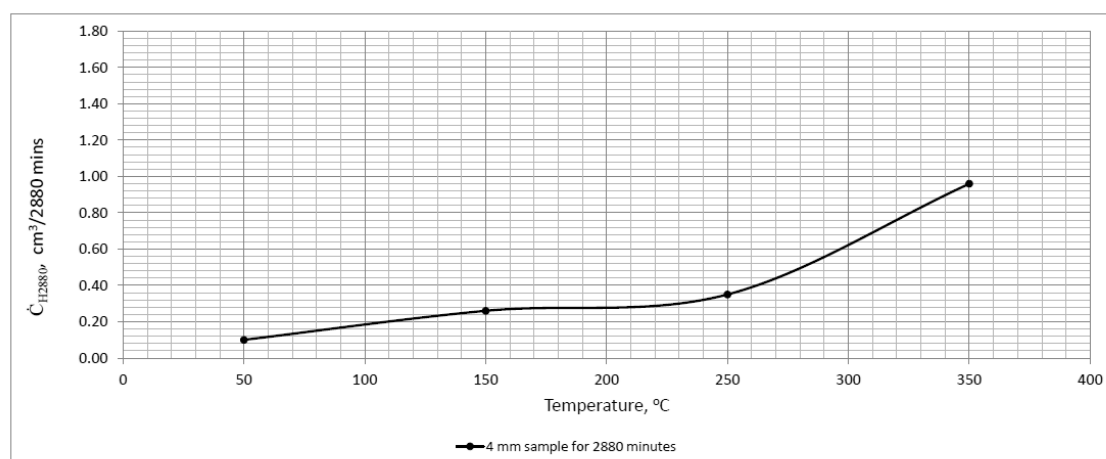


Figure 12.13: Rate of hydrogen egression at various test temperatures for 4 mm sample using 2880 minutes test results.

If it is assumed that the quantity of hydrogen egressed at different test temper-

atures at a constant time period is governed by the Arrhenius type rate equation that governs the rate processes, the hydrogen volumes egressed at a temperature for a constant time period can be written as follows:

$$\dot{C}_H = A \exp(-E_A/RT) \quad (12.2)$$

where A is pre-exponential factor, E_A is activation energy, R is the universal gas constant which is 8.314 J/molK, and T is the temperature in kelvin.

Also Rate ($\dot{C}_H$) can be determined by:

$$\dot{C}_H = \frac{V}{t} \quad (12.3)$$

where V is the volume of hydrogen egressed for a time period of t and t is the time period.

Thus, for the Fig. 12.13, the rate the hydrogen egressed can be written as follows:

$$\dot{C}_{H2880} = A_{2880} \exp(-E_A/RT) \quad (12.4)$$

Equ.12.4 can be re-written as

$$\ln \dot{C}_{H2880} = \ln A_{2880} - (E_A/RT) \quad (12.5)$$

Thus, a plot between $\ln \dot{C}_{H2880}$ and $1/T$ is produced for the results given in Fig. 12.13, and it is given in Fig. 12.14. If the rate equation is obeyed, a plot of $\ln \dot{C}_{H2880}$ versus $1/T$ should be a straight line with a slope of $-(E_A/R)$ and a Y intercept = $\ln A_{2880}$.

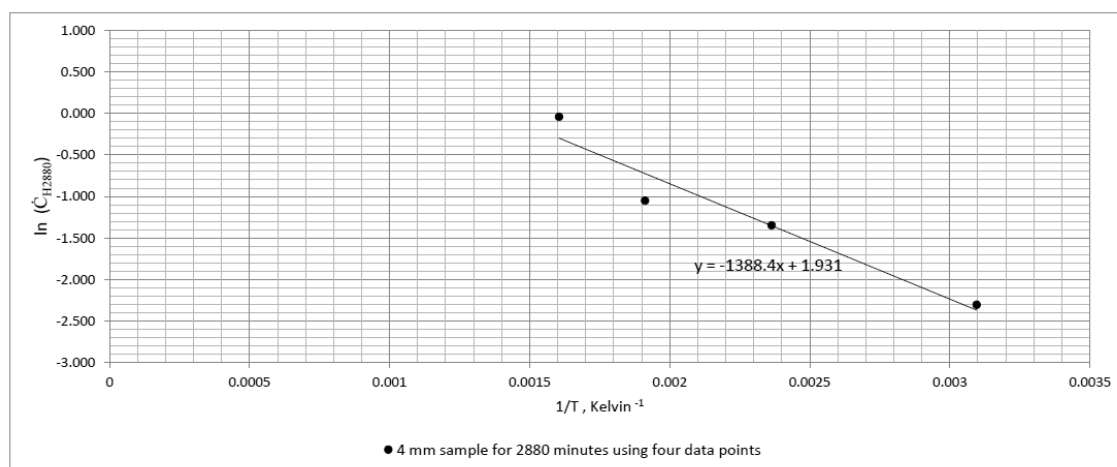


Figure 12.14: Plot of $\ln \dot{C}_{H2880}$ versus $1/T$ for four data points using the data provided in Fig. 12.13.

According to Fig. 12.14, the equation of the straight line that would best fit the data points is given by

$$y = -1388.4x + 1.931 \quad (12.6)$$

where $y = \ln \dot{C}_{H2880}$ and $x = 1/T$, where T , temperature, is measured in Kelvin.

Using Equ.12.5 and Equ.12.6, A_{2880} and E_A/R can be calculated.

Thus,

$$\dot{C}_{H2880} = 6.896 \text{ cm}^3 \text{ per 2880 minutes and } E_A/R = 1388.4 \text{ K}^{-1}$$

Therefore, the rate equation for the data in Fig. 12.13 can be represented from the following equation:

$$\dot{C}_{H2880} = 6.896 \exp(-1388.4/T) \quad (12.7)$$

However, as explained before, the significantly higher amounts of hydrogen collected at 350° C made it difficult to fit the results shown in Fig. 12.14 to a straight line that reasonably represents all the data points. Therefore, the same plot was made in Fig. 12.15 without using the data for the tests carried out at 350° C. From looking at Fig. 12.15, it is clear that the data points are a better fit to a straight line when the data point related to 350° C is omitted. Thus, the rate equation using the data in Fig. 12.15 can be derived as explained before, and it can be represented in the following equation:

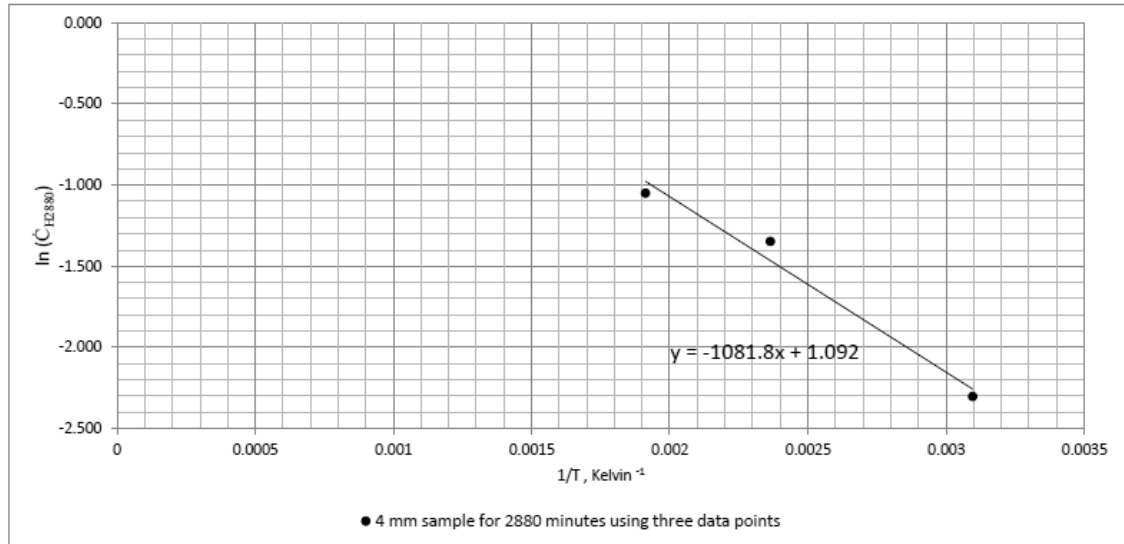


Figure 12.15: Plot of $\ln \dot{C}_{H2880}$ versus $1/T$ for three data points using the data provided in Fig. 12.13.

$$\dot{C}_{H2880} = 2.98 \exp(-1081.8/T) \quad (12.8)$$

Table 12.9 gives the amounts of hydrogen calculated using Equ.12.7 and Equ.12.8 compared to the actual amounts of hydrogen obtained from the test in identical

conditions. According to the test results indicated in the table, it is clear that Equ.12.8 closely represents the actual test values up to 250° C. Thus, the equation can be used to accurately predict the amounts of hydrogen at other temperatures (E.g.100° C, 200° C) at which the tests were not carried out. The hydrogen amounts at 350° C are calculated using the Equ.12.8: the answer is 0.45 cm³ where the test results indicated 0.96 cm³. Thus, as mentioned, the equation is accurate only up to 250° C.

Table 12.9: The amounts of hydrogen calculated using Equ.12.7 and Equ.12.8 compared to the actual amounts of hydrogen obtained from the tests

Test Temperature ° C (K)	Actual hydrogen amounts collected during tests cm ³	Hydrogen amounts calculated using Equ.12.7	Hydrogen amounts calculated using Equ.12.8
50 (323)	0.10 ± 0.01	0.09	0.10
150 (423)	0.26 ± 0.05	0.26	0.22
250 (523)	0.35 ± 0.04	0.48	0.35
350 (623)	0.96 ± 0.04	0.74	N/A

Equations for Other time durations

Similarly, equations can be developed for the other test durations: i.e., 720 minutes, 1440 minutes, 4320 minutes, 5760 minutes, and 7200 minutes. Thus, equations for calculating the hydrogen amounts at 5760 minutes are derived and given in Eqn.12.9 when four data points are used (that is when data for 350° C is included). Eqn.12.10 provides the same amounts when three data points are used (that is, when data for 350° C is omitted). Time duration of 5760 minutes was selected because that is the time needed for the hydrogen amounts to stabilize or start to stabilize for all

the selected test temperatures (see Fig. 12.2). The information used to derive the equations is given in Fig. 12.16, Fig. 12.17, and in Fig. 12.18. Fig. 12.16 show how much hydrogen was collected from the 4 mm thick test sample over a four-day period (5760 minutes) at different temperatures and and Fig. 12.17 gives $\ln \dot{C}_H$ vs $1/T$ plot for the four data points. Fig. 12.18 provides $\ln \dot{C}_H$ vs $1/T$ plot for three data points.

$$\dot{C}_{H5760} = 5.899 \exp(-1199.2/T) \quad (12.9)$$

$$\dot{C}_{H5760} = 1.4596 \exp(-688.65/T) \quad (12.10)$$

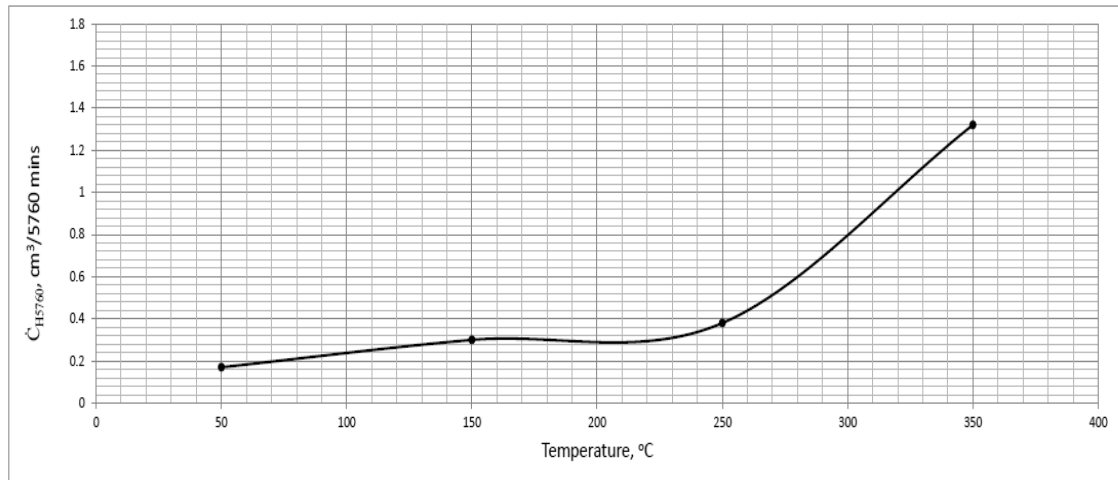


Figure 12.16: Rate of hydrogen egression at various test temperatures for 4 mm sample using 5760 minutes test results.

Table 12.10 gives the amounts of hydrogen calculated using Equ.12.9 and Equ.12.10 compared to the actual amounts of hydrogen obtained from the test in identical con-

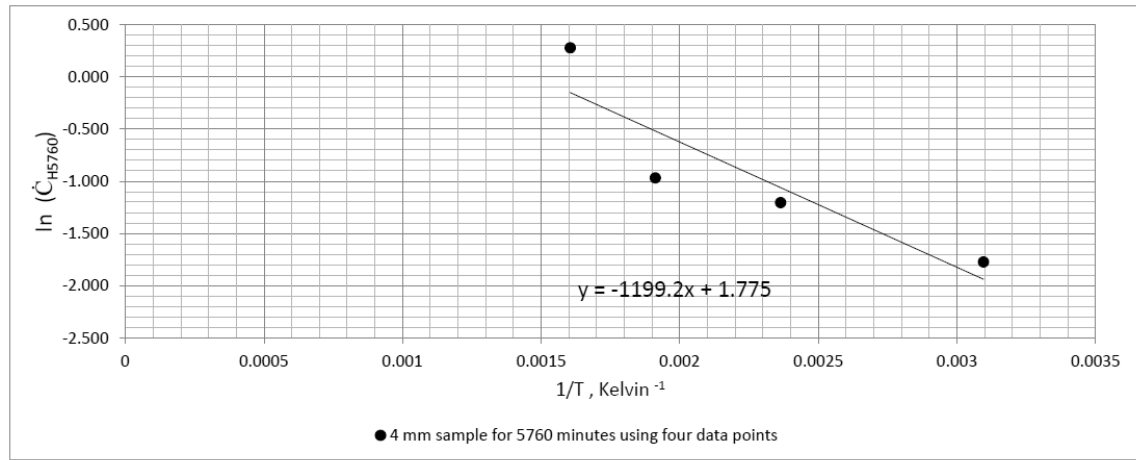


Figure 12.17: Plot of $\ln \dot{C}_{H5760}$ versus $1/T$ for four data points using the data provided in Fig. 12.16.

ditions. According to the results indicated in the table, it is clear that Equ.12.10 closely represents the actual test values up to 250° C. Thus, Equ.12.10 can be used to accurately predict the amounts of hydrogen at other temperatures (E.g.100° C, 200° C) at which the tests were not carried out.

Importance of finding

Equ.12.8 and Equ.12.10 are useful to predict how much hydrogen would egress at any temperature up to 250° C. For example, the predicted hydrogen amount that has egressed at 200° C at the end of four days' duration for identical test conditions would be 0.34 cm³ at STP. This is predicted using Equ.12.10. In addition, the method used to derive the equations above can be used to derive equations for predicting hydrogen amounts when limited test results are available at different test conditions. For example, if the hydrogen amounts that have egressed at 50° C and 150° C are known, an equation can be derived to predict the hydrogen amounts that egressed

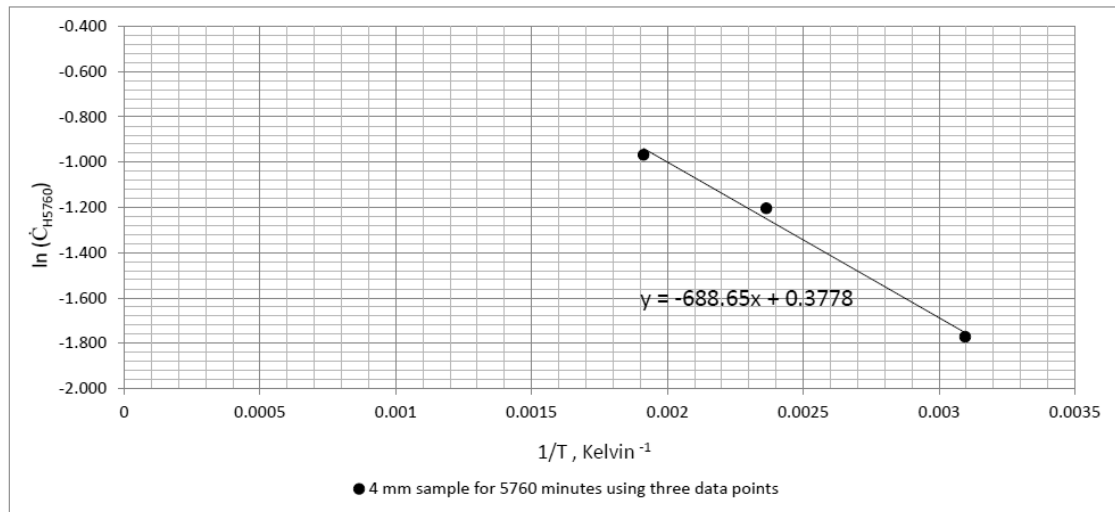


Figure 12.18: Plot of $\ln \dot{C}_{H5760}$ versus $1/T$ for three data points using the data provided in Fig. 12.13.

at any temperature up to 250° C.

12.7.2 Method 2

This method is similar to the above method except, this method used the hydrogen egress rates of the entire data set up to 250° C. Thus the hydrogen egress rate is calculated as the amount of hydrogen egressed per second. Fig. 12.19 provides $\ln \dot{C}_H$ vs $1/T$ plot for the data points. Thus, equation for calculating the hydrogen rates is derived and given in Eqn.12.11.

$$\dot{C}_H = 1.4E(-5)exp(-1007/T) \quad (12.11)$$

Table 12.11 gives actual hydrogen amounts, the amounts of hydrogen calculated using the Equ.12.11, and the amounts of hydrogen calculated using method 1 (i.e.

Table 12.10: The amounts of hydrogen calculated using Equ.12.9 and Equ.12.10 compared to the actual amounts of hydrogen obtained from the tests

Test Temperature ° C (K)	Actual hydrogen amounts collected during tests cm ³	Hydrogen amounts calculated using Equ.12.9	Hydrogen amounts calculated using Equ.12.10
50 (323)	0.17 ± 0.01	0.14	0.17
150 (423)	0.30 ± 0.04	0.35	0.29
250 (523)	0.38 ± 0.04	0.60	0.39
350 (623)	1.32 ± 0.06	0.85	N/A

Equ.12.8 and Equ.12.10) for comparison.

Importance of finding

Equ.12.11 is useful when it is required to predict how much hydrogen would egress at any temperature up to 250° C and at any time period up to 5760 minutes (4 days). For example, the predicted hydrogen amount that has egressed at 225° C at the end of 1560 minutes duration would be 0.17 cm³ at STP. Even though Equ.12.8 and Equ.12.10 predict amounts with a better accuracy, Equ.12.11 has better versatility during the calculations. The Equ.12.11 can be refined using more data points from additional tests as a future work. Refined- equation will provide better predications.

As an additional step, the activation energy for egression of hydrogen from steel, between 50° and 250° C was calculated using the Equ.12.11 and it is about 8.37 kJ/mol. The values obtained from literature [8] for activation energy of hydrogen that egress from iron and steel samples, at temperatures between 200° and 700° C varies from 6.91 to 13.63 kJ/mol.

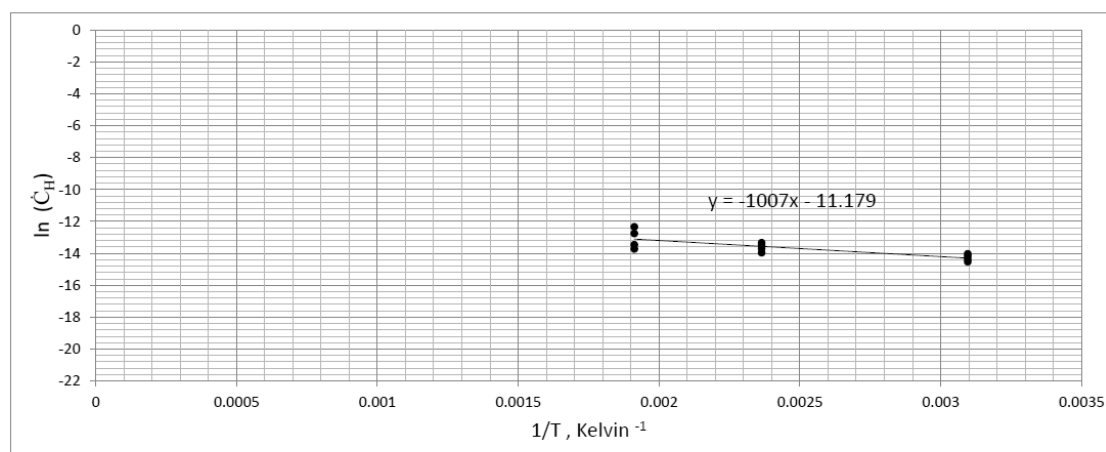


Figure 12.19: Plot of $\ln \dot{C}_H$ versus $1/T$ for all data points.

Table 12.11: The amounts of hydrogen calculated using Equ.12.11 compared to the actual amounts and amounts calculated using method 1.

Test Temperature ° C (K)	Actual amounts from tests cm ³	Amounts calculated using Method 1's Equ.12.8	Amounts calculated using Method 1's Equ.12.10	Amounts calculated using Method 2's Equ.12.11
50 (323)	0.10 ± 0.01	0.11	N/A	0.11
150 (423)	0.26 ± 0.05	0.23	N/A	0.22
250 (523)	0.35 ± 0.04	0.38	N/A	0.35
50 (523)	0.17 ± 0.01	N/A	0.17	0.21
150 (523)	0.30 ± 0.04	N/A	0.29	0.45
250 (523)	0.38 ± 0.04	N/A	0.39	0.71

Chapter 13

Conclusions and Suggested future work

13.1 Conclusions

The results obtained in this thesis work indicate that the hot vacuum extraction technique based on the new Thermal Vacuum Hydrogen System (TVHS) can be used to accurately measure hydrogen amounts in steel samples. The vacuum decay is a sensitive and responsive parameter that is directly related to the hydrogen flux. The groundwork related to operating the system has been completed, and the following conclusions are made based on this groundwork:

- Operating the TVHS can be currently done up to a temperature of 400° C.
- Using a secondary pressure gauge with a primary pressure gauge helps to overcome the problems related to drifting of pressure gauge readings.
- Bringing the entire system back to room temperature avoids the need to do complex calculations that are otherwise required to compensate for the effects of temperature on the parts of the TVHS.
- Using dummy samples helps in making the system's total volume constant. By using these, the vacuum decay graphs for the different thickness samples were able to be compared with each other.
- Enhanced vacuum chamber with vee apexes on the lips, annealed deoxidized copper gaskets, and the bolt tightening procedure resulted in achieving consis-

tent successful sealing in the vacuum chamber.

The TVHS was calibrated using the standard eudiometer method. The following conclusions were made using the calibration test results.

- When the amount of hydrogen collected using the TVHS method was compared with the eudiometer method, the TVHS method registered a slightly higher amount of hydrogen. Because this observation applied to all the sub-tests and similar observations are noted in some of the references, this finding is considered actual. The statistical variation of the TVHS test results is quite similar to the eudiometer test results and is not a factor in the variation between the two methods. Thus, the Equ. 8.1 can be used to correlate the measured amounts from the two methods.
- It is likely that the differences between the mediums (medium type and pressure) that the test samples were immersed have caused the above mentioned differences in the collected hydrogen amounts.

The following conclusions were made using the hydrogen amounts that were measured using the TVHS method. The results are based on the test results obtained from 4 mm and 12 mm thick, 31 mm in diameter, disk-shaped test samples made out of grade AISI 1020 steel.

- Temperature is a key parameter that affects the amount of hydrogen that egressed out from a sample. Each test temperature resulted in reaching its own steady state amount of hydrogen. Thus, it is unlikely that the amount of hydrogen that egressed from a test sample at a lower temperature would reach the same amount that egressed at a higher temperature with time.

- A significantly higher amount of hydrogen egressed at 350° C, compared to the amounts that egressed at 50° C, 150° C, and 250° C. Thus it is likely for the steels samples used in this research work, the majority of charged hydrogen would have been trapped in deeper traps in which elevation of temperature less than 350° C was not adequate to release the hydrogen.
- The ratios among the amounts of easily mobile hydrogen: progressively mobile hydrogen at 150° C: progressively mobile hydrogen at 250° C: progressively mobile hydrogen at 350° C is 1: 2: 3: 10.
50° C is taken as the temperature that collected the easily mobile hydrogen, and the ratios are based on the steady state hydrogen amounts.
- The ratio among the amount of hydrogen that egressed at the end of $\frac{1}{2}$ a day: 1 day: 2 days: 3 days: 4 days: 5 days is 1.0: 2.3: 4.2: 4.7: 4.9: 5.0. The ratio was calculated by using the mean value of the amounts of hydrogen that egressed at 150° C.
- At all the test temperature selected, it took much longer time to reach the hydrogen amounts to come to a steady state.

The following conclusions were made using the test carried out by the eudiometer method.

- Improvements implemented on the eudiometer system and related hydrogen measuring procedure increased the accuracy and efficiency of the eudiometer method and improved the user' safety.
- Analyzing of the powder samples collected from the mercury bath and the

immersed mild steel sample showed a possibility for hot mercury to dissolve carbon from the pearlite structure of the steel, leaving the iron in the structure.

13.2 Suggested Future Work

As explained in this thesis work, the TVHS can be used to correlate hydrogen amounts with different parameters (i.e. test temperature, test duration, material types, and so forth). Thus, the opportunities for future research using the TVHS in hydrogen measurement are endless. Following are few suggestions for areas of future research.

- Finding accurate optimum temperature ranges for hydrogen removal from different types of steels
- Finding the behavior of changing the rate of hydrogen egress from a test sample
- Finding how external pressure and type of the medium that a test sample is immersed would effect on the measured amounts of hydrogen
- Refining of the Equ.12.11 using more data points from additional tests to provide better predications on hydrogen amounts.

The following suggested improvements would help to further expand the uses of the TVHS:

- Investigation of different gasket materials those are suitable for use in the vacuum chamber assembly that could withstand higher temperatures
- Investigation of a commercially available vacuum chamber that could be assembled faster to replace the current vacuum chamber. (Even though the vacuum

chamber that was designed and fabricated for this research study works well, it needs a longer time to assemble before each test, so the assembly of the chamber has become a bottle neck in the test procedure.)

- Investigation of how the TVHS could convert to a unit that could measure total hydrogen amounts in a steel sample.

Finally, the findings in this research work on the interaction of steel with the mercury (especially the possibility of dissolution of carbon from steel by mercury at low-elevated temperature) are new knowledge; and further studies are needed to confirm these findings.

References

- [1] Lunarska, E., “Hydrogen-degradation of low carbon steels” in *Hydrogen Degradation of Ferrous Alloys*, ed. Oriani, R.A., Hirth, J., Smialowski, M., (NJ, USA: William Andrew Publishing, Noyes, 1985), 720.
- [2] Wang, M., Akiyama, E. and Tsuzaki, K., “Effect of hydrogen on the fracture behavior of high strength steel during slow strain rate test,” *Corrosion Science* 49 (2007): 4081-4097.
- [3] Senadheera, T., Ph.D. Thesis Proposal on *Accurate measurement of hydrogen in steels* (2006): 3.
- [4] Kim, G., “Failure of piping by hydrogen attack,” *Engineering Failure Analysis* 9 (2002): 571-578.
- [5] Craig, B., “Hydrogen damage” in *ASM Handbook of Corrosion: Fundamentals, Testing and Protection* (Ohio, USA: ASM International, 2003), 367-374.
- [6] Vehoff, H., “Hydrogen related material problems” in *Hydrogen in metals*, ed. Wipf, H. (Berlin: Springer-Verlag,1995), 215-278.
- [7] Nomura, T. and Sakai, T., “Theoretical and parametric methods for evaluating hydrogen attack limit” in *Fitness for Adverse Environments in Petroleum and Power Equipment*, 359, (NY, USA: Pressure vessel and piping division , ASME International, 1997), 315-334.
- [8] Shaw, W.J.D. and Matei, D.G., “Fundamental and Applied Studies of Hydrogen Embrittlement,” Special Report (*internal*),1998.

-
- [9] Steiner, J.E., "Control of flaking and other hydrogen problems in heavy forgings" in *Current Solutions to Hydrogen Problems in Steels*, ed. Interrante, C.G. and Pressouyre, G.M. (Ohio, USA: ASM International, 1982), 55-62.
- [10] Jha, K.N., Sardar, M.N., Jha, N.N. and Chakraborty, S., "Hydrogen control during steel making for medium carbon wheels," *Scandinavian Journal of Metallurgy* 32 (2003): 296-300.
- [11] Beloglazove ,S.M., "Absorbtion of hydrogen by steel during pickling and electroplating," *Soviet Material Scienec* 1 (1965): 192-196.
- [12] Bruce, D.C., "A contribution to the mechanism of hydrogen entry into steels in acid environments," *Corrosion* 34 (1978): 282-284.
- [13] Darken, L.S. and Smith, R.P., "Behavior of hydrogen in steel during and after immersion in acid," *Corrosion* 5 (1949): 1-17.
- [14] "Lincolon electric introduces new additions to the FCAW-G pipeliner® family," *Pipelines and gas journal* (2012): 107.
- [15] McKeown, D. and Waltham H., "Hydrogen and its control in weld metal," *Metal Construction* 17 (1985): 655-661.
- [16] Limacher, B., Dagbert, J. and Galland, J., "Hydrogen related problems in steels after different surface treatments," in *Current Solutions to Hydrogen Problems in Steels*, ed.Interrante, C.G., Pressouyre, G.M. (Ohio, USA: ASM International, 1982), 79-91.
- [17] Feng, T.Z. and Mei, H.C., "The relation between degassing baking treatment and fracture toughness of cadmium-plated high strength steel" in *Current Solu-*

- tions to Hydrogen Problems in Steels*, ed. Interrante, C.G. and Pressouyre, G.M (Ohio, USA: ASM International, 1982), 98-110.
- [18] Timmins, P.F., *Solution to Hydrogen Attack in Steels* (Ohio, USA: ASM International, 1997), 72-75.
- [19] Zakroczymski, T., "Entry of Hydrogen into Iron Alloys from the Liquid Phase" in *Hydrogen Degradation of Ferrous Alloys*, ed. Oriani, R.A., Hirth, J., Smialowski, M., (NJ, USA: William Andrew Publishing, Noyes, 1985), 215-251.
- [20] Townsend, H., "Hydrogen sulfide stress corrosion cracking of high strength steel wire," *Corrosion* 28 (1972): 39-47.
- [21] Dvoracek, L., "Sulfide stress corrosion cracking of steel," *Corrosion* 26 (1972): 177-182.
- [22] Jones, D.A., *Principles and Prevention of Corrosion*, (NY, USA: Prentice Hall, 1996), 334-345.
- [23] Beloglazov, S., "Peculiarity of hydrogen distribution in steel by cathodic charging," *Journal of Alloys and Compounds* (2003): 240-243.
- [24] Kiefer, J.H., "Effects of moisture contamination and welding parameters on diffusible hydrogen," *Welding Journal* 75 (1996): 155-161.
- [25] Hudgins, C.M., McGlasson, R.L., Mehdizadeh, P. and Rosborough, W.M. "Hydrogen sulfide cracking of carbon and alloy steels," *Corrosion* 22 (1966): 238-251.

-
- [26] Pressouyre, G.M., "Current solutions to hydrogen problem in steel" in *Current solutions to hydrogen problems in steels*, ed. Interrante, C.G., Pressouyre, G.M., (Ohio, USA: ASM International, 1982), 18-33.
- [27] Shaw, W.J.D., Class notes of "*Hydrogen measurement & interactions in BCC steels*".
- [28] Troiano, R.A., "The role of hydrogen and other interstitial in the mechanical behavior of metals," *ASM Transactions* 52 (1960): 54.
- [29] Pressouyre, G.M., "Trap theory of hydrogen embrittlement," *Acta Metallurgica* 28 (1980): 895-911.
- [30] Bernstein, M. and Pressouyre, G.M., "The role of traps in the microstructural control of hydrogen embrittlement of steels" in *Hydrogen Degradation of Ferrous Alloys*, ed. Oriani, R.A., Hirth, J. and Smialowski, M., (NJ, USA: William Andrew Publishing, Noyes, 1985), 641-685.
- [31] Shaw, W.J.D., Matei, D. and Fraser M.A., "Understanding the behaviour of the vacuum foil hydrogen permeation techniques," *Corrosion*, Paper no.: 00463 (2000): 463/1-463/11.
- [32] Shaw, W.J.D., Jayasinghe, D.M. and Matei, D., "Correlations between corrosion electrochemical hydrogen flux and a vacuum foil technique," *Corrosion*, Paper no.: 391 (1998): 391/1-391/12.
- [33] Addach, H., Bercot, P., Wery, M. and Rezrazi, M., "Quantitative determination of hydrogen in solids by gas chromatography," *Journal of Chromatography A* 1057 (2004): 219-223.

-
- [34] Quantana, M.A. and Dannecker, J. R., "Diffusible hydrogen testing by gas chromatography," in *Hydrogen Embrittlement: Prevention and Control*, ASTM STP 962, ed. Raymond, L., (Philadelphia, USA: ASTM International ,1988), 215-251.
- [35] Das, K.B., "A hydrogen detector for measuring surface and volume hydrogen content in metals," in *Proceedings of International Conference on the Effects of Hydrogen on Material Properties and Selection and Structural Design*, ed. Bernstein, I.M. and Thompson, A.W., (Ohio, USA: ASM International, 1973), 609-620.
- [36] Sohrman, B., Budhifvars, S., Dahlskog, H., Elvander, J. and Nilsson, G., "A new method for measuring diffusible hydrogen in weld metal," *A Welding Review* (1985): 8-10.
- [37] Unites Sates patent document 4142399: Method for automatic quantitative measurement of hydrogen in metal and an apparatus for carrying out the said method, Inventors: Sato, H.,Otsubo, M. and Goto, S., 1977.
- [38] Unites Sates patent document 4191175: Process and apparatus for measurement of diffusible hydrogen, Inventors: Godai, H. and Sugiyama, T., 1980.
- [39] Unites Sates patent document 7306951 B1: Method and apparatus for determining diffusible hydrogen concentration", Inventors: Benson, D.,Wildeman, T., Smith, D. and Olson, S., 2007.
- [40] Padhy, G., Ramasubbu, V. and Albert, S.K., "Hot extraction of diffusible hydrogen and its measurement using a hydrogen sensor," *Welding in the World* 56 (2012): 18-25.

-
- [41] Ransley, C.E. and Talbot, D.E., “Routine determination of hydrogen content of aluminium and aluminium alloys by hot-extraction method ”, *Institute of Metals-Journal* 84 (1956): 445-452.
- [42] Degrove,F., Carley,J. and Gonzalez,N., “New method for determination of hydrogen content of Aluminum and alloys: Part1 Improvements in the vacuum extraction method”, *Metallurgical Transactions B* 6 (1975): 535-545.
- [43] DH603, Residual and diffusible hydrogen determination by hot extraction, Leco Cooperation, USA, 2012,
www.leco.com/products/inorganic/hydrogen/dh603/dh603.html.
- [44] Hydrogen Analysis by Vacuum Hot Extraction (VHE), Federal materials research institute (BAM), Germany, 2011,
[www.bam.de/en/service/publikationen/publikationen – medien/unikale – pruef/upe – 506 – en – 5 – 4.pdf](http://www.bam.de/en/service/publikationen/publikationen%20-%20medien/unikale%20-%20pruef/upe%20-%20506%20-%20en%20-%205%20-%204.pdf).
- [45] Martin, J.F., Laben, M.M. and Albert, S.K., “Vacuum and inert-gas fusion,” *Chemical Analysis* 40 (1974): 113-221.
- [46] Hargrove, G.L., Shepard, R.C. and Farrar, H., “Determination of nitrogen and hydrogen at parts-per-million levels in milligram steel samples,” *Chemical Analysis* 43 (1971): 439-442.
- [47] EMGA-621W Hydrogen Analyzer, HORIBA Scientific, France, 2013,
[http : //www.labcompare.com/552 – Hydrogen – Analyzer/1426 – EMGA – 621W – Hydrogen – Analyzer](http://www.labcompare.com/552-Hydrogen-Analyzer/1426-EMGA-621W-Hydrogen-Analyzer).

-
- [48] Martin, J.F. and Melnicks, L.M., "Hydrogen," *Chemical Analysis* 40 (1974): 289-321.
- [49] Mallet, W., Gerd, F.A. and Griffith, C.B., "Determination of hydrogen in magnesium, lithium, and magnesium-lithium alloys," *Analytical Chemistry* 25 (1953):116-119.
- [50] Griffith, C.B. and Mallet, W., "Determination of hydrogen in wrought aluminum alloys," *Analytical Chemistry* 25 (1953): 1085-1087.
- [51] Carson, C.A., "Determination of hydrogen in steel comparison of tin-fusion and hot-extraction techniques," *Analytical Chemistry* 32 (1960): 936-939.
- [52] Jenkins, N. and Parker, D.H., "Measurement of diffusion hydrogen in manual arc metal welded metals," *Metal Construction* 18 (1986): 298-302.
- [53] Lunarska, E., "Hydrogen- induced blister cracking in linepipe steel" in *Hydrogen Degradation of Ferrous Alloys*, ed. Oriani, R.A., Hirth, J., Smialowski, M., (NJ, USA: William Andrew Publishing, Noyes, 1985), 737-762.
- [54] Mabho, N., Bergers, K., Flock, J. and Telgheder, U., "Determination of diffusible and total hydrogen concentration in coated and uncoated steel using melt and solid extraction techniques: Part I," *Talanta* 82 (2010): 1298-1305.
- [55] Ueno, H. and Kato, E., "Determination of hydrogen in liquid pure copper and liquid copper-tin alloy," *Report of the Castings Research Laboratory, Japan* 21 (1970): 29-33.
- [56] Martin, J.F., Takacs, R. Rapp, R. and Melnick, L.M., "Evaluation of methods for determining hydrogen in steels ," *Transactions of the Metallurgical Society*

- of AIME* 230 (1967): 107-112.
- [57] Lang, D., Gardner, M. and Holmes, J., “Mercury arising from oil and gas production in the United Kingdom and UK continental shelf,” A report by University of Oxford, Department of Earth Sciences, United Kingdom (2012).
- [58] Zettlitzer, M. and Klieinitz, W., “Mercury in steel equipment used for natural gas production amount, speciation and penetration depth,” *Oil & Gas- European magazine* 3 (1997): 25-30.
- [59] Wilhelm, M. and Nelson, M., “Interaction of Elemental Mercury with Steel Surfaces,” *The Journal of Corrosion Science and Engineering*, 13 (2010).
- [60] Mercury in Steel, Mercury Technologies Services (MTS), 2011,
www.hgtech.com/MTS%20Library/MTS%20Mercury%20in%20Steel%202008%20d2.pdf
- [61] Gurinsky, D., “The behaviour of materials in aggressive liquid metals,” *Nuclear Metallurgy - Special Report Series, AIME*, (1952): 5-20.
- [62] Kirshenbaum, N., “Materials compatibility of Hg for practical applications at elevated temperatures” in *Metallurgical Technologies*, ed. Branover, H., (1985), 336-342.
- [63] Reid, R.C., “Mercury boiler treatment with titanium and magnesium metals,” *American Society of Mechanical Engineers-Advance Papers*, (1951): 20-26.
- [64] Okamoto, H., “Fe-Hg binary phase diagram” in *Desk Handbook: Phase Diagrams for Binary Alloys*, (Ohio, USA: ASM International, 2000), 363.
- [65] Lopez-Garcia, R. and Radford, R., “Managing Mercury in Hydrocarbon Processing Plants During Turnaround,” *Hydrocarbon World* 7 (2010): 25-30.

-
- [66] Chaiyasit, N., “Decontamination of Mercury Contaminated Steel (API 5L-X52) Using Iodine and Iodide Lixiviant,” *Modern Applied Science* 4 (2010): 12-20.
- [67] Roseborough, D., Gothelid, M., Aune, R. and Seetharaman, S., “The surface behavior of mercury on iron systems,” *Metallurgical and Materials Transactions B* 37 (2006): 1049-1056.
- [68] Davis J.R., “Elevated-temperature corrosion properties of carbon and alloy steels ” in *Heat Resistant Materials, ASM Speciality Handbook*, (Ohio, USA: ASM International, 1999), 155.
- [69] Pawel, S.J., DiStefano, J.R., and Manneschildt, E.T., “Corrosion of type 316 L stainless steels in a mercury convection loop” in *a Special Report Prepared for the U.S. Department of Energy, 1999* 1-48.
- [70] Leak Detection Methods: A Comparative Study of Technologies and Techniques, VTech cool innovations.

www.vtechonline.com/pdf/VTech%20Leak%20Detection%20Methods.pdf
- [71] WIKIPEDIA *www.en.wikipedia.org/wiki/Atomic_radius*
- [72] *Metals Handbook- Desk Edition*, ed. Davin. J.R., (Ohio, USA: ASM International, 2003).
- [73] Caskey, G., “Hydrogen Effects in Stainless Steel” in *Hydrogen Degradation of Ferrous Alloys*, ed. Oriani, R.A., Hirth, J., Smialowski, M., (NJ, USA: William Andrew Publishing, Noyes, 1985), 822-862.
- [74] Langley, R., “Hydrogen trapping, diffusion and recombination in austenitic stainless steels,” *Journal of Nuclear Materials* 128 (1984): 622-628.

-
- [75] Danielson, P., "Choosing the Right Vacuum Materials," *A Journal of From Practical and Useful Vacuum Technology* (2003): 1-4.
 - [76] Howard, G., Nelson, M. and Stein, J., " Gas-phase hydrogen permeation through alpha iron, 4130 steel, and 304 stainless steel from less than 100° C to near 600° C," NASA Technical note, NASA TN 0-7265 (1973).
 - [77] Redhead, P.A., "Hydrogen in vacuum systems: An overview " in *Hydrogen in Materials and Vacuum Systems*, ed. Myneni, G.R., Chattopadhyay, S.,(USA: American Institute of physics, 2003),243-259.
 - [78] " Linear expansion coefficient of metals and alloys" in *Material expansion coefficient*, Laser and Optics User Manual, Agilent Technologies (USA: American Institute of physics, 2002).
 - [79] Fundamentals of Mechanical Engineering Experiments for Graduate Study, VTech cool innovations,Khon Kaen University, Thailand,

www.sites.google.com/a/kku.ac.th/fundamentals – of – mechanical – engineering – for – graduate – study/topics/signals – and – noise – in – measurement – systems
 - [80] ANSI/AWS A4.3-1993 (Superseding ANSI/AWS A4.2-86), " Standard Method for Determination of the Diffusible Hydrogen Content of Martensitic, Bainitic and Ferritic Weld Metals Produced by Arc Welding," Approved by American National Standard Institute, American Welding Society, FL.USA.
 - [81] ISO3690:2000E (Replacing ISO 3690:1977) International Standard, " Welding an Dalled Processes- Determination of Hydrogen Content in Ferritic Steel Arc Weld Metal," The International Organization for Standardization.

-
- [82] AS/NZS 3752:1996: Methods of determination of the diffusible hydrogen content of ferritic weld metal produced by arc welding (a standard of Australiana and New Zealand Standard institute)
- [83] BS 639:1986: Covered electrodes for the manual metal-arc welding of carbon and carbon-manganese steels, Appendix C: Method for the determination of diffusible hydrogen content (a standard of British Standard Institute)
- [84] Senadheera, T. and Shaw W. J. D., “Improvements in the mercury displacement method for measuring diffusible hydrogen contents in steels,” *Journal of Testing and Evaluation* 37 (2009): 1-9.
- [85] Fabling, F. T. and Chew, B., “Performance of collecting fluids in diffusible hydrogen analysis,” *Welding Research International* 3 (1973): 81-87.
- [86] Yaws, C., *The Yaws handbook of thermodynamic properties for hydrocarbons and chemicals*, (Gulf Publications, 2006).
- [87] Lvov, B., “Kinetics and mechanism of thermal decomposition of nickel, manganese, silver, mercury and lead oxalates,” *Thermochimica Acta* 364 (2000): 99-109.
- [88] Ming, C. and Simkovich, G., “Gibbs Free Energy of Formation of Cementite, Fe_3C analysis,” *Metallurgical Transactions A* 19 (1988): 2115-2117.
- [89] Peight, J.G., *Perry’s Standard Tables and Formulas for Chemical Engineers*, (McGraw-Hill Publishers, 2003), 373.
- [90] Gay-Lussac’s Law, Student Resources for General Chemistry, ChemPaths,

-
- www.chemed.chem.wisc.edu/chempaths/GenChem – Textbook/Gay – Lussac – s – Law – 952.html*
- [91] What is Accuracy?, Technical Notes by Arbiter Systems Inc, CA, USA.
www.arbiter.com/news/technology.php?id = 3
- [92] Metallic gasket materials, Technical Notes by Teadit Inc, Huston, USA.
www.teadit – na.com/catalog/index
- [93] Fend, H., “Progress in metal sealing techniques,” *Vacuum* 47 (1996): 527-529.
- [94] San Marchi C. and Somerday B.P., “Technical Reference on Hydrogen Compatibility of Materials Copper Alloys,” A technical report prepared by Sandia National Laboratories, USA (2006).
- [95] Schenck, H., *Theories of engineering experimentation*, 3rd Edition, (Hemisphere publishing, 1976), 14-16.
- [96] Blake, P.D., “Effect of sampling and analytical factors on reported hydrogen content of mild steel weld metal,” *British Welding Journal*, 9 (1962): 594-601.
- [97] Smialowski, M., *Hydrogen in Steels*, (Pergamon Press, 1962).
- [98] Hudson, M., Norris, W.G. and Stragand, G.L., “Effect of environment on the rate of hydrogen removal from steel,” *Journal of Industrial Engineering and Chemistry*, 51 (1959), 319-325.
- [99] Sastri, V.S. and Tjan, C., “Studies on the analysis of hydrogen in steels stored in various media,” *Werkstoffe und Korrosion-translated*, 39 (1959), 462-464.

-
- [100] Ohno, S. and Uda, M., "An examination of collection medium for determination of diffusible hydrogen in welded metals," *Transactions of National Research Institute for Metals*, 22 (1980), 32-39.
- [101] Scialdone, J., "Pressure and purging effect on material outgassing and evaporation," *Proceedings of the 9th International Symposium on Materials in a Space Environment, Netherlands*, (2003): 16-20.
- [102] Olden, V., Thaulow, C. and Johnsen, R., "Modelling of hydrogen diffusion and hydrogen induced cracking in supermartensitic and duplex stainless steels," *Journal of Materials and Design*, 29 (2008), 1934-1948.
- [103] Lee, K. and Jay-Young, L., "A new method of the calculation of the hydrogen trap activation energy in metals," *Journal of Materials Science Letters*, 2 (1983), 538-540.
- [104] Choo, W.Y., "Hydrogen trapping phenomena in carbon steel," *Journal of Materials Science*, 17 (1982), 1930-1938.
- [105] Glikman, L.A. and Orlov, V. A., "The mechanism of hydrogen embrittlement of steel due to hydrogen charging during pickling," *Journal of Soviet Material Science*, 299 (1965), 81-82.
- [106] Ishizaki, T. and Takeda, T., "Hydrogen evaluation from Iron and steel by continuous heating by vacuum," *Journal of Japan Institute of Metals*, (1981), 268-275.
- [107] Turnbull, A., Hutchings, R.B. and Ferriss, D.H., "Modelling of thermal desorption of hydrogen from metals," *Materials Science and Engineering A*, 238

- (1997), 317-328.
- [108] Bergers, K., Souza, C., Thomas, I., Mabho, N. and Flock, J., "Determination of Hydrogen in Steel by Thermal Desorption Mass Spectrometry," *Steel Research*, 81 (2010), 499-509.
- [109] Nagumoa, M., Takaib, K. and Okudaa, N., "Nature of hydrogen trapping sites in steels induced by plastic deformation," *Journal of Alloys and Compounds*, 293 (1999), 310-316.
- [110] Wang, M., Akiyama, E. and Tsuzak, K., "Effect of hydrogen on the fracture behavior of high strength steel during slow strain rate test," *Corrosion Science*, 49 (2007), 4081-4097.
- [111] Mishael,S.J., Dean, F.W.H. and Fowler, C., "Piratical applications of hydrogen permeation monitoring," *Corrosion*, Paper no.4476 (2004), 1-12.
- [112] Propagation of Error, ChemWiki.
*[http : //chemwiki.ucdavis.edu/Analytical_Chemistry/Quantifying_Nature/
Significant_Digits/Propagation_of_Error](http://chemwiki.ucdavis.edu/Analytical_chemistry/Quantifying_Nature/Significant_Digits/Propagation_of_Error)*
- [113] Error calculations using calculus.
[http : //www.rod.beavon.clara.net/err_comb.htm](http://www.rod.beavon.clara.net/err_omb.htm)
- [114] Jones, D.A., *Principles and Prevention of Corrosion*, Ed.2 (Prentice Hall, NJ, U.S.A, 1996) 334-343.