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# COMPRESSED HYDROGEN GAS VEHICLE CYLINDER DEVELOPMENT

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16. Abstract

This report presents a new standard for all-composite high pressure cylinders for on-board storage of hydrogen gas as a fuel for vehicles. The report also covers a rationale for the standard, design considerations to be addressed in the development of a cylinder for this application, and details on the design and testing of a cylinder that meets the new standard.

An important innovation during the project involved the development of an injected foam dome for the cylinder. Originally designed to prevent handling damage to the cylinder, it was also found to significantly enhance the performance of the cylinder when exposed to fire. A number of other design and fabrication features are discussed, with many of the recommendations confirmed through testing.

A cylinder was designed using the new standard, and recommendations are presented in the report. A number of cylinders were then produced to this design, and were successfully tested to the following requirements of the new standard: hydrostatic burst, drop, penetration, high temperature creep, bonfire performance, permeation, liner embrittlement, and pressure relief device performance.

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16. Résumé

Ce rapport présente un projet de norme visant les bouteilles en matériau composite pour le stockage sous pression d'hydrogène utilisé comme combustible par les véhicules routiers. Il expose les raisons qui ont motivé l'élaboration de cette norme, explique les critères à prendre en compte dans la conception d'une bouteille destinée spécialement au stockage d'hydrogène et décrit une bouteille conçue et éprouvée conformément aux prescriptions de la nouvelle norme.

Une des innovations de ce projet a été l'application sur les fonds de la bouteille d'un revêtement de protection en mousse moulée par injection. Conçu au départ comme protection contre les dommages physiques pouvant survenir en cours de manutention, ce revêtement a par ailleurs amélioré considérablement la tenue au feu de la bouteille. Le rapport décrit diverses autres caractéristiques de conception et de construction d'une bouteille à hydrogène comprimé, soulignant les cas où la validité d'une recommandation a pu être confirmée par des essais.

Un modèle de bouteille a été conçu conformément aux exigences de la nouvelle norme. Plusieurs exemplaires ont été fabriqués, et ils ont subi avec succès les épreuves prescrites par la norme, soit : essais de résistance aux pressions hydrostatiques, aux chocs, essais de pénétration, de fluage à température élevée, essais au bain de feu, essais d'étanchéité aux gaz, de fragilisation du chemisage et essais de fonctionnement du dispositif de protection contre les surpressions. Le rapport présente également des recommandations.

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## EXECUTIVE SUMMARY

Canada is in the forefront of research on the use of hydrogen as a fuel for vehicles. This project was initiated because of the lack of a standard for on-board hydrogen cylinders for use in vehicles.

Standards already exist for the design and testing of cylinders for the on-board storage of natural gas. However, there are unique requirements for the storage of hydrogen because of its small molecule size, low energy density, lower compressibility at high pressures, larger flammability range, lower minimum spark energy, and the fact that it can lead to hydrogen embrittlement and hydrogen-induced cracking in metals with which the hydrogen comes in contact. Therefore it was determined that a new standard and a new cylinder design were required for this application.

A new standard is proposed which is similar to that used for vessels which are designed for use with natural gas, but with several significant new requirements and tests, including a test for the effects of hydrogen embrittlement on liner and metal components, special pressure relief device (PRD) requirements and tests, and new requirements for the liner such as resistance to pin holes from electrical discharge.

Design of a composite shell for use with hydrogen must consider the unique properties of the gas. The low energy density means that many containers will be required per vehicle, so weight and volume efficiency of the vessel are important considerations. Aramid, glass, and graphite are all candidate fibres for this application. The advantages and disadvantages of each fibre must be assessed. It is essential to examine strength, density, safety requirements, and their influence on the resulting cylinder in terms of weight, cost, volume efficiency, and fire and chemical resistance. It was concluded that either an all-carbon reinforced structure or a hybrid of carbon and glass reinforced structure is the optimum design for the hydrogen application.

Other parameters in the design that must be examined for the hydrogen application include liner material, end boss, end plug, cylinder boss-to-valve adapter, PRD, and the resin system. Taking each of these in turn:

- For the liner, gas permeation is an important consideration because of the very small hydrogen molecule. Testing revealed that the liner material used for a lightweight natural gas cylinder was also suitable for use with hydrogen.

- For the metallic pieces (end boss, end plug, and boss-to-valve adapter), it is paramount to allow for the effects of hydrogen embrittlement. This can be accomplished by a careful choice of materials that meet the NACE MR0175 requirements for sour gas service.
- For the PRD, the small hydrogen molecule again affects the design. Several PRDs designed for natural gas were tested for use with hydrogen. Helium gas was used for the testing, which involved both hot and cold long-duration experiments. Only one of the PRDs passed the proposed tests.
- For the resin system, performance in a bonfire test was considered to be one of the crucial considerations. Tests were conducted to determine if changes to the resin system could enhance the performance of a composite in a fire situation. Five alternatives were examined including alternative epoxy resin systems, intumescent coatings, bromine-rich additives to epoxy, an extinguishing additive, and a bromine-rich vinylester. A bromine-rich vinylester combined with an extinguishing additive, a special alternative resin system, and the intumescent coating all enhanced fire performance in the sample testing. However, only the intumescent coating provided sufficient protection to meet the bonfire test in full-scale testing. A foam dome, developed to enhance the cylinder's handling durability, also worked to enhance performance in the bonfire test.

Another important safety feature for a hydrogen cylinder is its damage resistance. An all-composite cylinder is most vulnerable in the end-dome area. A 45° drop test onto concrete followed by pressure cycling is the established test to examine this feature. A number of design features were tested including metal reinforcement in the end-dome region, composite rings in the end-dome region, tough glass/epoxy composite embedded in the graphite/epoxy composite in the end-dome region, and an energy-absorbing material placed on the outside of the end dome. The latter two methods provided sufficient protection. However, the energy-absorbing material injection-molded on the end domes was found to be superior in terms of cost and ease of manufacture. It also resulted in enhanced performances in a fire situation.

Because of the small size of the hydrogen molecule, an improved seal technology over that used for compressed natural gas cylinders is needed to ensure a leak-free storage system. Several seal systems were analysed using finite element analysis, and the promising systems were selected for tests. Testing was conducted at -40°C as this was found to be the temperature at which obtaining a good seal is most difficult. An accelerated creep test (at high temperature) followed by a fast fill was also used to test seal performance. From the analysis and testing, it was concluded that a seal design employing an O-ring was adequate to maintain the cylinder pressure under the most severe loading conditions.

Based on all of the above tests, a new cylinder design was completed and produced. The design included:

- an O-ring incorporated into the seal system
- injection-molded foam-dome end caps
- a PRD which passed all the scale testing

The cylinders were then successfully put through the following tests outlined in the proposed hydrogen cylinder standard: hydrostatic burst, drop, penetration, high temperature creep, bonfire performance, permeation, liner embrittlement, and PRD performance.

## SOMMAIRE

Le Canada joue un rôle de chef de file dans la recherche sur l'utilisation de l'hydrogène comme combustible pour les véhicules routiers. Le présent projet a été lancé pour pallier l'absence de normes applicables aux bouteilles pour le stockage d'hydrogène à bord des véhicules.

Il existe des normes pour la conception et la mise à l'épreuve des bouteilles de gaz naturel embarquées. Toutefois, ces normes ne peuvent être appliquées telles quelles aux bouteilles devant servir au stockage d'hydrogène, en raison des caractéristiques particulières de ce gaz : molécule beaucoup plus petite, plus faible densité énergétique, plus faible compressibilité aux températures élevées, plus grande plage d'inflammabilité, limite inférieure d'inflammabilité moins élevée et potentiel de fragilisation et de fissuration des métaux avec lesquels il entre en contact. Il y a donc lieu de définir des exigences particulières de conception et de tenue en service pour les bouteilles à hydrogène.

L'équipe de recherche propose un projet de norme, inspiré de celle qui régit les bouteilles à gaz naturel comprimé mais comportant plusieurs exigences et épreuves supplémentaires, notamment un essai pour déterminer la fragilisation du chemisage et des éléments métalliques de la bouteille au contact de l'hydrogène, des exigences et des essais visant le dispositif de protection contre les surpressions et des exigences propres au chemisage de la bouteille, notamment de résistance aux piqûres causées par les décharges électriques.

Les critères de conception d'une bouteille à hydrogène en matériau composite doivent tenir compte des propriétés uniques de ce gaz. La faible densité énergétique de l'hydrogène signifie en pratique que le véhicule devra transporter plusieurs bouteilles. Par conséquent, le poids et le volume de la bouteille sont des critères de conception importants. En principe, les fibres d'aramide, de verre et de graphite conviennent toutes pour la fabrication de l'enveloppe. Il faut cependant peser leurs avantages et inconvénients respectifs. Il importe de vérifier la masse volumique, la résistance et les caractéristiques de sécurité de chacune et de déterminer l'incidence de ces caractéristiques sur le poids, le volume, la résistance au feu et aux produits chimiques et le coût de fabrication de la bouteille. Il a été déterminé qu'un matériau à fibres de carbone ou à fibres de carbone et de verre constituait le choix le plus judicieux pour les bouteilles à hydrogène.

D'autres critères intéressant notamment le matériau constitutif du chemisage, les bossages, les obturateurs, l'adaptateur entre le bossage et le robinet, le dispositif de protection contre les

surpressions et la matrice de résine, sont à prendre en compte dans la conception des bouteilles à hydrogène. Ainsi,

- pour le chemisage : la perméabilité aux gaz est un facteur important, vu la très petite taille de la molécule d'hydrogène. Les essais ont permis d'établir que le matériau utilisé pour la fabrication du chemisage d'une bouteille à gaz naturel légère conviendrait également pour les bouteilles à hydrogène;
- pour les éléments métalliques (bossages, obturateurs, adaptateur) : il est impératif de tenir compte de la fragilisation du métal causée par le contact avec l'hydrogène. Il faut choisir un matériau satisfaisant aux exigences de la norme NACE MR0175 pour les appareils en contact avec des gaz sulfureux;
- pour le dispositif de protection contre les surpressions : il faut encore une fois tenir compte de la petite taille de la molécule d'hydrogène. Plusieurs dispositifs de protection contre les surpressions conçus pour le gaz naturel ont été essayés en vue de leur utilisation avec l'hydrogène. Des essais de longue durée ont été effectués à basses températures et à températures élevées, avec de l'hélium. Un seul des dispositifs a résisté à ces essais;
- pour la matrice en résine : la tenue au feu est considérée comme primordiale. Des essais ont été menés pour voir si, en changeant la composition de la matrice, on pouvait obtenir une meilleure tenue au feu. Cinq possibilités ont été considérées : l'emploi de différentes résines époxydes, de revêtements intumescents, d'additifs riches en brome, d'un additif extincteur et d'un vinylester riche en brome. Le vinylester riche en brome combiné avec un agent extincteur, une des résines et le revêtement intumescent ont tous donné une meilleure tenue au feu lors des essais sur éprouvettes. Cependant, seul le revêtement intumescent a donné des résultats satisfaisants lors des essais au bain de feu de bouteilles. Un revêtement de fond en mousse conçu pour protéger la bouteille contre les dommages physiques en cours de manutention a également contribué à sa tenue au feu.

La résistance mécanique de la bouteille est une caractéristique de sécurité importante. Les zones les plus fragiles d'une bouteille en matériau composite sont les fonds. La méthode établie pour déterminer la résistance mécanique d'une bouteille à gaz comprimé comprend un essai de chute à $45^{o}$ sur une surface de béton, suivi d'une mise sous pression cyclique. Différents éléments destinés à renforcer la zone des fonds de la bouteille ont été essayés : renforcement métallique, anneaux en matériau composite, composite verre-époxyde ancré dans le composite graphite-époxyde et matériau amortisseur appliqué en surface selon la technique du moulage par injection. Ces deux dernières solutions ont assuré une protection suffisante. Toutefois, le matériau amortisseur présente un avantage du point de vue du coût et de la facilité de fabrication, en plus d'améliorer la tenue au feu de la bouteille.

Vu la taille de la molécule d'hydrogène, le dispositif d'étanchéité équipant les bouteilles à gaz naturel comprimé n'est pas suffisant pour assurer l'étanchéité des bouteilles d'hydrogène. Différents dispositifs d'étanchéité ont été analysés par la méthode des éléments finis, et les dispositifs les plus prometteurs ont été soumis à épreuve. Des essais ont été tenus à -40 $^{o}$C, température à laquelle il est le plus difficile d'obtenir une parfaite étanchéité. Ils ont été complétés par un essai de fluage accéléré (à température élevée) suivi d'un remplissage rapide. Les analyses et essais ont montré qu'un dispositif comportant un joint torique assure l'étanchéité de la bouteille et ce, aux plus fortes pressions de stockage du gaz.

Les résultats de cette campagne d'essais ont servi à la conception d'une bouteille destinée spécialement au stockage d'hydrogène ainsi qu'à la construction de prototypes. Cette bouteille présente les caractéristiques suivantes :

- un dispositif d'étanchéité comportant un joint torique;
- un revêtement de protection des fonds en mousse moulée par injection;
- un dispositif de protection contre les surpressions ayant subi avec succès toutes les épreuves prescrites.

Les prototypes ont résisté à toutes les épreuves prescrites dans le projet de norme visant les bouteilles à hydrogène comprimé : essais de résistance aux pressions hydrostatiques, aux chocs, essais de pénétration, de fluage à température élevée, essais au bain de feu, essais d'étanchéité aux gaz, de fragilisation du chemisage et essais de fonctionnement du dispositif de protection contre les surpressions.

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## 1.1 AN ALL-COMPOSITE LIGHT-WEIGHT CYLINDER

EDO Canada Limited (ECL), located in Calgary, Alberta, is a world leader in composite natural gas storage technology. ECL has successfully developed the design and manufacturing technologies for a composite light-weight high-pressure cylinder suitable for the on-board storage of fuel in natural gas vehicles.

ECL has performed extensive research and development with on-board storage containers for compressed natural gas. This has resulted in development of the world's first certified "all-composite"[1] cylinder and also most storage-volume-to-weight efficient cylinder. These cylinders have been certified to the CSA B51 standard [a] and the ANSI/AGA NGV2 [b] standard. Cylinders have been sold for use on buses, semi-trailer transports, garbage trucks, vans, light trucks, taxis, fleet vehicles, and river boats. In this project, the high-pressure composite cylinder technology developed by ECL for the all-composite natural gas cylinder is developed further for use in vehicular gaseous hydrogen applications.

Figure 1.1 is an illustration of the all-composite cylinders currently manufactured by ECL for the vehicular storage of compressed natural gas.

---

[1] "All-composite" cylinders are defined in the Canadian specification for natural gas cylinders [a] as "*composite cylinders using non-metallic liners*".

**Figure 1.1:**
**The ECL All-composite Family of Cylinders**

Figure 1.2 is an illustration of the basic components which make up an all-composite cylinder.

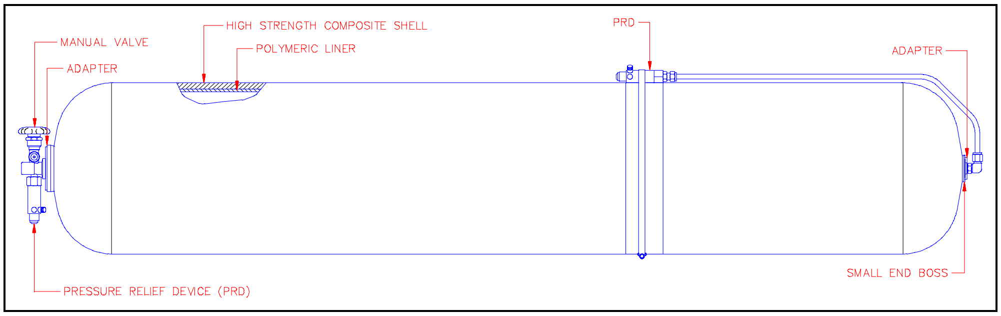

**Figure 1.2:**
**The Basic Components of an All-composite Cylinder**

The cylinder consists of:

1. A polymeric liner which is used as a barrier to prevent gas leakage through the composite material;
2. A tough composite fibre/epoxy structural shell;
3. A steel adapter and end plug which are used to attach fittings to the cylinder;
4. A high-pressure manual valve which is used for the manual closing and manual vent down of a cylinder; and
5. Two fusible plug pressure relief devices which are used for venting the cylinder in the advent of an accidental fire.

## 1.2 DIFFERENCES BETWEEN HYDROGEN AND NATURAL GAS

There are differences, however, in the storage of natural gas as compared to hydrogen gas:

- The hydrogen gas molecule is smaller than the natural gas molecule; thus, greater controls are required to ensure a leak-free storage system.
- Because of the small nature of the hydrogen gas molecule, the hydrogen ion can migrate into most metals causing effects such as hydrogen embrittlement, and hydrogen induced cracking.

- The energy density of natural gas is 37.1 MJ/SCM while only 11.3 MJ/SCM for hydrogen; thus, the hydrogen storage system must maximize fuel storage within a given physical envelope.
- At 24.8 MPa, the compressibility factor of natural gas is 0.82 but 1.16 for hydrogen; thus, more standard cubic meters (SCM) of natural gas than hydrogen gas can be compressed into one cubic meter of space. The hydrogen storage system must maximize fuel storage within a given physical envelope.
- The hydrogen gas, in air, has a large flammability range. The low flammability limit of hydrogen in air, vol%, is 4.0%. This, coupled with its low minimum spark energy, means that hydrogen is easily ignitable.

## 1.3 COMPRESSED HYDROGEN STORAGE DEVELOPMENTS

Several developments have been made in the design of a cylinder for compressed hydrogen storage and these developments are separated into the following chapters:

### *Chapter 2: Specification Generation*

Currently, there are no known standards available in the world dealing with the vehicular storage of hydrogen gas. This chapter presents: (1) a proposed standard for the vehicular storage of compressed hydrogen, and (2) a rationale for standard.

### *Chapter 3: Design Configuration Trade-Off*

There are several fibrous materials available for use in the composite shell of the cylinder. This section analyzes the material options and performs a design-to-cost trade-off study of the candidate design configurations which conform to the draft specification for the vehicular storage of compressed hydrogen outlined in chapter 2.

Additionally, there are trade-offs involving the overall resin and fibre quantity in the cylinder. This chapter also addresses the efforts made to reduce resin content in the cylinder while still maintaining the quality and strength of the composite shell.

### *Chapter 4: Structural Materials Analysis*

The structural components of the cylinder must be effective in a hydrogen environment. This chapter evaluates: (1) candidate liner materials for conformance to the requirements in the draft pressure vessel standard developed, (2) candidate materials for the metal end-bosses, adapters, and end-plugs, and (3) candidate pressure relief devices for use with hydrogen.

### *Chapter 5: Safety Enhancement*

A couple of scenarios are especially critical in the design of an all-composite hydrogen cylinder. The performance of a cylinder in a bonfire environment is one key concern as hydrogen is an easily ignitable and highly explosive substance. The performance of a cylinder after it has been dropped is also of concern because composite materials typically do not perform as do their steel counterparts in an impact condition. This chapter also looks at ways of improving the cylinder's resistance to degradation in a fire and its strength under a drop condition.

### *Chapter 6: Enhancing the Seal Design*

Because of the small nature of the hydrogen molecule, the seal technology must be designed, with this in mind, to ensure a leak-free system. The work in this chapter concentrated on work needed to create an effective seal for hydrogen gas. The new seal prototypes were tested using extreme loading conditions such as high temperature, low temperatures, and a situation where a cylinder was filled rapidly with gas.

### *Chapter 7: Prototype Design and Testing*

A prototype cylinder was designed, based on:

- the information obtained in the previous studies, and
- well established engineering principles and design software that ECL has developed over the years.

A detailed finite element analysis of the cylinder was performed using the ANSYS software. After the design was developed, cylinders were manufactured and tested to demonstrate the qualification requirements identified in the draft pressure vessel standard. The details of the design and the results of the testing are presented in Chapter 7.

## REFERENCES

[a] CSA B51-95 Part II, “High Pressure Cylinders for the Storage of Natural Gas as a Fuel for Automotive Vehicles”, January 1995.

[b] ANSI/AGA NGV2-1992, “Basic Requirements for Compressed Natural Gas Vehicle (NGV) Fuel Containers”, August 1992.

## 2.1 THE NEED FOR A HYDROGEN CYLINDER STANDARD

A technical standard to govern the design and fabrication of a compressed hydrogen cylinder for vehicular storage does not, to the best of ECL's knowledge, exist. As outlined below, there are sufficient differences between hydrogen and natural gas that a different standard is required.

## 2.2 THE RATIONALE FOR THE HYDROGEN STANDARD

To a certain degree, the properties of hydrogen govern the precautions that must be undertaken when designing a standard for compressed hydrogen storage systems.

### *2.2.1 General Properties of Hydrogen*

Gaseous hydrogen has the following characteristics:

1. Hydrogen is the smallest element in nature [b]. Because of hydrogen's small molecular size, it is the most difficult to contain. The small molecules can more easily pass through the shell of an all-composite cylinder and can more easily leak through a sealing system. Thus, all-composite pressure vessels designed for the storage of other gaseous fluids must be tested to ensure reliable containment of the gaseous hydrogen.

2. Hydrogen is colorless, odorless, and tasteless [c] and thus, the presence of a leak in a cylinder may go unnoticed by the user unless hydrogen sensors or hydrogen odorants are present.

3. At stoichiometric composition, the minimum spark energy of hydrogen is an order of magnitude lower than that of hydrocarbons [b]. Leaking hydrogen may ignite in the absence of any normally apparent ignition source and will burn with a nearly invisible flame [c].

4. The low flammability limit of hydrogen in air, vol%, is 4.0% [b,c]. This, coupled with its low minimum spark energy, means that hydrogen is easily ignitable.

5. Hydrogen can act as a simple asphyxiate by displacing air. The lower flammability limit of 4%, however, means that the explosive limit is reached long before asphyxiation becomes a problem [c].

6. The diffusivity rate of hydrogen is high. Thus, hydrogen permeating through the cylinder liner is quickly displaced into the atmosphere. In fact, it has been demonstrated that an excessive hydrogen leakage into open atmosphere has not resulted in any explosion, but has dispersed without causing any harm [b].

7. When confined, hydrogen is detonable over a wide range of concentration, but when unconfined, it is difficult to detonate [d].

### *2.2.2 The Compressibility of Hydrogen*

Figure 2.1 illustrates the compressibility characteristics of hydrogen [e].

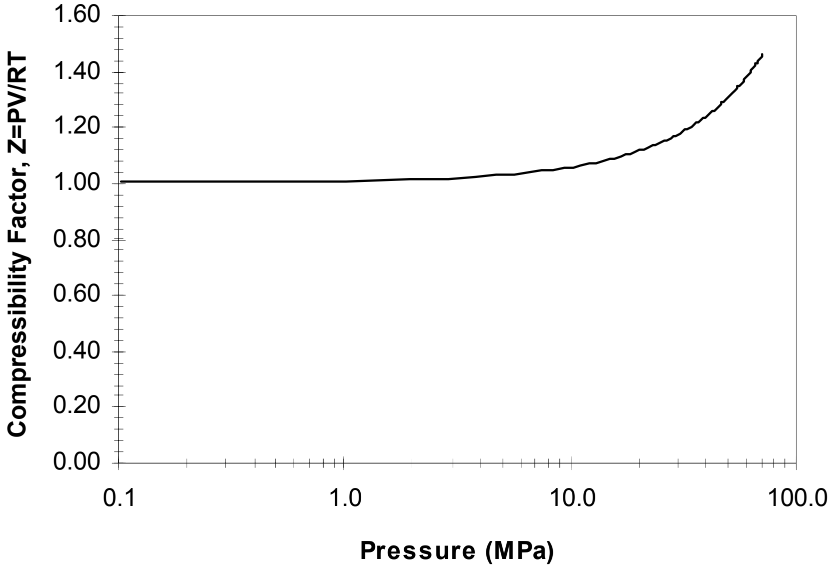

**Figure 2.1:**
**The Compressibility of Hydrogen**

As noted by Figure 2.1, with increasing pressure, the efficiency of storing hydrogen decreases and this would have a direct bearing on the service pressure desired.

### 2.2.3 Fast Filling and Discharging a Cylinder with Hydrogen

An experiment was performed at ECL to measure the temperature change in a cylinder when filled and discharged with hydrogen. A 45 L cylinder was filled with hydrogen at a rate such that the cylinder went from an initial charge of 1.1 MPa to a maximum fill pressure of 35.5 MPa within 30 seconds. Over this time, the temperatures of the gas within the cylinder increased a maximum of 83°C[f]. Additionally, when discharged the cylinder underwent serious cooling. The Joule-Thompson effect, which is the change in temperature of a gas undergoing adiabatic irreversible expansion through a partially opened valve [g], explains this change in temperature.

On days when the cylinder temperature is high, this increase in temperature can cause the temperature of the gas to exceed the material design temperatures and a potential hazard exists. In order to control the temperature increases and decreases in the cylinder (and to avoid variances between different systems), the cylinder fill rate and input gas temperatures (controlled by the filling stations) and discharge rates (controlled by the fuel systems) should be standardized.[1] From this, the valve geometry, cylinder geometry, and materials can then be designed by a cylinder manufacturer.

### 2.2.4 Permeation of Hydrogen Through the Cylinder

All engineering materials used in the construction of pressure vessels have a certain degree of permeability to the flow of gases through the vessel wall and to the atmosphere. This study sets a safe permeation limit of the flow of hydrogen out of the all-composite internally pressurized hydrogen storage tanks for vehicular fuel storage.

A simple model was used to determine the allowable permeability rate of the hydrogen through the cylinder wall. This model is based upon the model created by the AGA NGV2 [a] standard for the permeation of natural gas through the natural gas cylinder walls. The model assumes a worst case where the vehicle is placed into a one-car garage which is either sealed or has a low air infiltration/ventilation rate of 0.5 air changes per hour. In the first case, the time until the explosive limit is reached is calculated. In the latter case, the maximum concentration of hydrogen in the garage is calculated.

---

[1] This standard extends beyond the scope of this report.

*Input parameters:*

| | |
|---|---|
| Size of the garage: | 36.24 $m^3$ |
| Size of the fuel tank[2]: | 180 litre water capacity |
| Permeation rate: | 0.25 cc/hr/litre |

*Sealed Garage:*

With a hydrogen permeability rate of 0.25 cc/hr/litre, and a 180 L cylinder, the gas release rate is 45 cc/hr. The explosive volume of hydrogen in this garage, calculated to be 4% of the total volume of the garage, is equal to 1.45 $m^3$. Thus, an explosive limit would be created in the garage in around 3 1/2 years.

*Garage with Infiltration/Ventilation:*

Figure 2.2 shows this concentration of hydrogen as a function of time assuming an infiltration rate in the enclosed space of 0.5 air changes per hour and a permeability rate of 0.25 cc/hr/litre. The maximum volume concentration of hydrogen in the enclosed area is 2.50 PPM. This is well below the lower explosive limit of 400 PPM.

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[2] Note that a 100L cylinder pressured with gaseous hydrogen fuel to 34.5 MPa provides a decent range for a mid-size automobile.

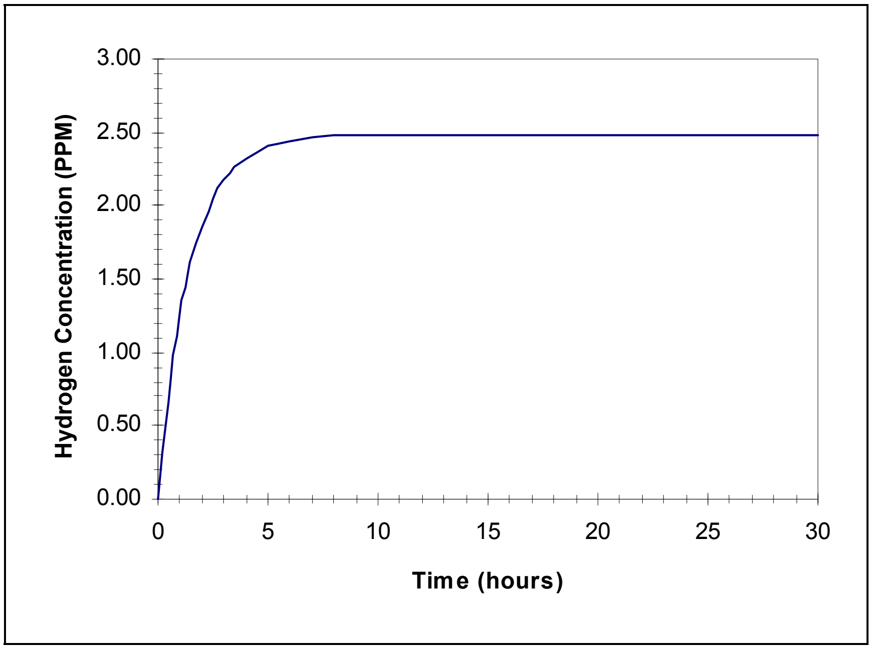

**FIGURE 2.2:**
**Concentration of Hydrogen in the Garage as a Function of Time**

A permeability rate of 0.25 cc/hr/litre ensures a safe discharge of hydrogen to the environment[3].

---

[3] Note that the design, by no means, should allow hydrogen which has permeated through the liner material to collect within air pockets in the cylindrical shell. Thus, it should be demonstrated that the permeation through the shell is greater than the permeation of hydrogen gas through the liner material.

## 2.3 A PROPOSED HYDROGEN CYLINDER STANDARD

A new standard, presented in appendix A, has been developed to initiate discussion for the development of a universally accepted standard for the fabrication of all-composite cylinders for the vehicular storage of compressed hydrogen. The format for the new standard is based upon the following rationale:

> The hydrogen standard borrows from the applicable sections of the current North American standards for the vehicular storage of compressed natural gas. More specifically, this standard closely follows the format of the document: AGA/ANSI NGV2-1992 [a]. The standard has been modified and additional sections have been applied to the standard to make accommodation for the inherent risks of storing compressed hydrogen over compressed natural gas.

## 2.4 COMMON SENSE GUIDELINES

In addition to the specifications set out in the proposed standard, some common sense guidelines should be used in designing and using a compressed hydrogen gas cylinder system.

1. A cylinder should be considered empty at 7.5 bar (0.75 MPa). Maintaining a positive operating pressure throughout the system protects against trapping ignitable mixtures within a closed system.

2. Hydrogen cylinders should be mounted on top of a vehicle or in a location so that any permeated or leaking gas is permitted to escape into the atmosphere. Any cover over the cylinder may trap leaking gas and would be a concern for danger [h].

3. A guideline for first fill conditions must be included with the cylinder. It is important that during the first fill of a cylinder with hydrogen, the system be purged with an inert gas such as helium so that an explosive $H_2$/air mixture cannot be reached.

4. It should be stated by the manufacturer that a leak test with soap solution or other appropriate leak detection system should be performed on a routine basis at maximum operating pressure.

5. Garages or other shelters used for the vehicles should be well ventilated in the case of a cylinder leak.

6. Because hydrogen is invisible and odorless, odorant should be added to the hydrogen gas (as is done with natural gas). [i]

7. Since leaks may occur, all possible sources of ignition should be removed from the compressed hydrogen system and the fuel system should be grounded where possible.

## REFERENCES

[a] ANSI/AGA NGV2-1992, *“Basic Requirements for Compressed Natural Gas Vehicle (NGV) Fuel Containers*”, August 1992.

[b] Das, L.M., *”Safety Aspects of a Hydrogen-Fueled Engine System Development”*, International Journal of Hydrogen Energy, Vol. 16, No. 9, pp. 619-624, 1991.

[c] *“Handbook of Compressed Gases: Third Edition”*, Compressed Gas Association, Inc., 1990.

[d] Hay, D.R., “*Emerging Requirements for Hydrogen Safety”, Codes and Standards for Safe Use of Hydrogen Energy*”, National Hydrogen Association Proceedings, Washington, D.C., January 25-26, 1995, pp. 15-24.

[e] Schaefer and Thodos, A. I. Ch. E. Journal, July 1959.

[f] EDO Technical Report TR4950005, “*Hydrogen Fast Fill/Discharge Test*”, EDO Canada Limited, May 1995.

[g] “*McGraw-Hill Dictionary of Scientific and Technical Terms: Fourth Edition*”, S.P. Parker (ed), McGraw-Hill Book Company, 1989.

[h] Wolf, C.J., “*Codes and Standards for Safe Use of Hydrogen Energy: Stationary Hydrogen Systems*”, Codes and Standards for Safe Use of Hydrogen Energy, National Hydrogen Association Proceedings, Washington, D.C., January 25-26, 1995.

[i] J. M. Norbeck et al., “*Hydrogen Fuel for Surface Transportation*”, Society of Automotive Engineers Inc., 1996, p. 281.

## 3.1 INTRODUCTION

Composite materials are good for the design of cylinders made for the on-board storage of hydrogen fuel because they are lightweight and strong. Despite the fact that all of the fibre materials display high strength-to-weight ratios (when compared to more conventional materials like steel), these materials are very different from each other in terms of their other material properties. To further sub-divide these fibrous materials, a closer look at their properties has to be made. The candidate materials for the structural shell of an all-composite cylinder designed for the vehicular storage of hydrogen fuel are: glass-fibre, aramid-fibre (Kevlar), carbon-fibre or combinations thereof. Figure 3.1 illustrates the different fibre types. The important variables to investigate include: the strength-to-weight ratio of the composite shell, the required thickness of the composite shell, the fatigue strength of the fibres, the creep strength of the fibres, the fire resistance of the composite shell, the corrosion resistance of the fibres, and the cost.

**Figure 3.1:**
**Carbon Fibre, Aramid Fibre, and Glass Fibre**

In addition to the fibre type, the resin/fibre content poses another trade-off issue: a trade-off can be made in the amount of resin put into a cylinder and the strength, weight, and outside dimensions of a cylinder. Optimizing the cylinder cost in terms of resin content and fibre content is governed closely by the manner of impregnation and the recycling of used resin.

This chapter analyses the effects of using different fibre types and different resin/fibre quantities on the cylinder performance and cost.

## 3.2 THE CANDIDATE FIBRE MATERIALS

Three sources of data were used to obtain the properties of the various fibres considered in the design of the all-composite cylinder:

- manufacturers' data,
- literature reviews, and
- in-house testing of filament wound composite laminates.

The following sections summarize the results obtained and provide a discussion of their importance in the design of a hydrogen fuel storage cylinder.

### *3.2.1 Material Supplier's Data*

Table 3.1 provides a summary of manufacturers' data for the tensile modulus, tensile strength, density, and yield of the glass fibres, aramid fibres (Kevlar), and carbon fibres investigated. Included, also, are the calculated fibre cross-sectional area and the cross-sectional area of the impregnated fibre assuming a 60% by volume fibre content.

**Table 3.1:**
**Material Properties of the Candidate Fibres**

| | **Glass Fibre** | **Aramid Fibre** | **Carbon Fibre** |
|---|---:|---:|---:|
| Tensile Modulus (Mpa) | 80,000 | 127,500 | 232,000 |
| Tensile Strength (Mpa) | 2,300 | 3,800 | 5,100 |
| Fibre Density (gm/cm$^3$) | 2.49 | 1.44 | 1.80 |
| Fibre Yield (gm/m) | 1.99 | 0.95 | 1.63 |
| Roving XC Area (cm$^2$) | 0.00794 | 0.00653 | 0.00896 |
| Assumed Fibre Volume (%) | 60 | 60 | 60 |
| Impregnated Roving Area (cm$^2$) | 0.00132 | 0.01088 | 0.01498 |

### 3.2.2 Tensile Properties of the Composite Laminates

Theoretical Determination of the Laminate Modulus of Elasticity

The following theoretical approximation can be used to determine the theoretical modulus of elasticity ($Ex$) of the unidirectional laminate from the supplied mechanical properties of the fibre [a]:

$$Ex = Ef1 \bullet Vf1 + Ef2 \bullet Vf2 + Em \bullet Vm$$

where:

$Efi$ = Young's Modulus of Elasticity of the Reinforcing Fibre ($i$)
$Vfi$ = Volume Fraction of the Reinforcing Fibre ($I$)
$Em$ = Young's Modulus of the Structural Matrix
$Vm$ = Volume Fraction of the Structural Matrix

As an example, for the all-carbon fibre laminate, assuming that $Vf1$ is equal to 0.6 and assuming, because $Ef1 >> Em$, that the modulus of the structural matrix ($Em$) is zero, the theoretical modulus of the laminate is calculated to be:

$$Ex = 232{,}360 * 0.6$$
$$Ex = 139{,}416 \text{ MPa}$$

Theoretical Determination of the Laminate Ultimate Tensile Stress

In general, the average tensile strength of a bundle of fibres is generally less than the average strength of the fibres when tested individually [b]. During loading of a laminate to failure, some of the fibres in the laminate begin to break prior to the ultimate failure of the composite laminate. This causes high shear stresses in the matrix surrounding the fibre and high stress concentrations in the adjacent fibres. Through both these mechanisms, the surrounding fibres and matrix tend to fail prematurely.

For these tensile coupons, other factors contribute to the reduced tensile properties of the sample:

- In these samples, the fibre angle is not parallel to the longitudinal axis of the specimen. For each sample, the fibre orientation was 0.05° from this axis.
- With the geometry of the tensile samples, the machined edges are a weak point. Edge effects, such as the lack of constraint of material at the edges and the broken fibres at the edges caused by machining the sample, reduce the overall strength of the fibre.

Because of these issues, the tensile strength of the laminate cannot be theoretically determined without employing the use of statistical analysis. The parameters needed for the statistical analysis varies for each fibre material, fibre manufacturing method, fibre length, fibre cross-sectional area, the quality of the fibre, and so on. These factors are not available for this study and so a theoretical approximation cannot be included.

Experimentally and Theoretically Obtained Material Properties

Standard tensile coupons were fabricated and tested as per ASTM D3039-95 [c] to determine the tensile properties of the various candidate composite laminates.

Table 3.2 lists the experimentally obtained average mechanical properties for the composite filament wound laminates for the glass, Kevlar, and carbon fibre composites. Listed also are the theoretical approximations for the tensile modulus for each and the error in this approximation when compared to the experimental results.

**Table 3.2:**
**Material Properties of the Filament Wound Tensile Specimens**

| | Glass Fibre | Aramid Fibre | Carbon Fibre |
|---|---:|---:|---:|
| Tensile Modulus (Mpa):experimental | 42,060 | 68,260 | 142,722 |
| Tensile Modulus (MPa):theory | 47,990 | 76,530 | 139,270 |
| Error in Theoretical Tensile Mod (%) | 14.1 | 12.1 | 2.4 |
| Tensile Strength (Mpa):experimental | 827 | 1520 (calc)[1] | 2130 |

### 3.2.3 Densities of the Composite Laminates

The density of each filament wound laminate was measured experimentally. The densities of the fibres, the density of the epoxy matrix, and the experimentally obtained average densities of each laminate are summarized in Table 3.3.

---

[1] Note that the ultimate tensile strength of the all-Kevlar laminate could not be determined using the standard tensile coupons. During testing, the coupons failed by interfibre splitting of the fibres to such an extent that load could no longer be supported by the coupon (note that the smoother surface of Kevlar and its lower transverse properties contribute to Kevlar's relatively low shear property levels [d]). Thus, as an approximation, the ultimate tensile strength of the all-Kevlar laminate was assumed to be 40% of the ultimate tensile strength of the Kevlar fibre. This is based on the fact that the ultimate tensile strength of the carbon fibre laminate was determined to be 41.9% of the strength of the fibre and the ultimate tensile strength of the glass laminate was determined to be 36.3% of the ultimate strength of the glass fibre.

**Table 3.3:**
**Densities of the Fibres, the Matrix, and the Laminates**

| | Glass Fibre | Aramid Fibre | Carbon Fibre |
|---|---|---|---|
| Density of the Fibre (gm/cm$^3$) | 2.49 | 1.44 | 1.80 |
| Density of the Resin (gm/cm)$^b$ | 1.135 | 1.135 | 1.135 |
| Laminate Density (gm/cm$^3$) | 1.83 | 1.300 | 1.550 |

$^b$ obtained from previous in-house testing

The following formulae can be used to determine the theoretical density of the laminate:

$$Dl = \left(Df1 \bullet Vf1\right) + \left(Df2 \bullet Vf2\right) + \left(Dm \bullet Vm\right)$$

where:

*Dl*= Density of the Laminate
*Df*= Density of the Fibre
*Dm*= Density of the Matrix

Table 3.4 compares the experimentally obtained laminate density values with those obtained theoretically, assuming that the volume fraction of the fibre (*Vf*1) is equal to 0.6:

**Table 3.4:**
**Experimental Verses Theoretically Determined Densities**

| | Glass Fibre | Aramid Fibre | Carbon Fibre |
|---|---|---|---|
| Laminate Density (gm/cm$^3$):exp | 1.827 | 1.329 | 1.522 |
| Laminate Density (gm/cm$^3$):theory | 2.05 | 1.301 | 1.550 |
| Error in theory approximation (%) | 6.7 | 2.1 | 1.8 |

### *3.2.4 Safety Factors*

In the current standards for the requirements of all-composite cylinders used in the vehicular fuel storage of natural gas [e,f,g], the required stress ratio[2] (SR) of the fibres in the design of the cylinder is different for each fibre type. These different SR's are rationalized by fact that the different fibres have different stress rupture characteristics. Carbon fibre is unique in that it has the highest resistance to stress rupture and, thus, it has the lowest SR of the three fibres.

Chapter 2 proposed that the same cylinder shell requirements as required by the compressed natural gas standards be used by compressed hydrogen. Table 3.5 lists the most rigorous SR's required by each fibre type by the current all-composite fuel storage

---

[2] The stress ratio (SR) is the ratio of the stress in the fibre at the specified minimum burst pressure divided by the stress in the fibre at working pressure.

cylinder for compressed natural gas [f,g]. It is proposed that these SR's are adopted by the hydrogen storage cylinders.

**Table 3.5:**
**Proposed Stress Ratios for the Hydrogen Cylinder Design**

| Material | Stress Ratio |
|---|---|
| Glass Fibre | 3.65 |
| Aramid Fibre | 3.1 |
| Carbon Fibre | 2.35 |

### *3.2.5 Other Fibre Properties to Consider*

The stress rupture strength of the fibre is not the only material property which will effect the strength of the cylinder. Other factors, such as the corrosion strengths of the fibre, impact resistance of the fibre, etc. also will effect the performance of the fibre laminate. Table 3.6 summarizes some of the potential sources of failure for each type of laminate and provides a value engineering approximation of the additional strength of laminate (ASL) required to withstand potential exposure to these variables.

**Table 3.6:**
**Additional Factors Affecting the Strength of the Fibres**

| Fibre Type | Potential Source of Failure | ASL |
|---|---|---|
| Glass Fibre | The general conclusion is that "glass filaments are not resistive to strong acids and bases and total filament destruction occurs in only a matter of days" [h].[3] | 20% |
| Kevlar Fibre | Exposure to certain strong aqueous acids and bases, over time, can cause degradation [i]<br>Kevlar has the tendency to gain moisture over time.<br>Extended exposure of Kevlar to UV light can cause loss in mechanical properties [i]. | 15% |
| Carbon Fibre | Carbon fibres are brittle. In an impact loading condition, it is more desirable to have a tougher material to absorb some of the energy upon impact. | 10% |

---

[3] In "all-composite" hydrogen fuel cylinders, the resin is the principal resistor to corrosion attack. However, in service, were the composite structure is placed in service, the resin can experience matrix cracking where microcracks develop in the resin due to the repeated loading. In this case, any contaminates can leach into the composite structure and attack the reinforcing fibre.

### *3.2.6 The Storage Capacity of the Cylinder*

Range is considered an important design consideration for hydrogen vehicles. Because of the low energy density of fuel when stored in a compressed gas state (compared to more conventional fuels such as gasoline or diesel fuels), the range of a hydrogen vehicle compared to a vehicle powered with gasoline or diesel fuels, with similar fuel tank sizes, will be smaller. Ideally, the storage capacity of a hydrogen cylinder, i.e. its volume capacity, should be maximized in order to approach the driving ranges that drivers are accustomed to.

The consequence of having a thicker composite laminate is that there internal storage capacity of the cylinder, for a given external storage volume, is reduced. The total volume of composite laminate needed in the design of a all-composite cylinder is determined by the strength of the laminate per unit thickness of the laminate and the SR required by the fibre used in the laminate construction.

Table 3.7 lists the different strengths/unit thicknesses (based on the geometry of the tensile coupon samples tested) for the three candidate fibre types.

**Table 3.7:**
**Strength/Thickness Ratios of the Different Fibres**

| | Glass Fibre | Aramid Fibre | Carbon Fibre |
|---|---:|---:|---:|
| Tensile Ultimate Strength (MPa) | 827 | 1517 | 2130 |
| Thickness of the Laminate (cm) | 0.188 | 0.152 | 0.178 |
| Strength/unit Thick (MPa/cm) | 4400 | 9980 | 11,970 |

For an all-carbon composite cylinder[4], 40.6 cm x 162.6 cm, designed for a service pressure of 24.8 MPa, the amount of carbon fibre required to meet the cylinder strength requirements was 0.0356 m$^3$. The total external volume consumed by the all-carbon cylinder was 0.1937 m$^3$. Using the strength/unit thickness values (SUTs) in Table 3.6, the additional strength factors (ASLs) in Table 3.5, and the stress ratios (SRs) listed in Table 3.4, the required volume of glass fibre and Kevlar fibre can be determined.

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[4] The cylinder is currently produced by EDO Canada Limited for the vehicular storage of natural gas.

$$V2 = \left(\frac{SR2}{SR1}\right) \bullet \left(\frac{1+\left(ASL2/100\right)}{1+\left(ASL1/100\right)}\right) \bullet \left(\frac{SUT1}{SUT2}\right) \bullet V1$$

where:

*V*i= Volume of the fibre i
*SR*i= Stress Ratio of the fibre i
*ASL*i= additional strength of laminate required for fibre i
*SUT*i= Strength/Unit Thickness of fibre i

The quantity of glass in an all-glass cylinder needed to meet the strength requirements of a all-glass cylinder is 0.118 $m^3$ . The quantity of Kevlar in an all-Kevlar cylinder needed to meet the strength is 0.0425 $m^3$. In terms of cylinder internal storage volumes, assuming that each cylinder meets the external dimensions of the 40.6 cm x 162.6 cm cylinder (total external volume of 0.1937 $m^3$), this corresponds to internal volumes of 0.0755 $m^3$, 0.1512 $m^3$, and 0.1681 $m^3$, for glass, Kevlar, and, carbon respectively. Figure 3.2 shows, graphically, these results.

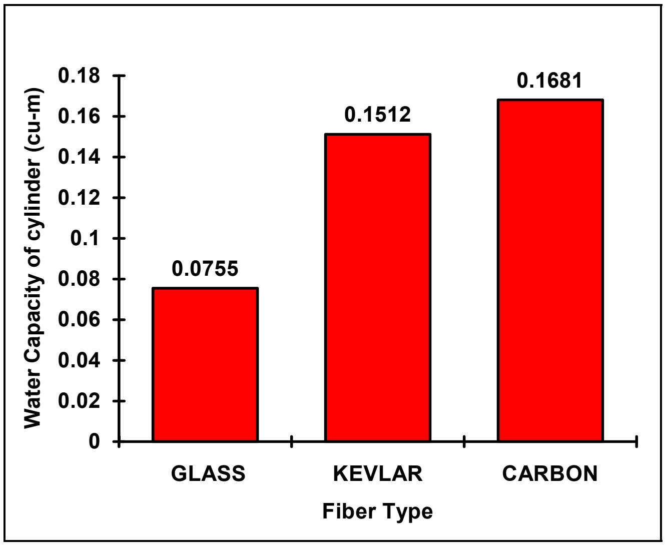

**Figure 3.2:**
**Water Capacities of the Hydrogen Cylinder Types**

It is clear that the all-carbon cylinder is much more efficient in terms of storage capacity than an all-Kevlar or all-glass cylinder.

### 3.2.7 *The Weight of the Cylinder*

In an optimal design, the fuel cylinders are designed to be as light as possible. Having a light cylinder increases the overall performance of the hydrogen vehicle in terms of vehicle fuel efficiency and the general maintenance of the vehicular components due to the additional wear and tear during operation.

In section 3.2.6, the composite volumes were determined to be 0.118 $m^3$, 0.0425 $m^3$, and 0.0256 $m^3$ for cylinders fabricated of glass fibre, Kevlar fibre, and carbon fibre respectively. Using the densities experimentally determined and listed in Table 3.4 above, the weight of the composite shell for each fibre type can be determined. Weights of 216 Kg, 57 Kg, and 39 Kg, were calculated for glass, kevlar, and carbon respectively. Figure 3.3 illustrates the weights of the different cylinder types graphically.

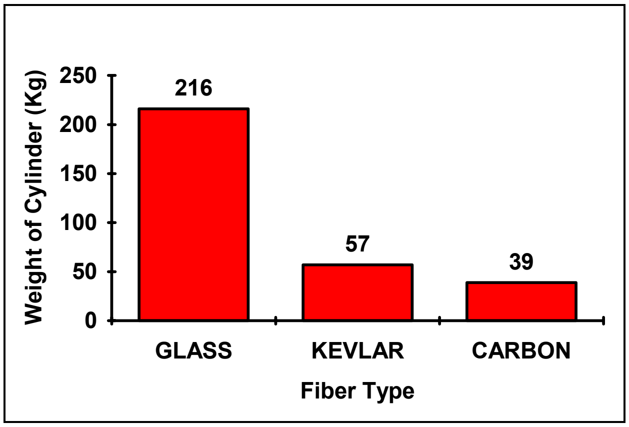

**Figure 3.3:**
**Weights of the Various Cylinder Types**

The carbon fibre is the best alternative for all-composite cylinders when compared on the basis of cylinder weight.

### 3.2.8 *The Fire Resistance of the Cylinder*

The ability of an all-composite cylinder to resist a bonfire situation is primarily a function of the resin used to bond the fibres together, not the fibrous material. In a bonfire application, the fire softens the epoxy resin to a point where the resin can no longer provide support to the fibres and the cylinder fails. In this analysis, the epoxy resin for each composite laminate is kept the same to provide consistency among the results.

### 3.2.9 The Cost of the Cylinder

The weights of the composite laminates needed for a 40.6 cm x 162.6 cm cylinder were 216 Kg, 57 Kg, and 39 Kg, for glass, kevlar, and carbon cylinders respectively (both the weight of the fibres and the weight of the resin matrix are included in these values). The following equation can be used to determine the weight of fibre (*Wf*) from the weight of the composite laminate (*Wt*):

$$Wf = \left[ \frac{Df \bullet 0.6}{\left(Dm \bullet 0.4\right) \bullet \left(Df \bullet 0.6\right)} \right] x\, Wt$$

By multiplying this weight of the fibre (*Wf*) by the cost per kilogram of carbon fibre, the cylinder cost can be determined. Table 3.8 lists the weight of the fibre needed for each cylinder type, and the total cost of the fibre needed for the fabrication of the cylinder.

**Table 3.8:**
**The Cost of the Fibre in the Cylinder**

| | Weight of Fibre (Kg) | Cost of Fibre[a] ($/Kg) | Cost of Fibre in Cylinder ($) |
|---|---|---|---|
| Glass Fibre | 152 | CAN $2.60/Kg | $395 |
| Kevlar Fibre | 36 | CAN $35.49/Kg | $1278 |
| Carbon Fibre | 26 | CAN $46.30/Kg | $1204 |

[a] quoted at the time of this report generation (Jan '97)

From this table, it is evident that the glass fibre, due to its low material cost, is the cheapest alternative for hydrogen cylinder manufacture.

### 3.2.10 Glass/Carbon Hybrid Cylinders

The above analysis assumed that the 40.6 cm x 162.6 cm cylinder designed by ECL utilized each layer of carbon fibre optimally in terms of stress in the fibres. In this cylinder design, however, some of the fibres used were for reasons other than supporting the loading from the internal pressure. As examples, some of the carbon fibres are used to support the metal end-fixtures and are built up to provide bulk material, not to be placed under severe stress conditions.

A hybrid cylinder design would replace some of the non-load bearing fibrous components of the current carbon fibre cylinder with the less expensive glass fibre filaments. A hybrid cylinder design may improve the overall cost of the cylinder design.

### *3.2.11 Properties of the Glass/Carbon Hybrid Tensile Coupons*

Hybrid tensile test coupons containing both carbon fibre and glass fibres were fabricated according the ASTM D-3039-95 standard to determine their mechanical properties. Figure 3.4 illustrates how the Young's Modulus of elasticity varies linearly with the percentage of carbon in the sample.

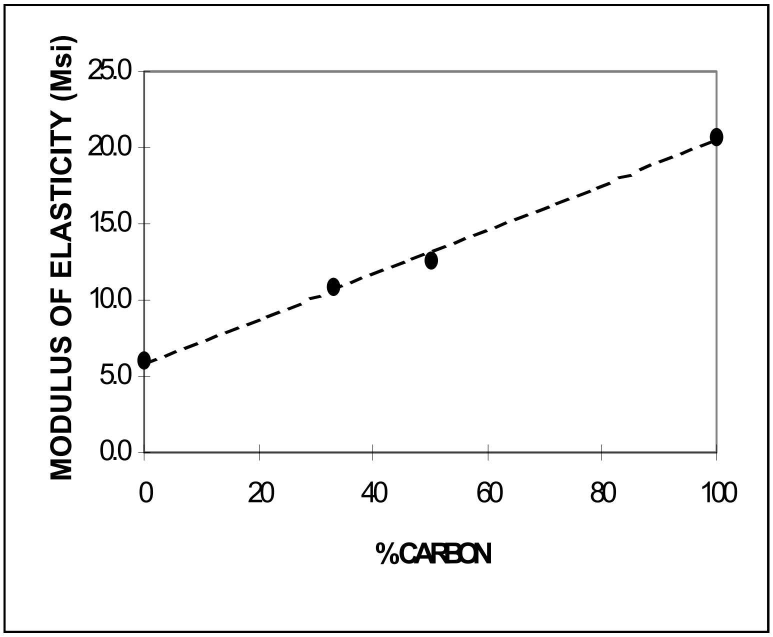

**Figure 3.4:**
**Tensile Modulus' of the Hybrid Laminate**

Figure 3.5 illustrates how the ultimate stress varies as a function of the percentage of carbon in the sample:

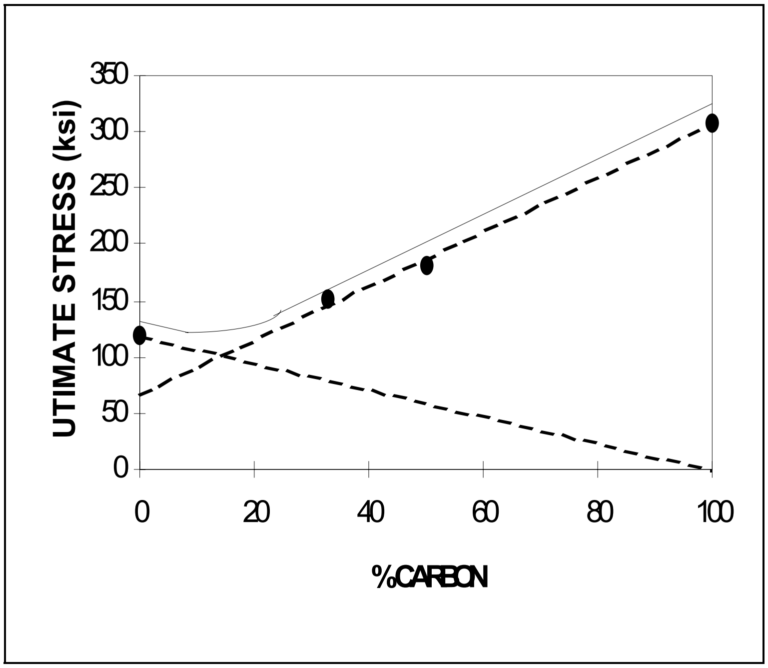

**Figure 3.5:**
**Ultimate Strengths of the Hybrid Samples**

For the samples with moderate to high volume ratios of carbon, the ultimate strength of the hybrid sample is a linear function of the percentage (%) of carbon. Under a strain controlled environment, the hybrid specimen will still fail when the carbon fibres, in the hybrid sample, reach their ultimate strain (experimentally determined to be approximately 1.5%). Glass fibre will strain further, but at this point, most of the load carrying capacity of hybrid laminate (i.e. the carbon fibres) has been destroyed.

Note that the strength of the hybrid tensile sample is not a linear function of the percentage of carbon (by volume) for hybrid samples which are low in carbon content (0<%CARBON<15%). This is because the behaviour of the laminate is predominately influenced by the glass fibre response. In this region, the addition of carbon fibre acts to reduce the strength of the laminate by reducing the cross-sectional area of the laminate when the carbon fibres break. At this point, the glass fibres are still capable of supporting the applied load.

### *3.2.12 Hybrid Cylinders*

Future work has to be performed for the development and testing of cylinders with hybrid composite shell designs.

## 3.3 REDUCING THE RESIN CONTENT

Another consideration in the optimization of the cylinder shell was through the reduced fibre and resin content through a more efficient manner of resin impregnation.

When the resin content of the composite laminate is too high, the strength of the composite is reduced. When the resin content of the composite laminate is too low, the strength of the composite is reduced. Precision wet filament winding of cylinders requires precise impregnation control to achieve an optimum resin content. In the case of the ECL LiteRider cylinder, the resin content is too high. Reducing the resin content ultimately leads to a reduction in resin and fiber used in manufacturing cylinders. This material reduction reduces the overall cost of the cylinder.

Figure 3.5 illustrates the current filament winding set-up. The winding consists of passing dry graphite fiber roving from a creel into a bath containing the resin and then onto the liner. Through a series of squeegees and combs, the resin content of the fibre as it is laid onto the cylinder is carefully controlled.

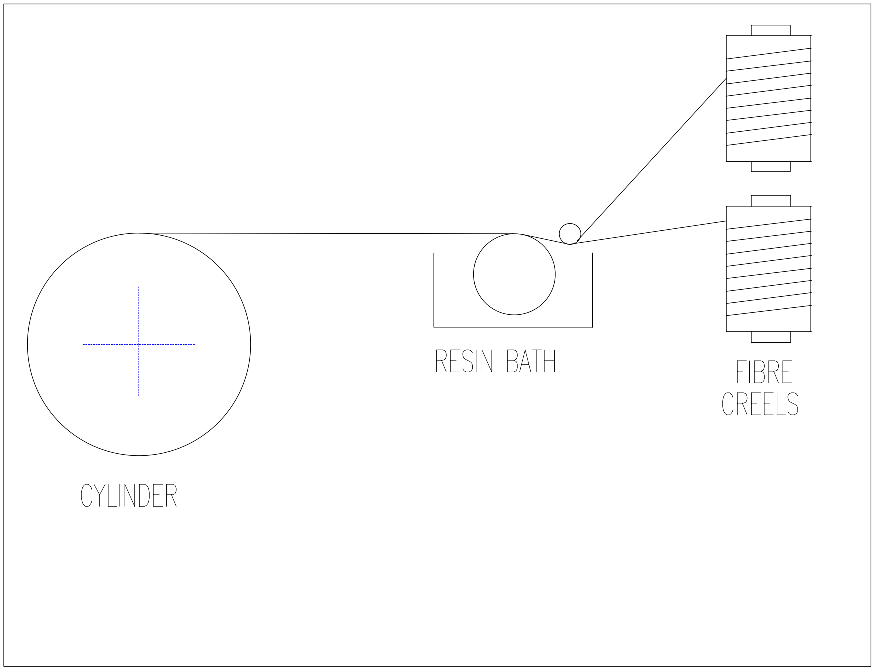

**Figure 3.6:**
**The Filament Winding Process**

By altering (1) the degree to which the fibre is worked prior to resin impregnation, (2) the manner of resin impregnation into the dry fibre, and (3) the degree to which resin is removed as it leaves the resin bath, the resin content of the composite can be controlled. As part of the hydrogen program, the resin bath design was optimized. The result of changes completed to the resin bath was a tremendous improvement to the resin content. The improved resin bath was used on several production runs and the resin content of the cylinders was reduced by approximately 30%.

Controlling the resin content not only reduces cost by reducing the resin used in the cylinder. By controlling the resin content, the amount of fiber required to maintain strength in the cylinder was reduced by 8-10% without compromising the final performance of the cylinder.

## 3.4 CONCLUSIONS

From the preceding analysis, the following conclusions can be made.

- All-carbon cylinders are the most optimal cylinder when compared to all-glass cylinders and all-Kevlar cylinders in terms of storage capacity, cylinder weight, and corrosion resistance, and cost.

- There may be room for improvement with the cylinder cost by employing the use of cylinders fabricated of both carbon fibre and glass fibre (hybrid cylinders). A hybrid cylinder design would replace some of the non-load bearing fibrous components of the current carbon fibre cylinder with the less expensive glass fibre filaments.

- Optimizing the resin content reduces the amounts of both the resin and fibre used in the cylinder. This reduces cylinder cost.

## REFERENCES

[a] R.M. Jones, “*Mechanics of Composite Materials*”, McGraw-Hill, 1975.

[b] “*Composite Design Handbook for Space Structure Applications*”, ESA PSS-03-1101 Issue 1, Structures and Mechanisms Division, European Space Research and Technology Centre, December 1986.

[c] ASTM D 3039-95, “*Standard Test Method for Tensile Properties of Polymer Matrix Composite Materials*”, February 15, 1995.

[d] Dupont Company*, “Filament Winding with Yarns or Rovings of Kevlar 49 Aramid Fiber*”, A Preliminary Information Memo, Number 431, September 1983.

[e] ANSI/AGA NGV2*, “Basic Requirements for Compressed Natural Gas Vehicle (NGV) Fuel Containers*”, 1992.

[f] CSA B51-95 Part 2, “*High Pressure Cylinders for the On-Board Storage of Natural Gas as a Fuel for Automotive Vehicles*”, 1995.

[g] ISO/TC 58/SC 3/WG 17, “*High Pressure Cylinders for the On-Board Storage of Natural Gas as a Fuel for Automotive Vehicles*”, July 1995.

[h] Kliger, H.S., and Barker, E.R., *“A Comparative Study of the Corrosion Resistance of Carbon and Glass Fibres”*, 39th Annual Conference, Reinforced Plastics/Composites Institute, The Society of the Plastics Industry, Inc., January 16-19, 1984.

[i] Dupont Company, "*Kevlar® Aramid Fibre*", Technical Guide, December 1992.

## 4.1 INTRODUCTION

Chapter 3 investigated the issues involved with the composite shell of the cylinder. This chapter will address the issues involved with some of the other components of the cylinder. More specifically, this chapter addresses the effectiveness of the following cylinder components in a compressed hydrogen gas environment:

- The liner material,
- The adapter, end plug, and end bosses,
- The pressure relief device.

## 4.2 THE LINER MATERIAL

In an all-composite cylinder used for the storage of compressed gas, a high-strength filament wound composite shell is lined internally with a polymeric liner. The purpose of this polymeric liner is to provide a barrier so that the contained gas is not permitted to escape through the cylinder shell sidewall. The liner, however, does not create a full barrier to the permeation of gas. The current liner used in the ECL cylinder for natural gas permits a small degree of permeation of low molecular weight hydrocarbons [a] and, thus, permeation of gas through the liner occurs. This is recognized by the standards for all-composite natural gas cylinders, AGA NGV2- 1996 [b] and CSA B51-95 Part 2 [c], and a small and safe degree of permeation is permitted.

This report details the experimental work used to determine where the current liner technology is suitable for hydrogen storage and to investigate other candidate materials which may be more suitable for hydrogen.

### *4.2.1 The Liner as a Barrier Film*

An understanding of permeation of hydrogen through the liner comes from previous experimental work and analytical models.

Previous Experimental Work

Previous experiments and investigations have been performed to gain a better understanding of the permeation rates of hydrogen and methane through the current liner material.

- Swain and Swain [d] performed some experimental testing of two grades of pipe (similar to the current liner material for the ECL natural gas cylinders) with both methane and hydrogen gas and illustrated that the permeation rate of hydrogen was 5.2 to 7.3 times the permeation rate for methane. Tests were conducted on pipe sections having the same geometry and loaded under the same external temperature range (23°C).

- Figure 4.1 illustrates data obtained from [e] and shows the relationship of the pressure gradient and temperature to the permeation rate of hydrogen through a liner sample. Note that this information was taken from samples which were 0.03mm thick (thin films) and cannot be extrapolated proportionately to thicker barriers because of the differing quality between the thin and thick films. However, the trends of the permeability relationships with pressure and temperature should be similar.

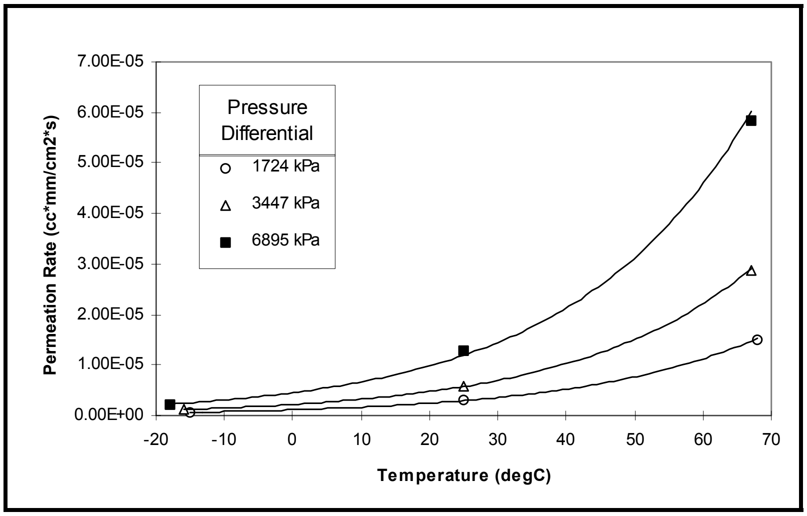

**Figure 4.1:**
**Hydrogen Permeation Through a Liner**

<u>The Transport of a Gas Through a Barrier (Fick's First Law)</u>

The transport of a penetrant in a barrier material can be described by Fick's first law stating that the volume (V) of a penetrant that penetrates a barrier wall is directly proportional to the area (A) of the wall, the partial pressure differential (p) of the penetrant and time (t), and inversely proportional to the wall thickness (s), if the wall is homogeneous in the direction of penetration:

$$V = D \cdot \left[ \frac{A \cdot p \cdot t}{s} \right]$$

D is a coefficient of diffusion and is a function of the barrier material, the penetrant surrounding the barrier, the penetrant inside the barrier, and stress level inside the material, and the temperature.

Assuming a constant thickness (s) and area (A), the differential equation for the diffusion is as follows:

$$\frac{\partial V}{\partial t} = D \cdot p$$

which indicates that assuming the same sample size, material, and penetrant properties, the rate of permeation of the gas through the barrier material is a function of the temperature and a linear function of the pressure.

The Viscous Flow Model

Fick's First Law explains how a particular penetrant behaves depending on the pressure and the temperature. The permeation rates (dV/dt) of different gases through a medium can be related to each other using the viscous flow model.

$$\left[\frac{\partial V}{\partial t}\right]_{(hydrogen)} = \left[\frac{\upsilon_{(hydrogen)}}{\upsilon_{(methane)}}\right] \cdot \left[\frac{\partial V}{\partial t}\right]_{(methane)}$$

The dynamic viscosity, $\mu$, of hydrogen and methane at atmospheric pressure and 20°C are given as [f]:

$\mu$ (hydrogen): 875 $n \cdot s/m^2$
$\mu$ (methane): 1087 $n \cdot s/m^2$

It should be noted here that the dynamic viscosity, $\mu$, is strongly dependent on temperature and essentially independent of pressure. The kinematic viscosity, $\upsilon$, is equivalent to the dynamic viscosity divided by the density of the material.

$$\upsilon = \frac{\mu}{\rho}$$

Where the densities of both gases at 20°C and 24.8 MPa are:

$\rho$ (hydrogen): 17.6 $Kg/m^3$
$\rho$ (methane): 200 $Kg/m^3$

Thus, the kinematic viscosity become:

$\upsilon$ (hydrogen): 6.86 $n \cdot m^2/s$
$\upsilon$ (methane): 0.744 $n \cdot m^2/s$

The ratio of viscosity can be used to relate the permeation rates for hydrogen and methane. Using the data above, the permeation rate for hydrogen at high pressure (24.8 MPa) and room temperature (20°C) is about 9.2 times the rate of permeation for methane through the same liner material.

### 4.2.2 Permeation Testing

The permeation rates of hydrogen through various liner technologies at high pressures was determined using experimental investigation. In this experimental set-up, the liner material sample was sandwiched between pressurized hydrogen on one side of the liner material and a permeation plate[1] on the other side. As gas permeated from the high pressure hydrogen side, through the liner, the gas was allowed to pass through the permeation plate and was sampled in a collection chamber. Gas was prevented from escaping out at the edges of the liner sample by using both compression of the liner and an o-ring seal.

Figure 4.2 illustrates the test set-up. In this set-up, pressurized hydrogen gas is held on one side of the liner in a stainless steel tubing configuration. The liner itself is encapsulated between this high pressure hydrogen tubing and a permeation plate. As the gas permeates through the liner, the gas is collected in a collection chamber. Gas is initially filled into the high pressure stainless steel line through a valve and the pressure is monitored using a pressure gage. As the gas permeates through the liner, levels of permeation are determined by measuring the gas composition in the collection chamber using a gas detection device.

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[1] The permeation plate was a rigid steel plate with holes drilled through. The purpose of this plate was to provide support for the plastic liner while still permitting gas to pass through. This, in essence, simulated the effect of the support from the composite shell on a liner.

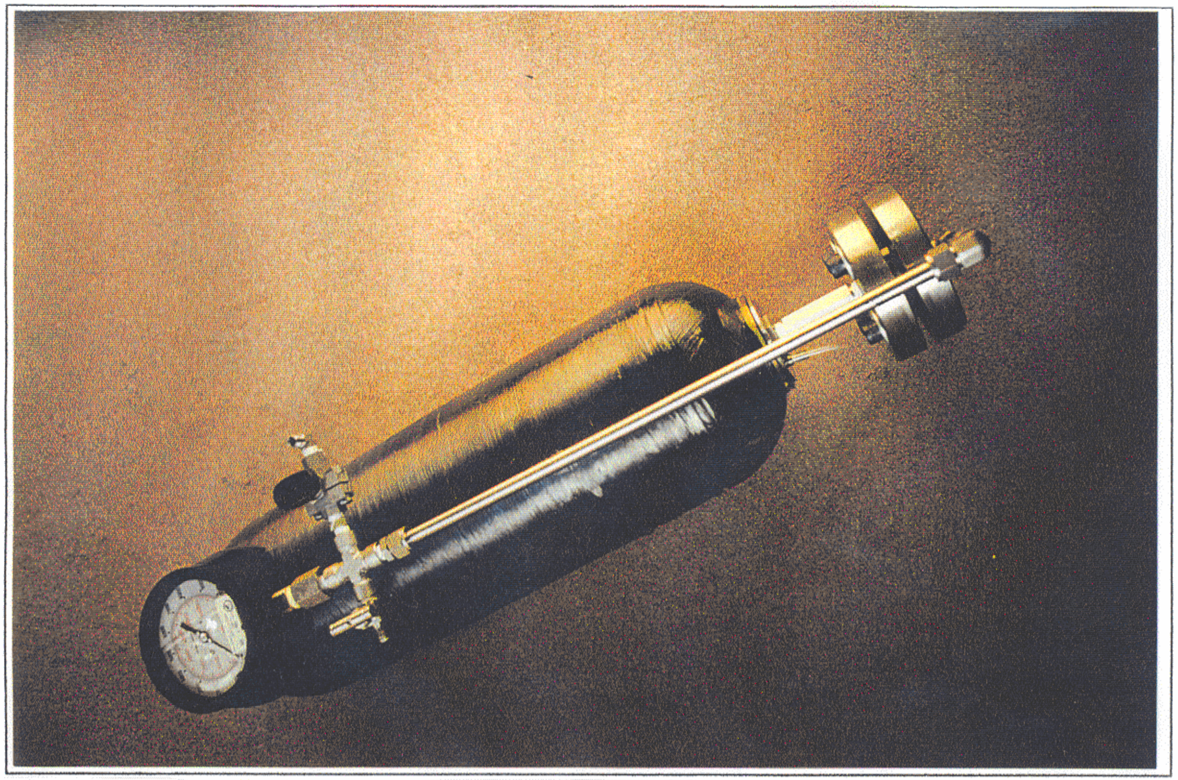

**Figure 4.2:**
**The Permeation Test Apparatus**

### *4.2.3 Permeation Test Results*

Two tests were performed on similar liner configurations. The liner material was rotomoulded to a 0.61 cm thickness and pressurized with hydrogen gas.

This was performed to determine the ability of the existing liner material (as used with the natural gas cylinders), to act as a barrier to the permeation of hydrogen. Figure 4.3 illustrates the drop in the pressure (P) of the hydrogen supply over time.

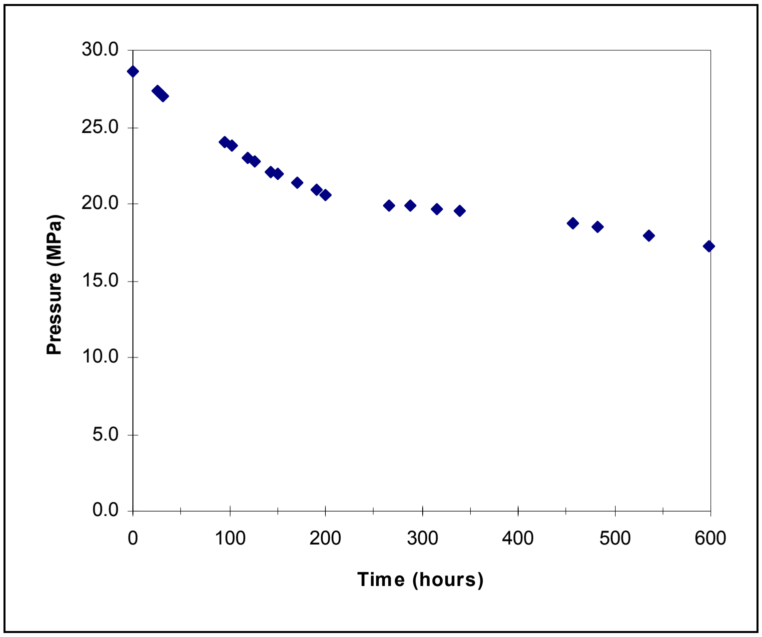

**Figure 4.3:**
**Pressure Drop in the Hydroden Supply Chamber Over Time**

Figure 4.4 illustrates the hydrogen concentration readings (%LEL) recorded in the collection chamber over time.

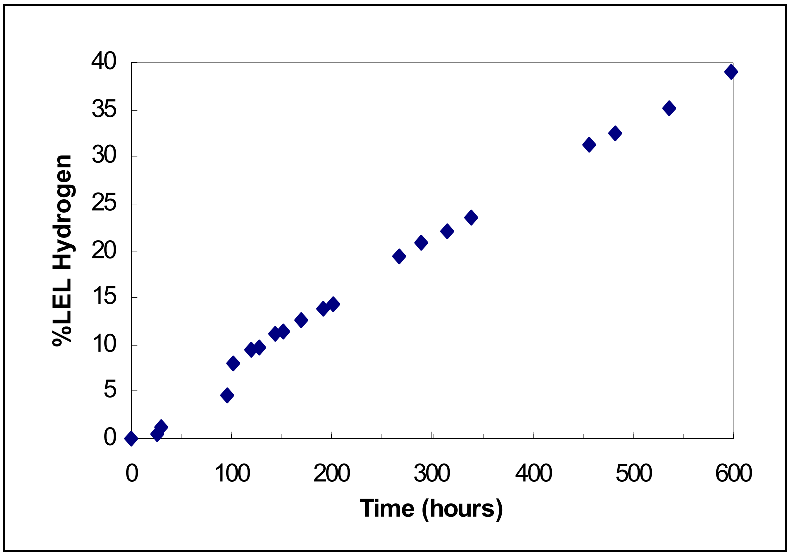

**Figure 4.4:**
**Hydrogen Concentration Readings in the Collection Chamber Over Time**

Using the volume of the chamber as being 12.5 L, the %LEL reading can be converted to a volume reading of hydrogen over time. This conversion is illustrated by Figure 4.5.

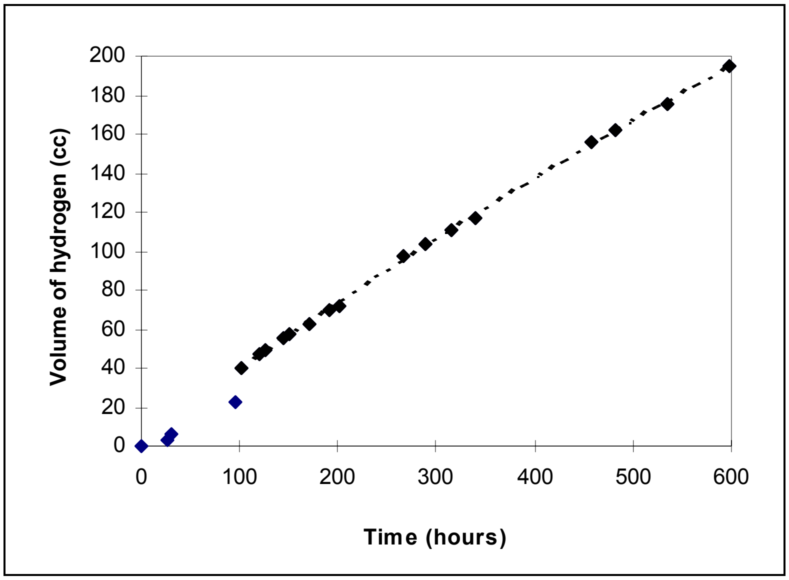

**Figure 4.5:**
**Volume of Hydrogen Permeating Through the Liner as a Function of time**

The fuel gas concentration profile through the thickness of the test section affects the permeability flow rates [d]. For this reason, near the initialization of the test, where the concentration of the hydrogen gas in the liner is changing with time, the flow rates are not steady-state and these data points were neglected in the determination of the steady-state permeation rate. The permeation rate can be plotted as a function of pressure. Figure 4.6 illustrates the permeation rate of the sample 1 as a function of hydrogen pressure. The trend appears to be linear.

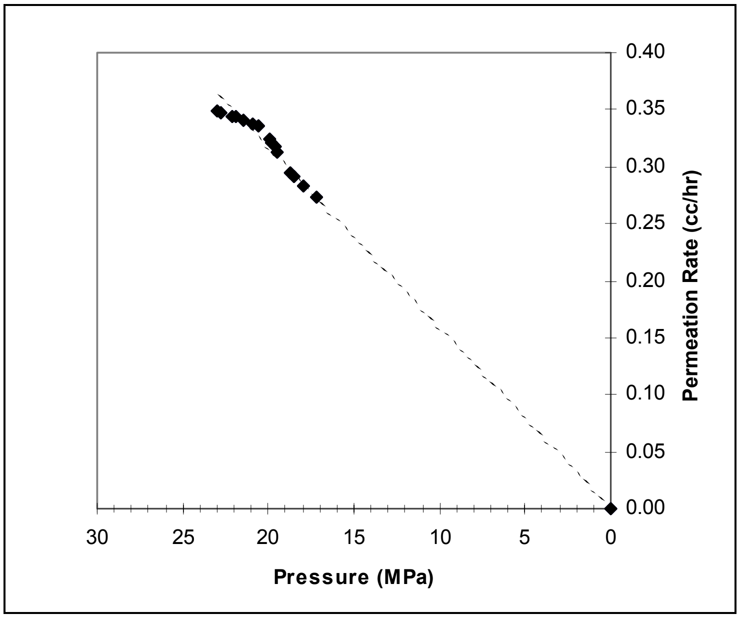

**Figure 4.6:**
**The Permeation Rate as a Function of Pressure**

Test 2 was performed to display repeatability with the test results found in Test 1. Figure 4.7 illustrates the volume of permeated hydrogen as a function of time for both Test 1 (circles) and Test 2 (solid dots) coupon samples.

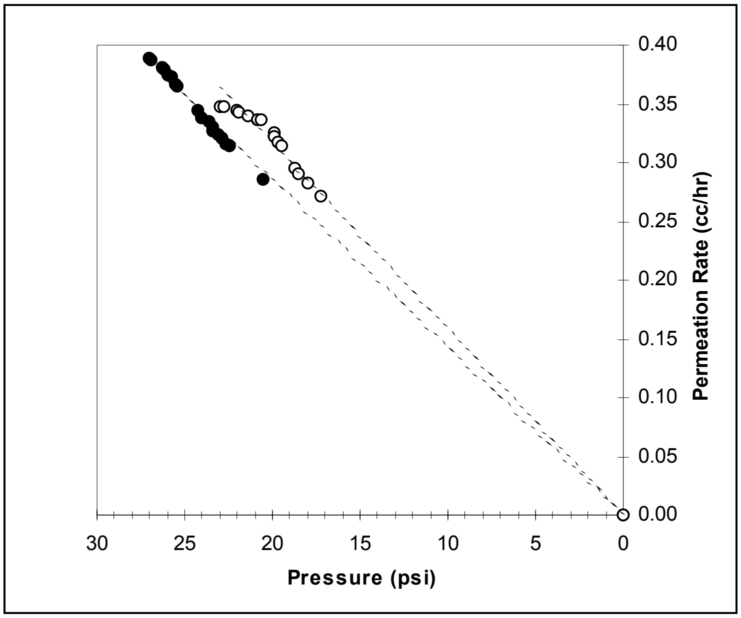

**Figure 4.7:**
**The Permeation Rate as a Function of Pressure**

At a service pressure of (24.8 MPa), the permeation rate for the couple samples were measured to be 0.39 cc/hr and 0.35 cc/hr for sample 1 and sample 2 respectively.

Note that the values obtained are preliminary. Additional testing of the material is necessary to verify permeation results.

### *4.2.4 The Liner in a Hydrogen Environment*

Previous testing at ECL determined the effect of a high pressure hydrogen environment on the liner material. A cylinder was pressurized with compressed hydrogen and heated so that the internal pressure was >17.2 MPa at >82°C. This pressure and temperature were held in the cylinder for 200 hours. The following conclusions were the results of the test:

- Following this conditioning, the cylinder was fatigue tested for 5,000 cycles from 0 MPa to 24.8 Mpa and burst at 67.2 Mpa. These requirements exceeded the requirements of the proposed hydrogen standard.

- Sections of the liner material were then taken from the burst cylinder. No degradation of the liner material's tensile strength and elongation were observed.

### *4.2.5 Alternative Liner Materials*

The use of alternative materials for the liner may be a more effective barrier to hydrogen. The use of a nylon material was examined by ECL for this application.

Nylon material has a lower permeation rate than the current liner material. However, upon further investigation, the following was established:

- Nylon material became quite brittle at temperatures around -40°C.
- The nylon material only came in the black colour which made inspection of the liner product difficult.
- The nylon part was difficult to form using the current liner manufacturing process. The part was difficult to remove from the mold, and the part was spotted with pin-holes which would reduce the effectiveness of the nylon material as a barrier.

## 4.3 THE ADAPTER, END PLUG, AND TWO END BOSSES

Due to hydrogen's unique molecular properties, it is capable of diffusing into most materials and cause structural damage to the material in the form of reduced ductility, ease of crack initiation and propagation, creation of surface blisters, surface cracks, and internal voids, and a lowering of the yield strength [g]. This is most commonly known as hydrogen embrittlement.

Although there are now known to be many alloy systems in which the behaviour is altered by the presence of hydrogen, hydrogen effects are most pronounced in steel. Hydrogen diffuses extremely rapidly in iron and steel and accumulates at a wide variety of locations in the microstructure [g].

The resistance to hydrogen embrittlement can vary widely and, in fact, different tempering treatment can cause different resistances to hydrogen damage. General rules of thumb with hydrogen and steel are [g]: "Embrittlement becomes more severe as strength levels increase, ... [and] steels with strengths below 700 Mpa show no significant embrittlement." However, these general rules must be used with caution.

The adapter, end plug, and the end-bosses[2] are manufactured from steel (for strength) and are exposed to the compressed hydrogen gas. As recommended by an external testing agency [h] only the materials that meet the NACE MR0175 material requirements for sour gas service should be used for the hydrogen environment.

## 4.4 PRESSURE RELIEF DEVICES (PRDS)

Almost all compressed gas containers are fitted with pressure relief devices (PRDs). A pressure relief device is a pressure- and/or temperature-activated device used to vent a charged cylinder safely in the event of a fire. Due to the nature of an all-composite cylinder, the PRD needs to be thermally-activated because when the all-composite shell is exposed to a fire environment, the cylindrical shell degrades significantly before the pressure in the cylinder can rise sufficiently to burst a rupture disk.

One of the concerns with thermally activated PRD's is that the eutectic material used in the PRD may creep over time and cause the PRD to release.

A proposed PRD-1 standard [i] includes an accelerated life test which is used to verify that the rate of creep of the eutectic material in the PRD is sufficiently low[3]. From the PRD-1 standard, the following creep test was extrapolated and adapted for hydrogen use. The purpose of this test was two-fold: (1) initially, the test examined the performance of the PRD to maintain pressure in a hydrogen environment, and (2) the test examined the ability of the PRD to hold pressure at high temperatures over a period of time.

### *4.4.1 The PRD Samples*

All PRD samples tested were of the type CG-9 which are described in the CGA Pamphlet S-1.1-1989 [j] as "*a fusible plug for use at cylinder service pressures above (3,450 kPa) utilizing a fusible alloy with a yield temperature not over 224°F (106.7°C), nor less than 208°F (97.8°C). Nominal yield temperature: 212°F (100°C).*"

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[2] As part of the design, the end bosses are separated from the hydrogen gas with the liner material. Thus, the end boss does not make direct contact with the hydrogen gas. However, the hydrogen gas is permitted to permeate through the cylinder liner. For this reason, consideration must be given to the end-boss material as well.

[3] The test is set up to ensure that the device can perform reliably for at least 1 year at 82°C and at least 20 years at 57°C.

Four different PRD samples were selected from 4 different PRD suppliers. The PRD samples used in this study are labeled and described in Table 4.1:

| PRD | DESCRIPTION OF PRD | Tm |
|---|---|---|
| PRD 1 | PRD1 is characterized by a straight cavity with a special composite alloy in the straight cavity. The composite alloy consists of fusible alloy matrix with a low melting point reinforced with solid, strong, stiff shots. | 100°C |
| PRD 2 | PRD2 is characterized by a fusible alloy that when melted, permits an o-ring seal to disengage. | 104°C |
| PRD 3 | PRD3 is characterized by a fusible alloy that when melted, permits a pressure retaining disk to rupture. | 102°C |
| PRD 4 | PRD4 is characterized by a fusible alloy that when melted, permits an sharp pin to penetrate a rupture disk and the cylinder can be fully vented. | 102°C |

**Table 4.1:**
**The PRD Samples**

### *4.4.2 Testing on the PRD Samples*

The test procedure was as follows:

1. One PRD was assembled onto a hydrogen storage tube, shown in Figure 4.8, that supported a supply of hydrogen gas.

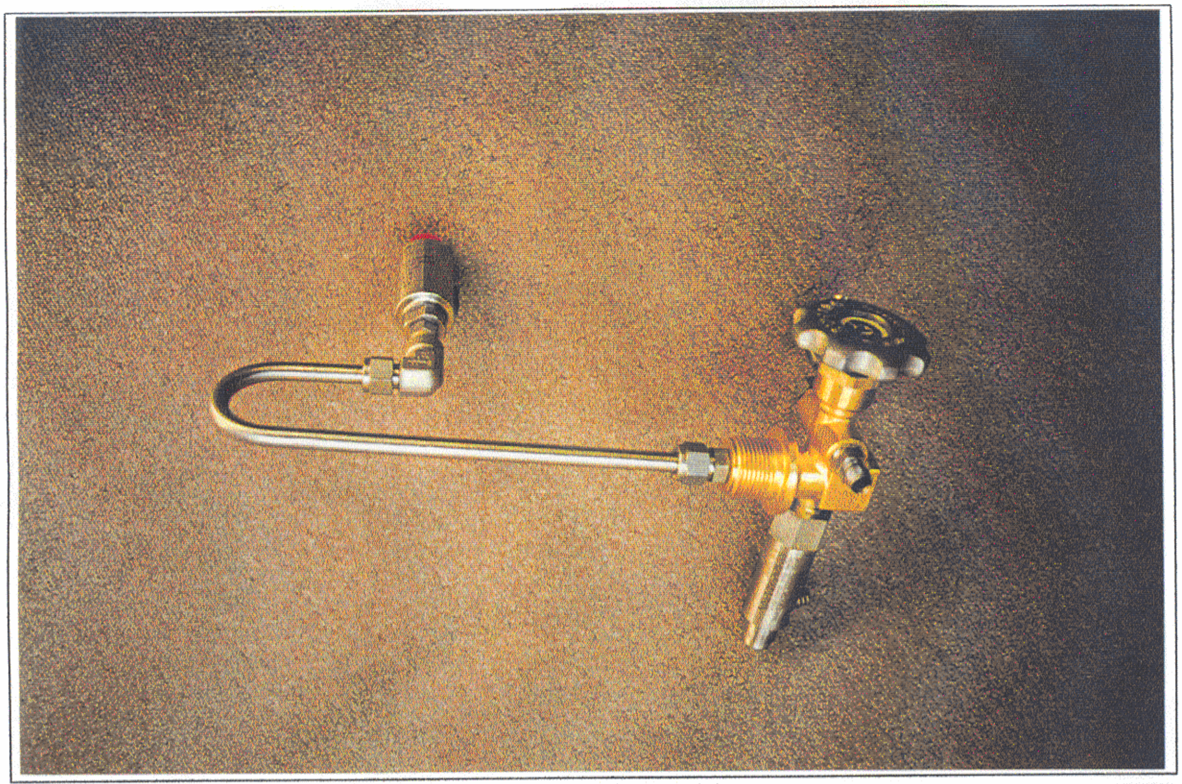

**Figure 4.8:**
**The PRD/Tube Assembly**

2. The PRD/tube assembly was then filled with hydrogen gas to a pressure of 24.8 MPa ± 1.4 MPa. Each PRD/tube assembly was checked with soapy water for leakage. None were detected.

   The PRD was then submerged into an oil bath that had a temperature of 22°C. Figure 4.9 illustrates a schematic view of the PRD test set-up. The PRD was fully submerged into the oil. A controller was used to maintain the oil temperature and a mixer was used constantly to ensure that the oil temperature was uniform throughout. Note that the PRDs were placed so that they were not in contact with the bath, mixer, or the heater.

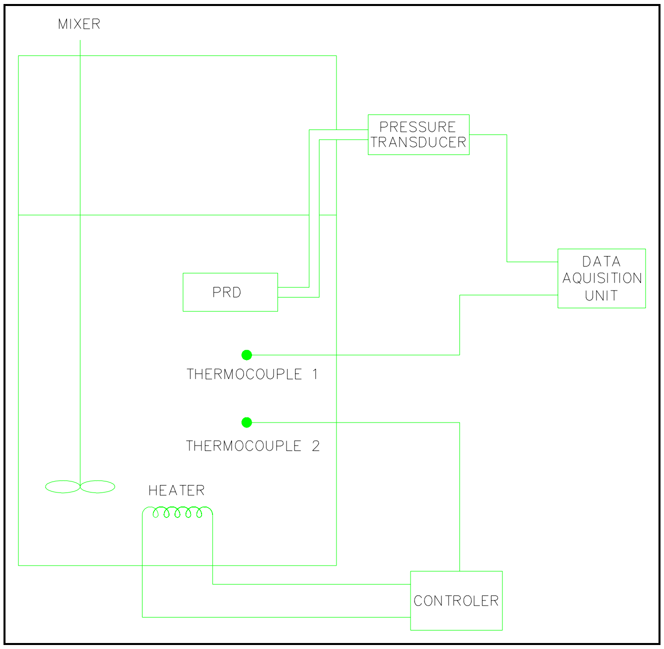

**Figure 4.9:**
**The PRD Test Set-Up**

3. The oil temperature was then heated to 90.2°C ± 2.5°C. Both the oil temperature and the pressure inside the hydrogen storage tubes were monitored over time using a data acquisition system. Figure 4.10 illustrates the oil temperature as a function of time. Note that the maximum temperature of the oil bath recorded was 92.7°C.

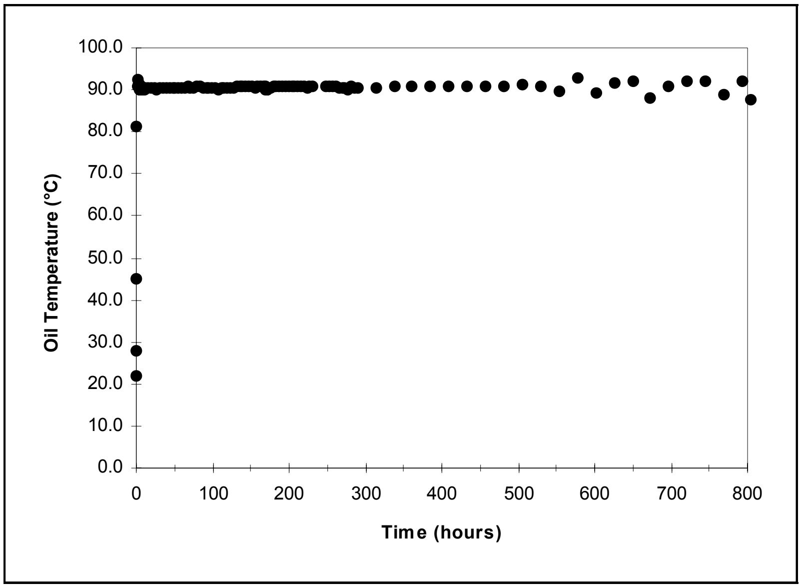

**Figure 4.10:**
**The Oil Temperature as a Function of Time**

### *4.4.3 Results of the PRD Testing*

Figure 4.11 illustrates the pressure in three of the PRDs as a function of test time.

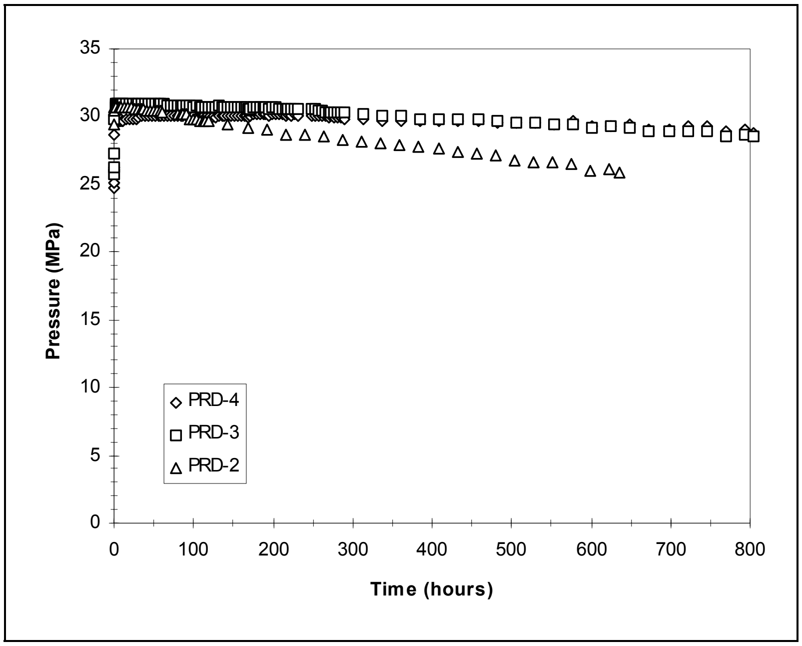

**Figure 4.11:**
**The PRD Pressure as a Function of Time**

Table 4.2 summarizes the results of the test.

**Table 4.2:**
**PRD Test Results**

| PRD | RESULTS |
|---|---|
| PRD 1 | PRD 1 began venting between 50 and 80 minutes from the beginning of the test. The PRD was fully vented by 110 minutes. After the hydrogen storage tube had fully vented from the PRD, the hydrogen storage tube was repressurized and the failure noted. Microcracking in the fusible eutectic material had caused the PRD to leak the hydrogen. |
| PRD 2 | PRD 2 did not trigger but steadily lost pressure over time. This loss in pressure was most likely attributable to loss of pressure through the o-ring seal. |
| PRD 3 | PRD 3 did not trigger but steadily lost a small degree of pressure over time. |
| PRD 4 | PRD 4 maintained its pressure for duration of test |

### *4.4.4 PRD Materials*

In general, the PRD samples are manufactured from either a brass or a stainless steel material. PowerTech Laboratories performed the tests from the proposed PRD-1 standard on PRD samples from 8 different suppliers. One of the conclusions of the study was that all of the brass PRDs tested, excluding one, did not pass the proposed SCC test [k]. The stainless steel seems to be a more reliable choice of material for the PRD.

## REFERENCES

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[b] ANSI/AGA NGV2-1992, *“Basic Requirements for Compressed Natural Gas Vehicle (NGV) Fuel Containers*”, August 1992.

[c] CSA B51-95 Part 2, “*High Pressure Cylinders for the On-Board Storage of Natural Gas as a Fuel for Automotive Vehicles*”, 1995.

[d] Swain, M. N. and Swain, M. N.,”Fuel Gas Permeability of Non-Metallic Pipes”.

[e] “Permeability and Other Film Properties of Plastics and Elastomers”, Plastics Design Library, 1995.

[f] E.A. Avallone and T. Baumeister II,“Mark’s Standard Handbook for Mechanical Engineers”, Ninth Edition, McGraw-Hill Company, 1986.

[g] H.K. Birnbaum, *“Encyclopedia of Material Science and Engineering*”, Permagon Press Ltd., 1986.

[h] Fax correspondance with Craig Webster, PowerTech Laboratories, February 29, 1996.

[i] “Basic Requirements for Pressure Relief Devices for Natural Gas Vehicle (NGV) Fuel Containers”, Proposed PRD-1 Standard, Draft Version 2.0, February 16, 1996.

[j] CGA Pamphlet S-1.1-1989, “Pressure Relief Device Standards: Part 1-Cylinders for Compressed Gases”, Compressed Gas Association, Inc., 1989.

[k] Conversation with Livio Gambone, PowerTech Laboratories, March 4, 1997.

## 5.1 IMPROVING THE SAFETY OF THE CYLINDER

The safe operation the composite cylinders when filled with compressed hydrogen needed to be addressed in this program. In particular, two issues were highlighted by ECL as being key areas of concern for the safe use of compressed hydrogen in a cylinder:

- the performance of the hydrogen cylinder in a bonfire environment, and
- the performance of the hydrogen cylinder after the cylinder has been damaged due to drop or to some other impact scenario.

Work was performed to examine these safety concerns and are summarized in the following sections.

## 5.2 COMPOSITE MATERIALS IN A BONFIRE ENVIRONMENT

Composite materials are degraded in a fire environment. Primarily, the mechanism of degradation is that the resin material, which supports the carbon fibre, becomes weakened and burnt in the extreme temperatures of the fire. With the lack of support, the structural integrity of the laminate is severely compromised and the cylinder may rupture in a matter of minutes.

Because a composite material degrades quickly during a fire exposure, a rupture disk style PRD cannot be used because this is not a sufficient time to build up the pressure in the cylinder before the cylinder fails. To overcome this problem, ECL retrofitted their all-composite cylinders with:

- a thermally activated PRD to trigger when the PRD was heated above a certain temperature, and
- copper strips to help conduct the heat from a fire to the PRD location.

However, the copper strips were awkward and could easily be mishandled causing damage to the copper strip and the PRD to which it was attached. Other systems had to be investigated.

### *5.2.1 Increasing the Strength of a Cylinder in a Fire*

Ideally, the life of a cylinder when pressurized and placed in a bonfire environment could be increased. This increased cylinder life would allow for more time for the PRD to activate and vent the cylinder contents safely. Increasing the cylinder life would reduce the risk of a cylinder rupture when exposed to a bonfire condition.

Several fire performance enhancements methods were applied to the cylinder and tested. These solutions and their rationales are listed in Table 5.1:

| **Fire Performance Enhancement Method** | **Rationale** |
|---|---|
| Alternate Resin Systems | Some resin systems are inherently better at resisting fires than others. |
| Intumescent Coating | The intumescent material coats the composite material and, when burned, provides an insulative layer between the composite laminate and the flame. |
| Bromine-Rich Additive | Bromine rich additives are added to the resin material in the composite, making it more resistant to burning. |
| Extinguishing Additive | The extinguishing additive is added to the resin material in the composite and attempts to extinguish the resin if ignited. |
| Bromine-Rich Vinylester | The vinylester is applied instead of the current resin system for the outer layers of the composite. The bromine, again, makes it resistant to burning. |

**Table 5.1:**
**Bonfire Performance Enhancers**

### *5.2.2 Testing the Fire Resistance of Different Systems: A Coupon Test*

In order to test the effectiveness of each of the above mentioned methods to improve the performance of a cylinder in a bonfire test, a simple test was set up. The goal of the test was to find a way to increase a cylinder life, without copper strips, to a minimum of five minutes. Theoretically, this 5-minute threshold would give enough time for the PRD to reach required temperature to trigger and have a safe venting of gases.

The test set-up is shown in Figure 5.1. A composite laminate beam was simply supported at each end and weighted in the middle. A fire source was then applied to the centre of the laminate sample. After exposing the flat composite laminate beam sample to a fire condition, the time which the laminate fails was recorded.

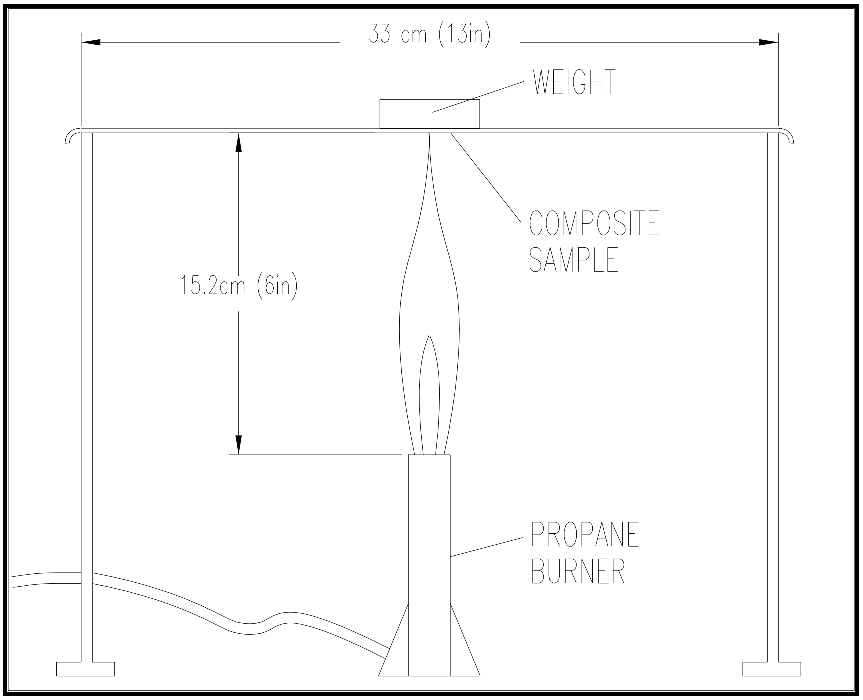

**Figure 5.1:**
**The Fire Test Set-Up**

The flat composite laminate samples were made by filament winding four layers of carbon fibre composite, with the appropriate fire protection systems, onto a flat panel so that the fibres were aligned in one direction. The composite coupons were then cured and then cut into strips (5 cm) so that dimensions of the samples were 5 cm wide by roughly 33 cm long.

These coupons were then tested for fire resistance by simply supporting them at each end on a frame. Figure 5.1 illustrates this test assembly. A weight (126 g) was then centered on top of the composite sample and a propane burner was placed approximately 15 cm below the composite sample. The burner was lit and the flame was adjusted so that the tip of the visible flame just touched the composite sample. Over time, most of the samples began to slump under the weight. An indicator was used to help determine when the sample had slumped 2.5 cm. The time required from the start of the fire until sample achieved 2.5 cm slump was recorded. Note that for each sample, the time it took the sample to reach 2.5 cm slump until total failure of the sample was always within one to two seconds. Note that the test was continued for 5 minutes at which time, if the specimen had survived, the testing was stopped.

### *5.2.3 The Results of the Coupon Testing*

Table 5.2 summarizes the results of the coupon testing performed.

**Table 5.2:**
**Fire Survival Time of Specimens with Various Fire Performance Enhancers**

| Coupon | Fire Performance Enhancement Method | Time (min:sec) |
|---|---|---|
| 1 | Current Resin | 0:56 |
| 2 | Current Resin + 10% Bromine-Rich Additive | 1:00 |
| 3 | Current Resin + 20% Bromine-Rich Additive | 0:54 |
| 4 | Alternative Resin ‘A’ | 1:05 |
| 5 | Alternative Resin ‘A’+ 10% Bromine-Rich Additive | 1:06 |
| 6 | Alternative Resin ‘A’ + 20% Bromine-Rich Additive | 1:11 |
| 7 | Alternative Resin ‘A’+ 20% Bromine-Rich Additive + 3% Extinguishing Additive | 1:34 |
| 8 | Alternative Resin ‘A’ + 8% Bromine-Rich Additive + 4% Extinguishing Additive | 1:30 |
| 9 | Bromine-Rich Vinylester ‘A’ | 2:05 |
| 10 | Bromine-Rich Vinylester ‘B’ | 2:03 |
| 11 | Bromine-Rich Vinylester ‘A’ + 10% Extinguishing Additive | No Failure |
| 12 | Bromine-Rich Vinylester ‘A’ + 20% Extinguishing Additive | No Failure |
| 13 | Alternative Resin ‘B’ | No Failure |

In general, the following results were observed:

- The addition of the bromine-rich additive did not enhance the composite’s resistance to failure in a bonfire environment.

- Alternative resin ‘A’ did not significantly enhance the performance of the composite.

- The specimens with both the bromine-rich additive and the extinguishing additives were capable of providing some resistance for retardation of the degradation of the cylinder in a bonfire environment. However, despite the fact that the resin material did not burn as readily, the heat from the bonfire softened the supporting resin matrix and the composite failed shortly thereafter.

- The specimens with both the bromine-rich vinylester and the extinguishing additives were capable of providing an even higher resistance for retardation of the degradation of the cylinder in a bonfire environment. However, as with the specimens with both the bromine-rich additive and the extinguishing additives, the heat from the bonfire softened the supporting resin matrix and the composite failed shortly thereafter.

- The specimens which used both the bromine-rich vinylester and an extinguishing additive and the specimen with alternative resin "B" survived the prerequisite 5 minutes in the fire environment.

### *5.2.4 Bonfire Testing*

From the results of the tests on the coupon samples, bonfire testing was performed on cylinders with similar protective systems. Five cylinders[1] were prepared and subjected to a vertical bonfire test. To test the fire performance enhancement system the cylinders were all pressurized with a combustible gas (natural gas), and all had their pressure relief devices plugged to enable testing of the tank for five minutes without the cylinder venting. Culverts were placed around the tank to block wind and which also created a swirling fire column effect which would totally envelope the cylinders being tested. Note that the bonfire test was continued for 5 minutes at which time, if the specimen had survived, the testing was stopped.

The following table summarizes the results of the test:

**Table 5.3:**
**Bonfire Survival Time of Cylinders with Various Fire Performance Enhancers**

| Cylinder | Fire Performance Enhancement Method | Time (min:sec) |
|---|---|---|
| 1 | Bromine-Rich Vinylester 'A' | 4:18 |
| 2 | Bromine-Rich Vinylester 'A' + 5% Extinguishing Additive | 3:00 |
| 3 | Bromine-Rich Vinylester 'A' + 20% Extinguishing Additive | 3:12 |
| 4 | Alternative Resin 'B' | 4:25 |
| 5 | Intumescent Coating | No Failure |

The cylinder with the intumescent coating was the only cylinder that passed the requirements of the test.

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[1] Note that the size and shape of the cylinders were not consistent among tests.

## 5.3 IMPROVING THE DROP RESISTANCE OF THE CYLINDER

Bonfire performance was one area of concern for ECL with regard to hydrogen cylinder safety. The other area of concern was how resistant the cylinder was to handling damage. For example, the cylinder could be dropped or mishandled when the cylinder is being transported from the manufacturing plant to the vehicle or could be dropped when being installed into a vehicle. Traditionally, with all-composite cylinders, the cylinders have been significantly weakened by dropping the cylinder on the end-dome location[2]. To address this issue, the proposed hydrogen standard requires that a cylinder undergo a 45° drop test and then subsequently be fatigue cycled without rupture failure. A method of protecting or reinforcing the dome was necessary to make the cylinder strong under any impact loading.

### *5.3.1 Methods to Increase the Impact Resistance*

Various methods of strengthening the impact resistance of the composite cylinder in the end-dome region were examined. These methods included:

- Placing a strong continuous metal reinforcement on the inside of the cylinder in the end-dome region.
- Placing strong reinforcing composite rings on the inside of the cylinder in the end-dome region.
- Placing layers of a tough composite within the carbon fibre composite matrix in the end-dome region.
- Placing a energy-absorbing material on the outside of the end-dome.

Essentially these reinforcement techniques fall into two categories:

- reinforcement to stiffen the composite matrix, and thereby not allowing the composite material to flex and crack under impact loading, and
- placing a material external to the composite which absorbs all the impact energy, rather than letting the composite material absorb this energy.

### 5.3.2 Drop Testing the Various Strengthening Mechanisms

Drop testing at 45° to the horizontal was performed, per CSA B51-95 Part II [a], on cylinders which were fabricated using the various reinforcement options listed above. Apart from the reinforcing technique, the cylinders were otherwise similar. After fabrication, each of the cylinders (unpressurized) was dropped so that the centre of gravity was 1.83 m above the ground and at 45°.

The cylinders were then cycled from 3 MPa to 31 MPa for 15,000 cycles or until the cylinder ruptured, whichever came first. Cylinders which did not rupture were considered a successful test.

### 5.3.3 The Results of the Drop Testing

*Continuous Metal Reinforcement on the Inside of the Cylinder*

The cylinders with the continuous metal reinforcement on the inside of the cylinder ruptured upon the first pressurization cycle of the cyclic loading. This cylinder did not meet the requirements of the proposed standard.

*Strong Composite Rings on the Inside of the Cylinder*

The cylinders with the composite rings on the inside of the cylinder ruptured upon the first pressurization cycle of the cyclic loading. This cylinder did not meet the requirements of the proposed standard.

*Layers Of Tough Composite Within the Carbon Fibre Composite Matrix*

The cylinders with the layers of tough composite material passed or failed, depending on the number of layers of reinforcement used. Table 5.4 summarizes the results of this testing.

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[2] Note that the cylinders traditionally have no problems with horizontal and vertical drops.

**Table 5.4:**
**Degree of Reinforcement and the Number of Cycles to Failure**

| Number of Layers | Cycles to Failure |
|---|---|
| 8 | 3,000 |
| 12 | 1[3] |
| 12 | 1,579 |
| 14 | 1,803 |
| 16 | No Failure |
| 16 | No Failure |

The cylinders with 16 layers of reinforcement were able to withstand cyclic loading up to 15,000 cycles without rupture. These cylinders also had no leakage during the cyclic loading.

### *Energy-Absorbing Material on the Outside of the End-Dome*

The final method employed the use of a energy-absorbing foam on the external surface of the composite cylinder at the end-dome location. Figure 5.2 illustrates the injected foam dome material. Foam material was injected onto both the large and small end-domes of a cylinder and the drop test was performed. This cylinder was then cycled for a minimum of 15,000 cycles without rupture failure or leakage. To further test the end-dome protection, the cylinder was dropped and cycled a second time without rupture failure or leakage.

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[3] It was assumed that the cylinder had a manufacturing defect which caused the cylinder to fail prematurely.

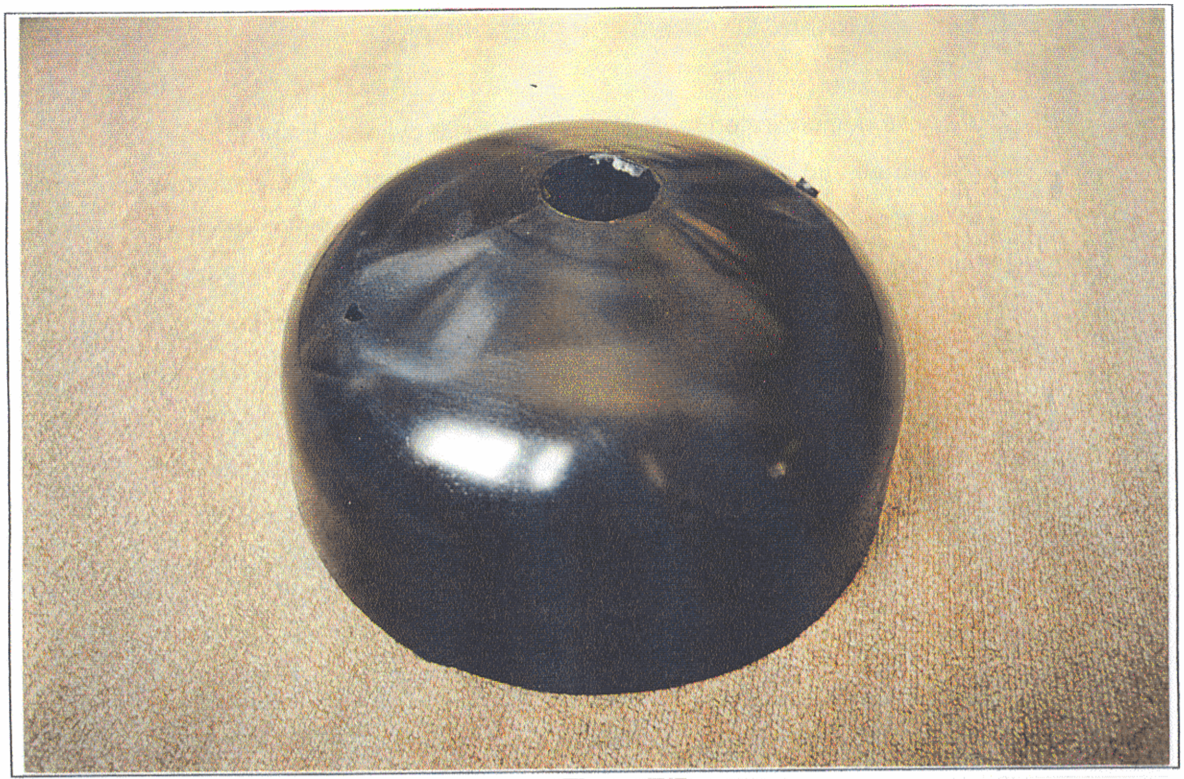


**Figure 5.2:**
**The Foam Dome Material**

The cylinder, upon visual inspection after impact, revealed no visual signs of damage except that the foam dome material, at the point of impact had lost some of its rigidity.

### *5.3.4 A Summary of the Drop Testing*

Two of the four methods attempted met the proposed drop test requirements: (1) layering tough layers of composite (16 in total) between the carbon fibre composite layers, and (2) injecting a energy-absorbing foam dome onto the external surface of the cylinder. In general, the former method was difficult to process due to the hand-lay-up requirements of the tough composite layer. Additionally, because this layer was embedded into the carbon fibre composite shell, there is still the chance of damage to the outer layer of carbon fibre composite upon impact. These two points make the injectible foam dome a desirable option. Upon impact, in this case, the foam dome absorbs most of the energy of the impact and little energy is imparted to the composite shell.

## 5.4 FOAM DOMES FOR ENHANCED FIRE/DROP PERFORMANCE

The foam dome was demonstrated to protect a composite cylinder from a 45° impact. The foam dome system served another purpose as well; to enhance the performance of the cylinder in a bonfire environment. Fire testing was performed on cylinder with foam domes in place. A flammable gas was placed in two cylinders and pressurized to 24.8 MPa. Each cylinder was then placed into a bonfire, one in the horizontal position and one in the vertical position. Both cylinders vented the contents of the cylinder safely to the environment.

In previous testing of this cylinder size without foam domes, the cylinder required the use of a copper strip to conduct heat from the fire to the PRD device. In this case, the copper strips were not required. The foam dome material, in this case, acted as a shield for the composite material and protected the cylinder from direct flame impingement, and provided a flammable source so that, if ignited, could concentrate the flame around the PRD.

Thus, both safety issues, the strength of the cylinder in the bonfire environment and provisions for increasing the impact resistance of the end-dome area are both addressed and successfully met with the injected foam dome solution.

## 5.5 CONCLUSIONS

The use of the injectable foam dome material onto the end-domes of the composite compressed hydrogen cylinder greatly improves its safety. The foam dome, because of its dual purpose of increasing the cylinders resistance to impact and increasing the cylinders strength in a bonfire, is a key addition to the hydrogen cylinder design.

### REFERENCES

[a] CSA B51-95 Part II, "*High Pressure Cylinders for the On-Board Storage of Natural Gas as a Fuel for Automotive Vehicles*", January 1995.

## 6.1 INTRODUCTION

Because of the small nature of the hydrogen molecule, a greater seal technology than the seal used in the compressed natural gas cylinders is needed to ensure a leak-free storage system. The work in this chapter concentrated on efforts necessary to create an effective seal for hydrogen gas.

The greatest potential for gas leakage in the cylinder occurs at the end of the cylinder where a large steel end boss in embedded into the liner. At this location, the geometry of the cylinder is composed of three parts: (1) the steel end-boss, (2) a steel adapter, and (3) the polymeric liner (see Figure 6.1). During manufacture of the cylinder, the liner is cast around the end-boss. During assembly of the cylinder, an adapter is screwed into the end-boss and compressed onto the liner. This compression creates a "compression-set" seal between these two materials, preventing pressurized gas within the cylinder from traveling between them. Pressurization of the cylinder further increases the degree of compression.

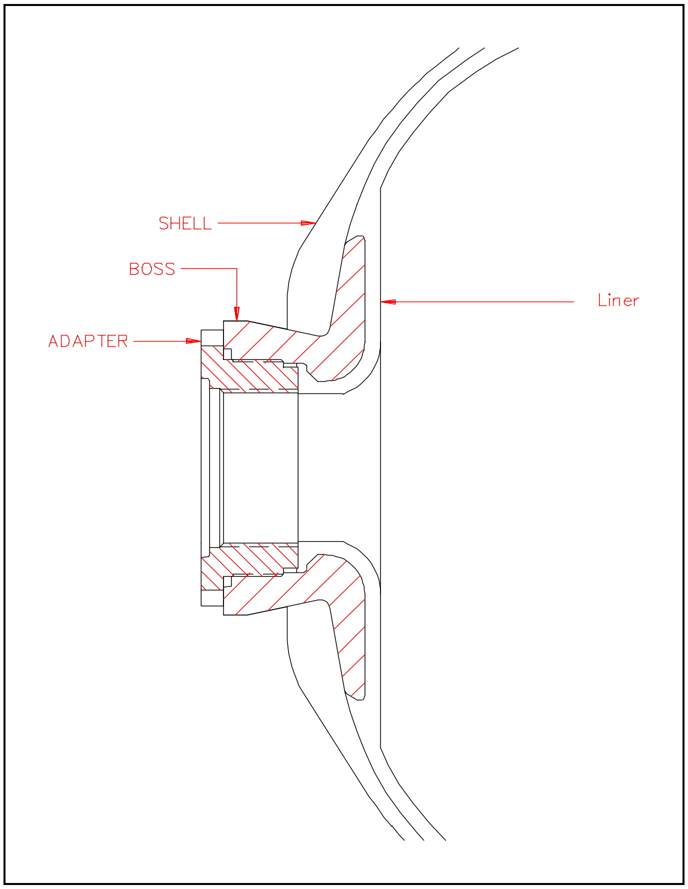


**Figure 6.1:**
**The Current Sealing Mechanism for the Compressed Natural Gas Cylinders**

In this chapter, new sealing designs were analysed using finite element analysis and tested using extreme loading conditions such as high temperature, low temperatures, and a situation where a cylinder was filled rapidly with gas.

## 6.2 FINITE ELEMENT ANALYSIS OF THE SEAL

Initially, a finite element analysis was generated to understand the mechanism of the seal between the plastic liner. From here, the finite element analysis was further expanded to include different sealing options (i.e. modifying the geometry of the adapter, modifying the geometry of the end-boss). The finite element analysis also examined the effectiveness of the seal under cold (-40°C) and warm (82°C) operating conditions.

### *6.2.1 The Finite Element Model*

Figure 6.2 illustrates one of the finite element models used to examine the sealing effectivity.

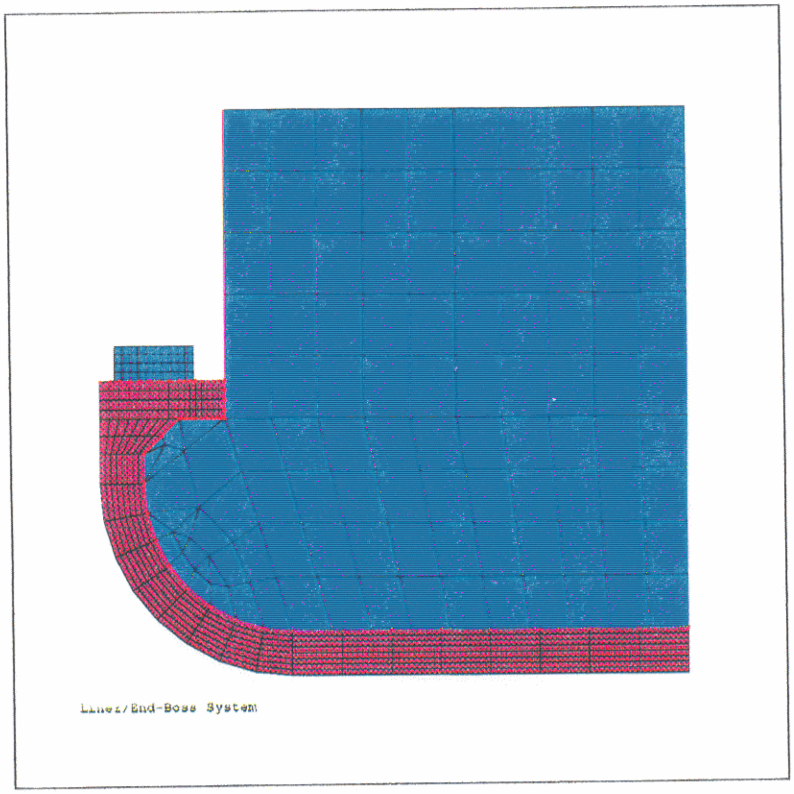


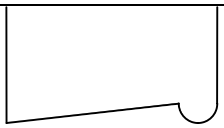
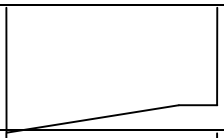
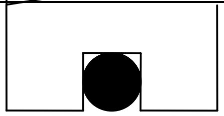
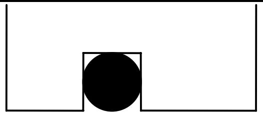
**Figure 6.2:**
**The Finite Element Model of the Cylinder Seal**

Just the portion of the cylinder around the sealing surface was modeled. The liner, adapter, and end boss were all modeled as two-dimensional axisymmetric isotropic elements. The loading on the cylinder lliner consisted of both applied internal pressure and adapter displacement onto the liner. To simulate the worst case loading condition, the liner is fully separated from both the end-boss and the adapter by gap elements.

### *6.2.2 Different Designs Modeled*

Various adapter geometries were investigated in order to understrand the sealing behaviour and to optimize the sealing quality of the end-boss/liner system. Table 6.1 illustrates, schematically, the various adapter geometries along with their prescribed displacements. The original adapter was analysed under room temperature, low temperature, and high temperature conditions. The other adapter designs were analysed under low temperature conditions.

**Table 6.1:**
**Alternative Adapter Designs**

| **Adapter Geometry** ϒ | **Revision #** | **Displacement** |
|---|---|---|
|  | Original Adapter | 0.030 cm |
|  | Revision #1 | 0.064 cm |
|  | Revision #2 | 0.094 cm |
|  * | Revision #3 | 0.089 cm |
|  * | Revision #4 | 0.089 cm |

ϒ The schematic drawing shows the cross-sectional view of the adapter base where it contacts the liner.

* symbolizes the addition of an o-ring to the adapter design. Note that the o-ring is there for illustration only. The o-ring was not modelled as part of the design.

### *6.2.3 Discussion of the Sealing Mechanism*

In general, the finite element analysis was effective at explaining the mechanism behind the seal and possible adaptations that could be made to the seal to improve its performance with any gas. The following observations were a result of the finite element analysis:

*Sealing Mechanism*

- The seal is created primarily by the clamping of the liner material between the adapter and the seat on the end-boss.
- Internal pressure increases the seal at room temperature.
- Increasing the adapter displacement onto the liner increases the seal.
- The seal in the end-boss/adapter system can be improved with the use of a larger adapter/liner contact area and possibly with the use of an o-ring.

*Low-Temperature Response*

- At lower temperatures, a reduced internal pressure and a thermal contraction of the liner material causes the material to displace away from the adapter. This reduces the quality of the seal.

*High-Temperature Response*

- At high temperatures, the liner material will undergo a stress relaxation. This relaxation will not degrade the quality of the seal at high temperatures.

## 6.3 INITIAL TESTING WITH CYLINDERS

### *6.3.1 Seal Options Tested*

A finite element analysis does not provide enough information for the design of a hydrogen seal. The finite element analysis must be backed up with experimental testing. Using the results of the finite element analysis, three seal designs were selected, with the following rationale in mind:

There are two potential mechanisms being investigated for sealing: (1) the compression of the liner material between the adapter and the steel end-boss as explained with the finite element analysis, and (2) the addition of an o-ring to the sealing surfaces. The first mechanism has advantages because it is simple. However, with hydrogen gas, the seal created by this compression set may not be enough to hold the small hydrogen molecules. The second mechanism, the o-ring seal, is good because it does not require the same degree of sealing surface quality as the compression set seal. However, there may be problems with o-ring extrusion, improperly seated o-rings, and contamination of the o-ring which all affect its performance. With the following tests, each of the seals incorporated one or both of these mechanisms into the design.

Figure 6.3. 6.4, and 6.5 illustrate the cross-sections of each design tested:

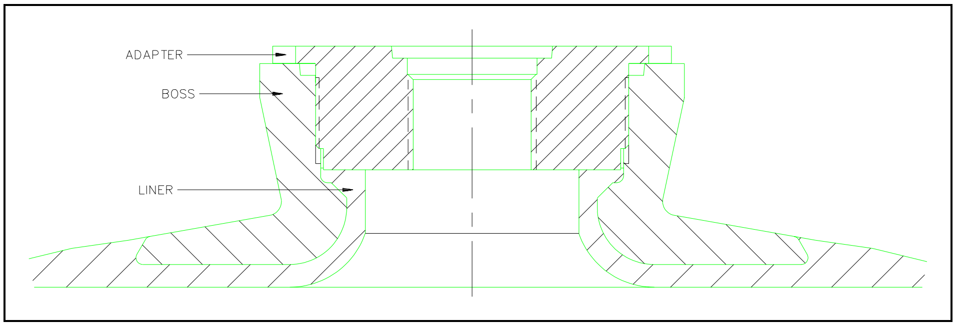


**Figure 6.3:**
**The Flat Seal**

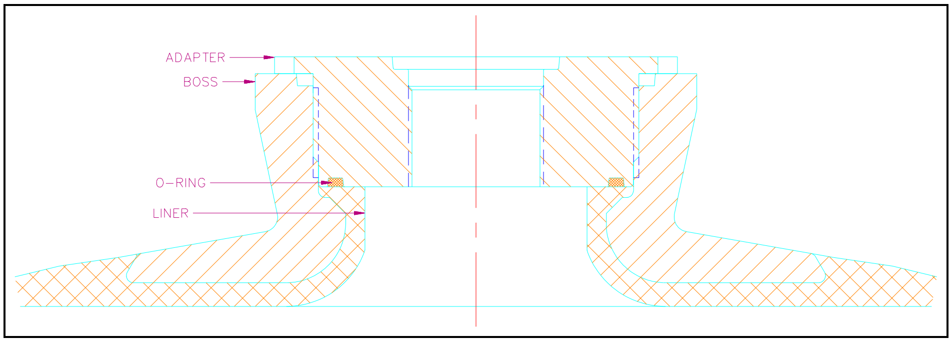


**Figure 6.4:**
**The O-Ring Seal**

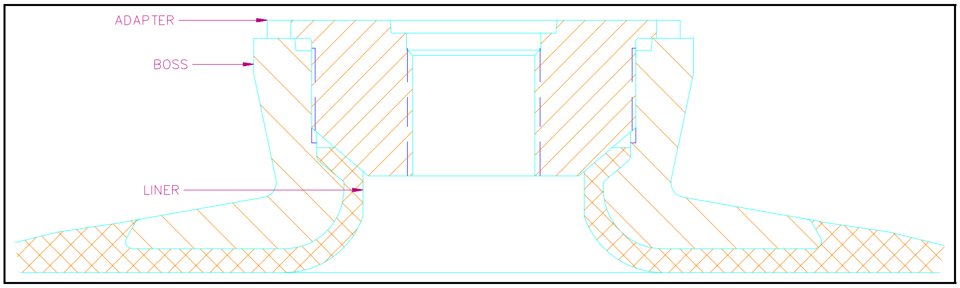


**Figure 6.5:**
**The Conical Seal**

### *6.3.2 Cold Temperature Testing*

A cold temperature environment was the first harsh environment for the seal testing. In general, under cold test conditions, both the steel and the liner material may contract causing the "compression" seal to be compromised. In this test, cylinders with the above mentioned seal designs were pressurized with helium gas and then cooled to determine if the seal would leak. Helium gas was used instead of hydrogen gas because testing with helium is safer than testing with hydrogen gas. Note that the helium molecule is the element most similar in size to hydrogen.

The test procedure was:

- Assemble the cylinder seal by threading the adapter into the boss and compressing the boss onto the liner for a measured amount of compression. A valve (for filling the tank with gas) with a pressure gauge (for monitoring pressure) was then fitted into the adapter.
- Pressurize the cylinder with a helium gas.
- Place the cylinder into a cooling chamber and monitor the pressure as a function of temperature.

Table 6.2 summarizes the seal type used in each test, the amount of compression on the liner, the pressure of helium gas put into the cylinder, and the temperature at which the cylinder seal leaked. Note that -40°C was selected as a pass/fail temperature because it is the proposed temperature at which the the materials are to be designed to (see Chapter #1).

**Table 6.2:**
**Results of the Cold Temperature Test**

| Seal Type | Compression | Pressure | Temperature |
|---|---|---|---|
| Conical | 0.137 cm | 25.5 MPa | > -40°C |
| Conical | 0.168 cm | 27.2 MPa | > -40°C |
| O-Ring | 0.099 cm | 27.2 MPa | < -40°C |
| O-Ring | 0.099 cm | 21.4 MPa | < -40°C |
| O-Ring Groove[1] | 0.076 cm | 22.2 MPa | < -40°C |
| Flat | 0.076 cm | 26.8 MPa | > -40°C |

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[1] The o-ring design without the o-ring

In general, both the o-ring design and the o-ring groove design were able to hold helium gas down to -40°C and lower.

### *6.3.3 Creep Followed by a Fast Fill*

Another predicted harsh environment for the cylinder seal was to assemble the cylinder, expose it to an elevated temperature, and then follow this with a fast-filling of the cylinder with gas. Because the liner material is a polymeric material, the liner material may creep (or relax) over a period of time after being assembled and this may compromise the cylinder seal. During a fast filling of the cylinder with gas, extreme temperatures get introduced at the cylinder throat, near the cylinder seal, and this may further compromise the seal. The following test was used to simulate these loading conditions:

- Assemble the cylinder seal by threading the adapter into the boss and compressing the boss onto the liner for a measured amount of compression. A valve (for filling the tank with gas) was then fitted into the adapter.
- The cylinders were then placed into an oven at 82°C for a total of 200 hours.
- The cylinders were then taken to a compressor station and filled with natural gas[2].

Table 6.3 summarizes the results of the creep/fast-fill testing:

**Table 6.3**
**Creep/Fast Fill Test Results**

| Seal Type | Compression | Oven Temp | Creep Time | Max Pressure Achieved | Result |
|---|---|---|---|---|---|
| Conical | 0.137 cm | 82°C | 200 hours | 6.21 MPa | Leakage |
| O-Ring | 0.074 cm | 82°C | 200 hours | 23.1 MPa | No Leakage<br>(Fill Time: 1:26) |
| Flat | 0.168 cm | 82°C | 200 hours | 18.6 MPa | Leakage |

## 6.4 TESTING THE CYLINDER SEAL WITH THE TEST POTS

Testing the seal of the cylinder on cylinders was costly and time-consuming. To simplify the process, test pots were created to continue testing the alternative sealing systems.

---

[2] Note that the compressor station was capable of filling an 80 L cylinder up to 20.7 MPa in approximately 5 minutes.

### *6.4.1 The Test Pot*

The test pots were machined from steel and designed so that the sealing area in the test pot was geometrically similar to the sealing area in the large end boss of a cylinder. Figure 6.6 illustrates the geometry of one of the test pots without the liner material in place

After their fabrication, the test pots were finished in the following manner:

- The cylinders were rotomolded with the same liner material as used in the "all-composite" cylinder. Figure 6.7 is a photograph of one of the test pots that was used for testing with the liner material rotomoulded in place.
- The liners in the test pots were then spotfaced (machined) to the required depth.
- The test pots were assembled with an adapter which is threaded into the top of the test pot. It is this compressing of the adapter material onto the liner material that forms the primary seal in the system.
- After assembling the adapters, each test pot was fitted with a manual valve (used to fill and vent the test pot) and a pressure transducer (used to monitor the pressure in the test pot).

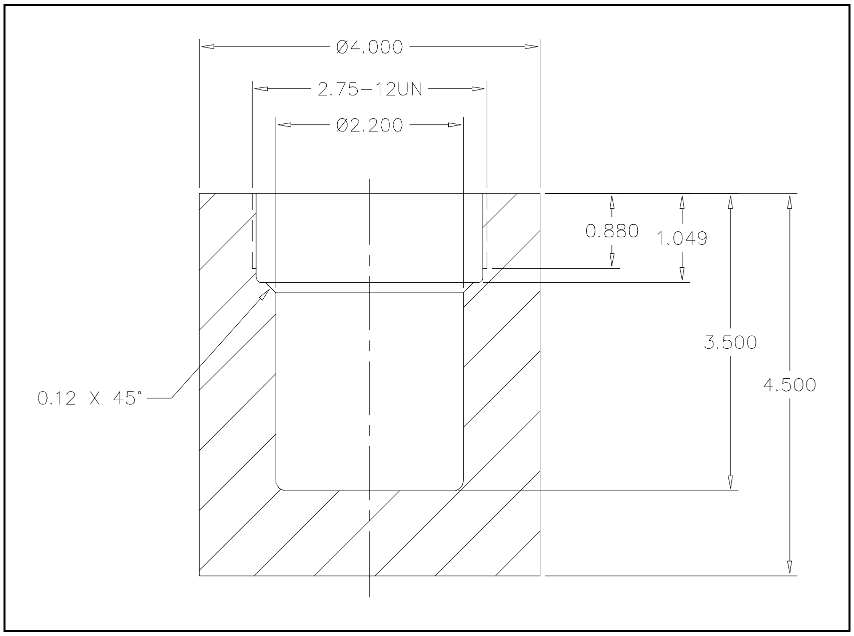

**Figure 6.6:**
**The Geometry of the Test Pot**[3]

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[3] Note that all dimensions are in inches.

**Figure 6.7:**
**The Rotomoulded Test Pot**

### *6.4.2 A Description of the Test*

To test the seal under some of the worst case senarios, the following test was devised:

1. In service, the liner material is compressed by the adapter several years, the liner material in the cylinder may creep. After the test pots had been assembled, the test pot was then placed in a hot environment for a minimum of 108 hours at a minimum of 82°C; the purpose being to accelerate creeping action in the liner and to simulate the long-term loading on the liner.

2. The test pots were then pressurized with a 50% helium/50% air mixture to approximately 17.9 MPa. This He/air mixture was used instead of hydrogen gas because testing with helium is safer than testing with hydrogen gas. Note that the helium molecule is the element most similar in size to hydrogen.

3. The pressurized test pot was then placed into a cooling chamber and cooled until the seal failed or until the limit of the cooling chamber was reached (approximately -115°C).

### *6.4.3 The Seal Systems Tested*

There were several sealing systems tested using the test pots. In general the sealing systems tested can fall within one or more of the catagories listed in Table 6.4:

**Table 6.4:**
**The Sealing Mechanisms**

| Sealing System | Seal Philosophy |
|---|---|
| Liner Compression | Liner compression is the primary sealing mechanism in the cylinder. This seal is formed by having the adapter compress down on the polymeric liner material. With sufficient compression, gas in not permitted to escape between the adapter and liner interface. |
| Sealant on the Liner Face | Sealant placed between the adapter and the liner face prior to compression will provide a better seal to prevent gas from escaping, and allow for less friction between the adapter and the liner material. This will allow for larger compression loading. |
| O-ring Seal | The o-ring seal acts as a secondary seal to the primary liner compression seal meantioned above. |
| O-Ring Groove without O-Ring | The geometry of the adapter sealing face will have an effect on the seal. This adapter geometry had performed well with the previous testing (section 6.2). |
| Tube | The tube is inserted into the throat of the liner prior to adapter compression. A tube placed in this location will prevent the liner material from migrating inwards during compression. This will increase the compressive force placed on the polymeric liner material. |

The following Table 6.5 is a matrix which lists the variety of seals tested and which of the above sealing mechanisms that they employed:

**Table 6.5:**
**The Test Scenarios**

| # | Liner Compression | Sealant | O-Ring Seal | O-Rg Groove w/o O-ring | Tube |
|---|---|---|---|---|---|
| P1 | X | | | | |
| P2 | X | | | X | X |
| P3 | X | X | | X | |
| P4 | X | X | | | X |
| P5 | X | | X | | |
| P6 | X | | X | | X |
| P7 | X | | X | | X |
| P8 | X | | | X | |
| P9 | X | | | X | |
| P10 | X | | X | | |
| P11 | X | | X | | |

### *6.4.4 The Results of the Test*

Test #1: Initial Testing of the Different Sealing Mechanisms

Testing units P1 to P5 were tested initially to determine the relative effects of each of the above sealing mechanisms.

Each of the adapters in the test is assembled so that there was a total of 0.076 cm compression onto the liner surface. In this case, the accelerated creep conditioning was not performed. The test pots were then pressurized with the He/Air mixture to 17.9 MPa then cooled in the cooling chamber. Leakages were noted in test pots P1-P4. Test pot P5 (with the o-ring) was cooled to below -80°C and the test pot did not leak. The following lists the temperatures at which the test pots P1-P4 leaked:

P1= 0°C
P2= -40°C
P3= -22°C
P4= -40°C

From this test, it is noted that (assuming that no effect is detrimental to the seal performance), the two sealing mechanisms that had the most positive effect on seal performance were the o-ring (P5) and the tube (P2 and P4).

### Test #2: Testing Seals which Employ an O-Ring and a Tube

Test Pots P6 to P7 were tested next. Both of these test pots had o-rings and tubes as part of their design.

Each of the adapters in the test were assembled so that there was a total of 0.076 cm compression onto the liner surface. After the accelerated creeping of the liner was performed, the test pots were pressurized to 17.9 MPa using the He/Air mixture. The test pots were then cooled down to determine the leak temperature which were noted as follows:

P6= -105°C
P7= -125°C

The seal with the o-ring and the tube obviously is a rugged seal design, capable of withstanding extremely cool temperatures.

### Test #3: The Effect of Compression on the Seal (O-ring with Tube)

Three test pots with both an o-ring and a tube were tested again to determine the compression needed to maintain a seal. The test pots were fitted with adapters that were compressed to 0.025 cm, 0.051 cm ,and 0.076 cm compression and pressurized with the He/air mixture to 17.9 MPa. The test pots were then cooled down to determine the leak temperature. The following were the leak temperatures for the test pots:

P7= -70°C (.025 cm compression)
P7= <-110°C (.051 cm compression)
P7= <-110°C (.076 cm compression)

### Test #4: Testing With the O-Ring Without the Tube

The effect of the o-ring without the tube needed some futher study because in Test #1, the assemblies were not creep tested initially.

Each adapter was compressed approximately 0.051 cm onto the liner. This assembly was followed by a high temperature creep test and then the pressurized with the He/Air mixture to 17.9 MPa. The test pots were then cooled down to determine the leak temperature.

The following was the leak temperature for the seal systems:

P8= -40°C
P9= -40°C
P10= -48°C
P11= -55°C

### *6.4.5 Conclusions from the Test Pots*

From the series of tests performed with the test pots, the following can be concluded:

- The o-ring seal and tube with 0.076 cm compression is the combination of sealing mechanisms that will give the best seal under low temperature conditions.
- The o-rings without the tube had marginal performance at .051 cm initial compression, but was more than adequate with 0.076 cm compression.

## 6.5 CONCLUSIONS

From this analysis, it was concluded that a seal design employing the use of an o-ring was adequate to maintain the cylinder pressure under the most severe loading conditions.

## 7.1 INTRODUCTION

In the previous chapters, a new hydrogen cylinder standard is proposed, rationale for the standard is presented, many design issues are discussed, test results are presented, and design recommendations or conclusions are established. This chapter describes the design of a cylinder which incorporates all information presented and outlines the results of full scale testing of cylinders built to the design.

## 7.2 THE PROTOTYPE DESIGN FOR HYDROGEN STORAGE

Figure 7.1 illustrates the prototype hydrogen cylinder design.

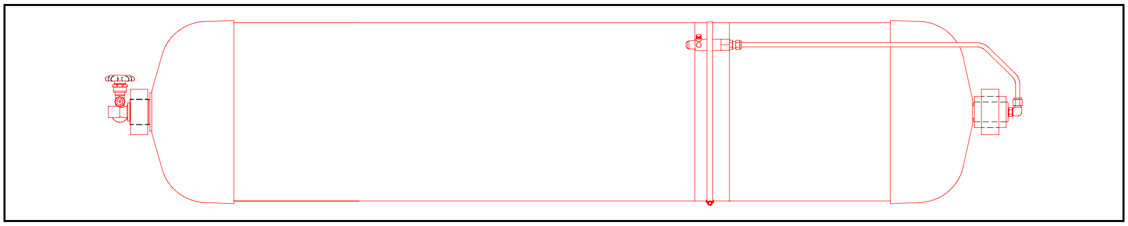

**Figure 7.1:**
**The Hydrogen Cylinder**

The figure represents the following cylinder components:

- the composite shell which is over top of a liner,
- the protective foam dome end caps,
- the encapsulated end-bosses, the end-plug and the adapter,
- a manual valve, and
- two pressure relief devices, one at each end of the cylinder.

## 7.3 COMPONENTS OF THE COMPRESSED HYDROGEN STORAGE CONTAINER

In handling hydrogen gas, all the general rules for compressed gas cylinders apply, but extra precautions are necessary in the handling of hydrogen gas. Storing hydrogen requires special details in the design. The following points detail these requirements and rationalize the prototype design in terms of these requirements.

- Chapter 3 outlined testing performed with various fibre types: carbon-fibre, Kevlar-fibre, and glass fibre. In summary, it was outlined that the development of a hybrid cylinder for the storage of compressed natural gas may be the most economical of the options provided. This cylinder incorporates a glass/carbon hybrid shell in its design.

- The composite material is not capable of acting as a barrier to hydrogen gas. Thus, a liner material is added to the design to act as a barrier for gas leakage. Testing of the liner material was conducted in Chapter 4.
- The adapter and end-plug in this cylinder design are metallic and are exposed to the hydrogen gas. Chapter 4 reviewed the material requirements for the metal in contact with high pressure hydrogen gas. This material has be integrated as part of the hydrogen cylinder design.

- Initially, the all-composite cylinder needs a sealing surface at the valve end of the cylinder that performs well with hydrogen. Because the hydrogen molecule is so small, it is difficult to contain hydrogen gas at high pressures without small degrees of leakage. Chapter 6 discussed optimization of the sealing system so that it could contain hydrogen. This seal design is incorporated into the prototype cylinder design.

- With an all-composite cylinder, the end-domes are particularly susceptible to impact damage on the domes. Protected the cylinder domes in the case of an accidental drop was discussed in Chapter 5. This prototype cylinder incorporates the foam dome end caps as a safety feature.

- Almost all compressed gas containers are fitted with pressure relief devices (PRDs). A pressure relief device is a pressure- and/or temperature-activated device used to vent a normally charged cylinder safely in the event of a fire. Due to the nature of an all-composite cylinder, the PRD needs to be thermally-activated. When the all-composite shell is exposed to a fire environment, the cylindrical shell gets degraded significantly before the pressure in the cylinder could rise high enough to burst a rupture disk. Due to the nature of hydrogen, the PRD needs also to contain the hydrogen gas without leakage Chapter 7 discussed the PRD selection with hydrogen and rationalizes the choice of PRD in this section.

## 7.4 THE DETAILS OF THE PROTOTYPE DESIGN

The prototype cylinder has the following specifications:

**Table 7.1:**
**Cylinder Specifications**

| Dimension | Value (Metric) | Value (Imperial) |
|---|---|---|
| Cylinder Length | 1.803 m ± 0.003 m | 71.0 in ± 0.1 in |
| Cylinder Diameter | 0.403 m ± 0.006 m | 15.85 in ± 0.25 in |
| Cylinder Weight | 48.5 kg ± 2.3 kg | 107 lb ± 5 lb |
| Cylinder Water Volume | 180 L ± 3 L | 6.36 $ft^3$ ± 0.11 $ft^3$ |
| Cylinder Service Pressure | 24.8 MPa | 3,600 psi |
| Cylinder Service Life | 15 years | 15 years |
| Cylinder Capacity @ Service Pressure[1] | 37,600 L | 1328 $ft^3$ |

## 7.5 DESIGN QUALIFICATION TESTING

Table 7.2 summarizes the design qualification testing required for the hydrogen cylinder:

**Table 7.2:**
**Design Qualification Tests**

| DESIGN QUALIFICATION TEST |
|---|
| Pressure Cycling, Ambient Temp |
| Pressure Cycling, Extreme Temp |
| Hydrostatic Burst Test |
| Bonfire Test |
| Flaw Tolerance Test |
| Drop Test |
| Penetration Test |
| High Temperature Creep |
| Permeation Test |
| Accelerated Stress Rupture Test |
| Environmental Test |
| Gas Cycling Test[2] |
| Boss Torque Testing |
| Embrittlement Test |
| PRD Test at Elevated Temperature |

Of these tests, the hydrostatic burst test, the drop test, the penetration test, the high temperature creep test, and the bonfire test were tested on the new cylinder design and are discussed below. Of these tests, the permeation test, the embrittlement test (of the liner material), and the PRD test were described in previous chapters of this report. Table 7.3 provides a rationale as to how the remaining cylinder test requirements have been met.

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[1] Note that this neglects the additional capacity due to cylinder expansion.
[2] Note that ECL was not capable of performing this test with hydrogen.

**Table 7.3:**
**Testing Rationale**

| TEST | RATIONALE FOR APPROVAL |
|---|---|
| Pressure Cycling, Ambient Temp | With all-composite cylinders, failure in a cycling test typically occurs, if it is going to happen at all, in the first 10 cycles. The cylinder in the drop test was cycled for 15,000 cycles without failure. It can be assumed safely that the cylinder would not fail in 45,000 cycles. |
| Pressure Cycling, Extreme Temp | The hybrid cylinder was designed so that the carbon fibre alone would take all of the required load for an acceptable burst strength. With the “all-carbon” cylinders, the extreme temperature cycling was not detrimental to the cylinders’ performance. It is assumed that the hybrid cylinder will have the same results. |
| Flaw Tolerance Test | The fibres effected by the flaw are the carbon fibres wound in the hoop direction. From previous experience, the flaw only causes the cut fibres to delaminate around the flaw. This has minimum bearing on the burst strength of the cylinder. |
| Accelerated Stress Rupture Test | The stress rupture test and the high temperature creep test are similar in nature. The high temperature creep test was chosen because it was considered the more severe of the tests. Therefore, it is assumed that if the cylinder can pass high temperature creep, it can pass stress rupture. |
| Environmental Test | Internally, the liner material is the same liner material used in the current LiteRider design. Externally, the carbon fibre/resin material is the same material used in the current LiteRider design. These facts, coupled with the fact that the glass fibre is not relied on for burst performance, dictates that the current hybrid design would pass the environmental test. |
| Gas Cycling Test[3] | ECL does not have the capacity to test the cylinder as per this test requirement. |
| Boss Torque Testing | The boss torque test is a function of the adhesive bond between the liner and the boss. Because this test is performed on ECL’s natural gas cylinders which have the same liner/boss configuration, it is assumed that this will apply to the hydrogen cylinder as well. |

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[3] Note that ECL was not capable of performing this test with hydrogen.

### 7.5.1 Hydrostatic Burst Test

Multiple cylinders were hydrostatically burst prior to finalizing the cylinder design. The following procedure was used with each cylinder:

- The cylinder was filled with water at ambient temperature.
- The cylinder was pressurized until a pressure of 20.7 MPa was reached. At this point, the pressure system was monitored for leakage.
- If the cylinder was capable, the cylinder was pressurized further until a pressure of 60.0 MPa was achieved; at this time, the pressure was held for 10 seconds.
- The cylinder was pressurized further until rupture.
- The ruptured cylinder was inspected for failure location.

Of the final prototype design, two cylinders were burst. Table 7.4 summarizes the results.

**Table 7.4:**
**Cylinder Burst Pressures**

| Cylinder | Burst Pressure |
|---|---|
| Cylinder A | 59.3 MPa |
| Cylinder B | 60.0 MPa |

The prototype cylinder was designed to operate at a service pressure of 24.8. With a 2.25 stress ratio requirement for the carbon fibres, this corresponds to a design burst pressure of 55.9 Mpa. With a 2.35 stress ratio requirement for the glass fibres, this corresponds to a 58.4 MPa design burst pressure. This cylinder design has met both of these design burst requirements.

### 7.5.2 Drop Test

One cylinder was drop tested. The following procedure was employed:

- Foam domes were injected onto both end-domes of the cylinder.
- The cylinder was then dropped horizontally such that the bottom of the cylinder was at a height of 1.83 m from a concrete floor. The cylinder was not restrained from secondary impact.

- The cylinder was then dropped twice vertically, once on each end, from a height such that the potential energy was 488 J. The cylinder was not restrained from secondary impact.

The cylinder was then dropped at a 45° onto a dome from a height such that the centre of gravity was 1.83 m from the concrete floor. The cylinder was not restrained from secondary impact. Figure 7.2 illustrates the 45° drop test set-up.

**Figure 7.2:**
**The 45° Drop Test**

- The cylinder was filled with oil and fatigue cycled from a maximum of 1.9 MPa to a minimum of 31.8 MPa for 11,307 cycles and an additional 3,697 cycles from a maximum of 0.9 MPa to a minimum of 25.2 Mpa. The cycling rate was 4 cycles per minute.
- The cylinder was then hydrostatically burst per the procedure outlined in section 7.5.1.

The results of the drop testing were as follows:

- The cylinder was cycled without leakage or rupture.

### 7.5.3 Penetration Testing

The following penetration test procedure was used to test the hydrogen cylinder:

- A cylinder was pressurized with compressed air to 24.8 MPa pressure.
- The cylinder was then mounted in its brackets and secured to a palette. Figure 7.3 illustrates the cylinder set-up.

**Figure 7.3:**
**The Cylinder Set-up for the Penetration Test**

- Lee Enfield Rifle (303 British Caliber) gun with full metal jacketed 180 grain bullets was used to fire the cylinder. Figure 7.4 illustrates the gun set-up.

**Figure 7.4:**
**The Rifle Set-up for the Penetration Test**

- The cylinder was shot in the cylindrical section at approximately 45° to the to the cylinder sidewall.

The following results were observed:

- The bullet entered the cylinder sidewall cleanly and lodged itself into the liner on the opposite side of the cylinder interior surface. Figure 7.5 illustrates the entry location of the bullet hole.
- The cylinder vented safely, without rupture.

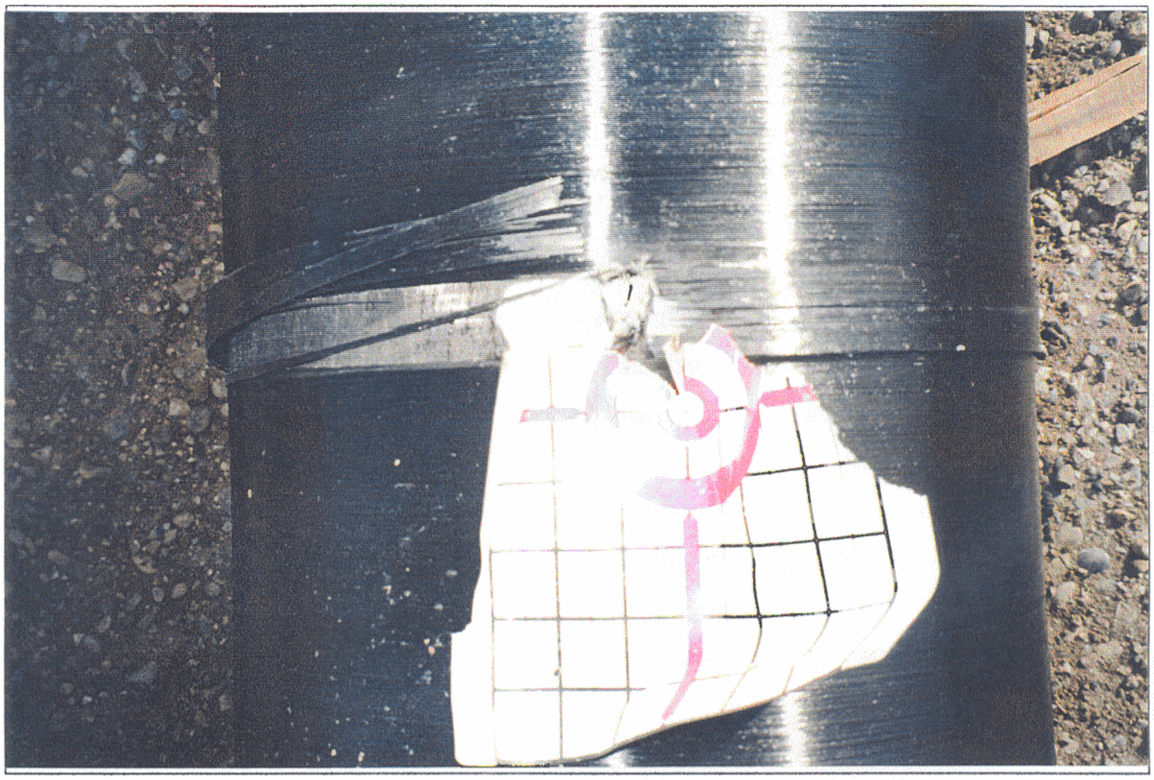

**Figure 7.5:**
**The Bullet Hole**

### 7.5.4 The High Temperature Creep Test

One cylinder was tested. The following procedure was used.

- The cylinder was filled with water.
- The cylinder was placed into an insulated bath which was filled with a water/ethylene glycol mixture.
- The bath was heated using two immersion heaters. The control point was 100°C.
- The bath temperature rose to a temperature of 81.5 °C ± 1.5°C.
- The pressure was increased to 31.0 MPa.
- The cylinder was placed in this condition for 200 hours. The bath temperature and the cylinder pressure were monitored for the entire duration of the test.

The cylinder did not rupture.

### 7.5.5 Bonfire Test

One cylinder was bonfire tested. The following procedure was employed:

- The cylinder was pressurized with hydrogen gas to a pressure of 24.2 Mpa at the environmental temperature which corresponded to 24.8 MPa at 21°C.
- A 165 cm long pan was filled with diesel/gasoline fuel mixture.
- The cylinder was placed horizontally and approximately 10 cm above rhe fire source. The cylinder was placed so that the centre of the fire source was placed midway between the two pressure relief devices.
- Three thermocouples were mounted on the bottom of the cylinder. Metallic shielding was used to prevent direct flame impingement on the thermocouples.
- A pressure transducer was used to monitor pressure in the cylinder during the duration of the test.
- Metallic shielding was used to protect the PRDs from direct flame impingement.
- The fire was ignited using a length of fuse cord.

Figures 7.6 and 7.7 show the set-up of the hybrid cylinder. Figure 7.8 shows the hydrogen cylinder in a bonfire environment. Figure 7.9 shows the pressure and temperature relationship of the cylinder with time. Figures 7.10 and 7.11 show the cylinder after the bonfire was extinguished.

**Figure 7.6:**
**The Hydrogen Hybrid Cylinder Bonfire Set-up**

**Figure 7.7:**
**The Hydrogen Hybrid Cylinder Bonfire Set-up**

**Figure 7.8:**
**The Hydrogen/Hybrid Cylinder in a Bonfire Environment**

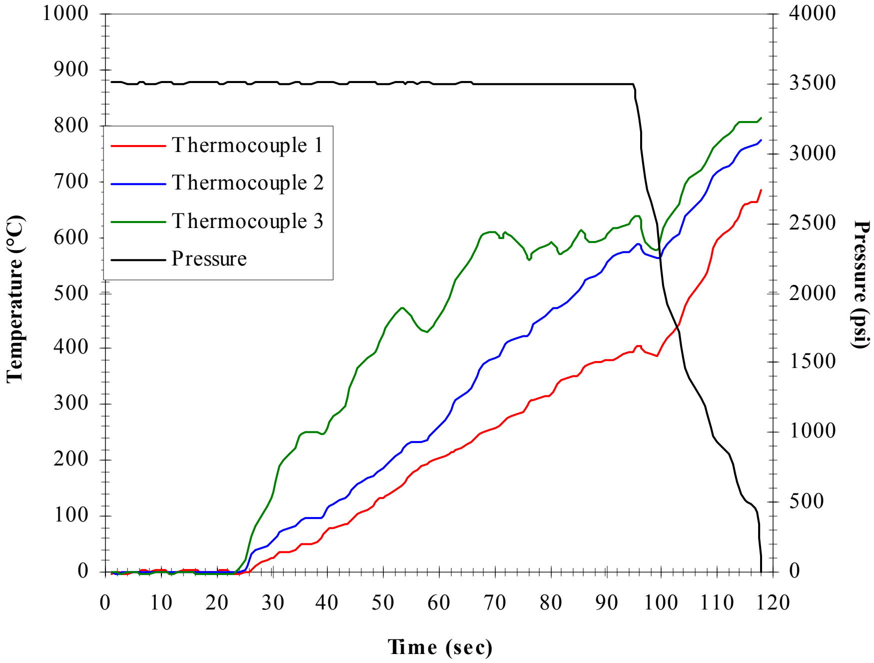

**Figure 7.9:**
**The Pressure/Temperature Responses of the Cylinder**

**Figure 7.10:**
**The Burnt Cylinder**

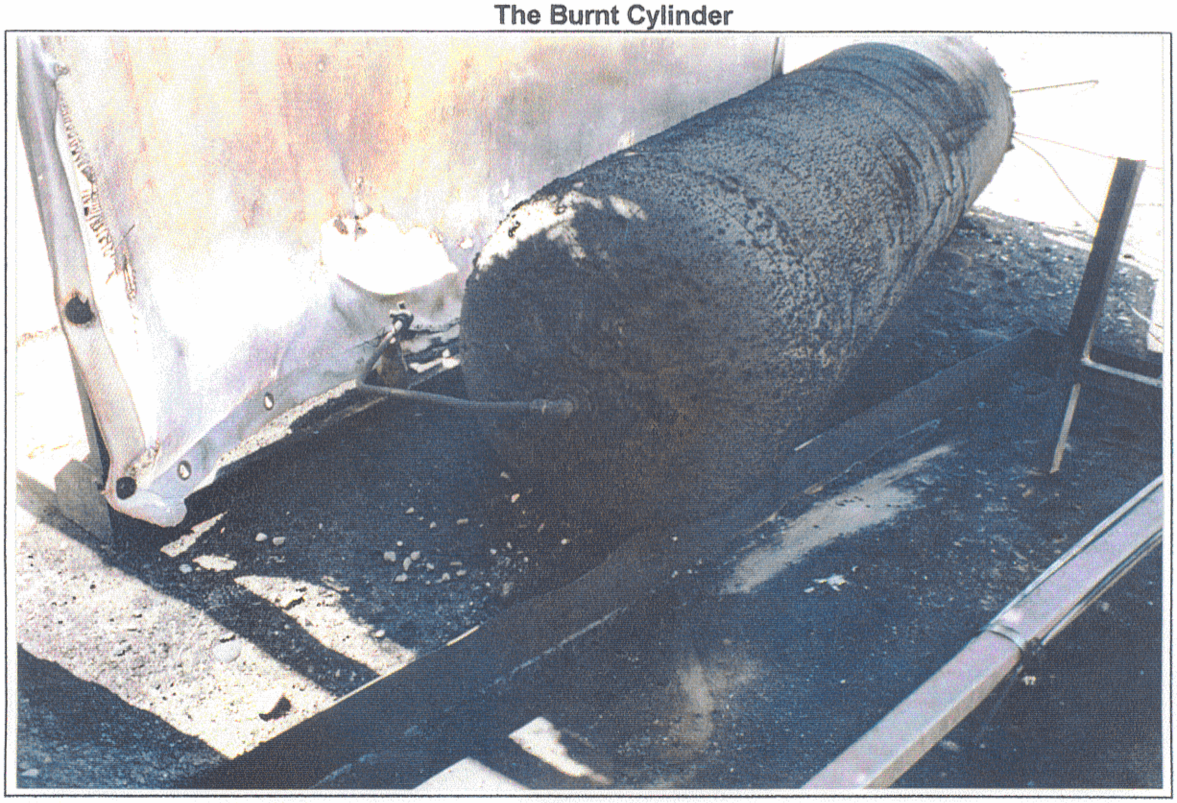

**Figure 7.11:**
**The Burnt Cylinder**

The results of the bonfire test were as follows

- The first PRD released after 74 seconds.
- The cylinder vented in 67 seconds.
- The cylinder did not rupture but vented its contents safely to the environment.

## 7.6 CONCLUSIONS

The tests conducted on the cylinders designed to incorporate all the features discussed throughout this report were carried out successfully. Final verification of the applicability of the standard, and of cylinders designed and tested to the standard, for hydrogen use, can only be accomplished through long term field trials. However, the successful testing of the cylinders goes a long way toward establishing credibility of the proposed standard and of the design issues raised throughout this report.

# APPENDIX A:
# A PROPOSED HYDROGEN CYLINDER STANDARD

## A.1 INTRODUCTION

This standard is for high pressure cylinders for permanent on-board storage of hydrogen gas as a fuel for automotive vehicles.

## A.2 SCOPE

This standard sets out the unique requirements for light weight refillable gas cylinders having a water capacity of not more than 1000 L intended only for the on-board storage of high pressure hydrogen gas as a fuel for automotive vehicles to which the cylinders are to be fixed.

This standard covers the use of cylinders with non-metallic liners with composite fibre overwrapping (all-composite cylinders).

## A.3 SERVICE CONDITIONS

The following service conditions form the basis of design validation tests for the cylinders intended for storing gaseous hydrogen on-board vehicles. Thus, cylinders fabricated and tested according to this standard shall only be used under conditions not exceeding the limitations prescribed in this section.

### A.3.1 Service Life

The service life for which containers are safe shall be 20 years.

### A.3.2 Service Pressure Guidelines

The cylinder may be filled to a pressure not exceeding any of the following:

Pressure Design Option #1

- a pressure that would settle to 248 bar (24.8 MPa) at a settled temperature of 21°C;
- a settled pressure of 310 bar (31 MPa) at 57°C. Note that this pressure is 125% of the maximum rated service pressure at ambient temperature and is imposed to limit the maximum pressure that the cylinder will see.

- a maximum pressure of 310 bar (31 MPa), immediately after filling, regardless of temperature. This statement is imposed because this is the loading condition during the service life of the cylinder where the gas temperature will be the highest.

Pressure Design Option #2:

Other pressures may be used provided that the pressure limits, as prescribed by “Pressure Design Option #1” are factored accordingly.

### A.3.3 Maximum Number of Filling Cycles

Cylinders may be filled a total number of 15,000 times.

### A.3.4 Service Temperature

Settled temperature of gas in cylinders may vary from a low of -40°C to a high of 57°C.

The temperature of container materials may vary from a low of -40°C to a high of 82°C. Temperatures of the container materials over 57°C shall be sufficiently local, or short enough duration, that the temperature of gas in the cylinder never exceeds 57°C.

Developed temperatures during filling and discharge will be predetermined by the manufacturer so that the maximum or minimum gas temperature may not vary beyond the material limits listed above.[1]

The developed temperatures during the filling and discharge cannot degrade the strength or leak-integrity of the cylinder. The maximum allowable filling temperature during a fast-fill situation is based on the environmental temperature, input gas temperature, mass flow rate of the fill, and thermal conductivity of the cylinder walls. The cylinder manufacturer must take this into account when designing the cylinder. This peak temperature has to be limited so that it does not reduce the quality of the cylinder.

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[1] Note that the fill rate of the gas into the cylinder is fixed and thus the developed temperatures depend on the cylinder’s materials and geometry.

### A.3.5 Gas Composition and General Corrosion

Grades of hydrogen gas range from 99.8 to 99.9997 percent $H_2$ (mole/mole) with various trace elements [a]. This subject of gas quality is important in the design of fuel cylinders primarily because the moisture content in the gas (and, thus, the oxygen content, as well) may accelerate the corrosion of the cylinders. This condition must be recognized in the design of the cylinder. No component of the cylinder shall be subject to general corrosion due to the presence of liquid water in the hydrogen fuel within the design service life of the cylinder.

Cylinders made to this standard are intended to be used with hydrogen gas that meets or exceeds the following composition:

- hydrogen shall be 99.95% pure;
- water $\leq$ 32.0 PPM at dew point -60°C atm;
- oxygen $\leq$ 10 PPM;
- nitrogen $\leq$ 400 PPM;
- hydrocarbons $\leq$ 10 PPM;
- carbon dioxide $\leq$ 10 PPM;
- carbon monoxide $\leq$ 10 PPM;

### A.3.6 Hydrogen Permeation

The allowable permeation rate for hydrogen gas through the cylinder shall be 0.25 cc/hr/L

### A.3.7 Hydrogen Leakage

Because of hydrogen’s small molecular size, insurance must be made so that the hydrogen will have no measurable leakage through the cylinder seal.

### A.3.8 Hydrogen Embrittlement

In the all-composite cylinders, the stored high pressure hydrogen gas comes in contact with both the liner material and the metal end-bosses. The material selection for the cylinder design must ensure the following:

- The performance of the liner material under service conditions must not be degraded due to the presence of hydrogen fuel.
- Under high temperature and pressure, the exposure of the hydrogen fuel to the steel end-bosses may create hydrogen embrittlement. The metal end-boss material has to be selected so that it would be ensured that hydrogen embrittlement will not occur to the end-boss connections during the cylinder's design life to a degree that would compromise the strength of the cylinder.

### A.3.9 Electric Charge Accumulation

If impurities or suspended particles are present in the fuel, a potential exists for and electrical charge to build-up in the liner during filling and high rate discharges. Since the thermoplastic liner material may be insulative, charge dissipation needs to happen through surface migration. If the charge exceeds the dielectric strength of the plastic material, corona discharges may occur, causing "pin-holing" in the liner and creation of leak paths. Cylinders should be fabricated such that the cylinder liner is resistant to "pin-holing" from the electric charge accumulation that the cylinder is susceptible to during operation.

## A.4 DESIGN

The all-composite cylinders are comprised of 4 components: (1) the composite shell, (2) the liner, (3) the end-bosses, and (4) the valve and pressure relief assembly (see Figure A.1).

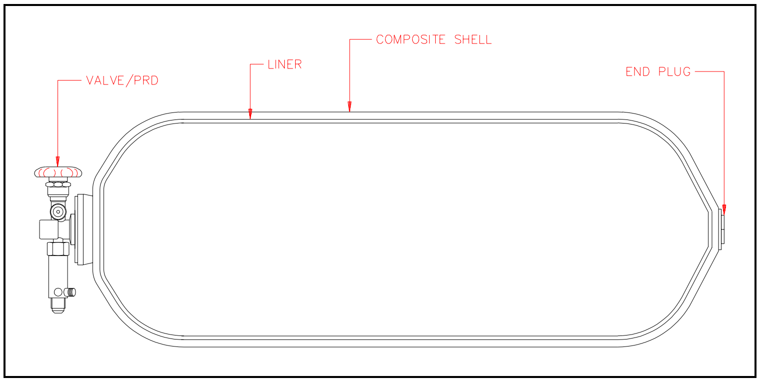

**FIGURE A.1:**

**Components of the all-composite Cylinder**

### A.4.1 The Composite Shell

The fibres used in the construction of the outer shell shall be made of carbon fibre, aramid fibres, glass fibres, or a combination thereof.

With storage of compressed hydrogen fuel, the structural load is taken primarily by the composite shell. Because the loading conditions specified in Pressure Design Option #1 (section A.3.2) are similar to those required of the all-composite cylinders for natural gas storage, and because the fuel constituency has no bearing on the design of the composite shell, the design requirements of the composite shell used in the hydrogen cylinder construction shall be similar to that used in the natural gas cylinder construction. The requirements for Pressure Design Option #2 will also be similar.

### A.4.2 The Liner

The liner material is not intended to carry a significant amount of the structural load of the cylinder. The liner is to be made of a material which meets the same mechanical properties required of the liners of cylinders used in the storage of natural gas. In addition, the liner material should meet these additional requirements:

- the liner material shall be selected to resist degradation caused by exposure to hydrogen fuel,
- the liner, as part of the cylinder, shall be selected to provide a barrier to contain the hydrogen fuel under pressure and resist the permeation of hydrogen to acceptable levels,

- the liner shall be both selected and designed to resist the development of “pin-holes” caused by both the build-up of electric charge on the liner and inadequate resistance of the liner to the magnitude of this electric charge build-up, and
- the liner material shall withstand the high temperatures developed during fast-fills, especially with a gas with a high “approach” temperature.

### A.4.3 The Metal Components

The metal components shall be manufactured from a material which resists degradation (both general corrosion and hydrogen embrittlement) due to the hydrogen fuel, or shall be protected from the hydrogen fuel using a barrier which is durable and protects the end-boss from the fuel for the design life of the cylinder.

The openings in the cylinder shall contain threads which, in combination with the cylinder seal system, allow no measurable leakage of hydrogen gas through the end-boss.

### A.4.4 The Valve and Pressure Relief Assembly

The Pressure Relief Device shall be selected to ensure:

- compatibility with the hydrogen fuel in terms of resistance to general corrosion and hydrogen cracking,
- an ability of the eutectic material (if applicable) to resist creeping under sustained loading and high temperatures. Note that the maximum temperature by which the eutectic material should resist creep is defined as the upper limit described in the fast-fill condition (section A.3.4).
- timely release of the hydrogen fuel only in a fire situation and only such that the fuel passes passively to the atmosphere without explosion.

## A.5 DESIGN QUALIFICATION TESTS

### A.5.1 Design Qualification Tests Previously Defined for Natural Gas

The following design qualification tests shown in Table A.1 are already required of all-composite cylinders for natural gas vehicles in industry [b,c,d]. It is noted that the majority of the tests, with the exception of the bonfire test, the natural gas cycling test, and the permeation test, measure the design of the cylinder indifferent to the fuel contained inside. In each case, the pressurized natural gas fuel required in the tests shall be replaced by pressurized gaseous hydrogen fuel and the test commenced. It is noted in each case that the acceptable results in terms of the natural gas standards are acceptable in the case for hydrogen fuel, as well.

**TABLE A.1**

**Currently Developed Tests for all-composite Fuel Cylinders**

| | CSA B51-95 Part II [b] *(January, 1995)* | ISO/TC 58/SC 3/WG 17 [c] *(July, 1995)* | AGA NGV2 1996 [d] *(Draft, 1996)* |
|---|---|---|---|
| Pressure Cycling, Ambient Temp | X | X | X |
| Pressure Cycling, Extreme Temp | X | X | X |
| Hydrostatic Burst Test | X | X | X |
| Bonfire Test | X | X | X |
| Flaw Tolerance Test | X | X | X |
| Drop Test | X | X | X |
| Penetration Test | X | X | X |
| High Temperature Creep | X | X | X |
| Permeation Test | X | X | X |
| Accelerated Stress Rupture Test | X | X | X |
| Environmental Test | X | X | X |
| Gas Cycling Test | | X | X |
| Boss Torque Testing | | X | X |

Note that X indicates which tests are included in the standard

The all-composite cylinder, designed for the storage of hydrogen fuel, shall meet or exceed the requirements set out by each of the above standards for cylinder storage of natural gas.

### A.5.2 Additional Tests Required for Hydrogen

#### A.5.2.1 Embrittlement Test

One finished cylinder shall be internally pressurized with gaseous hydrogen fuel to the working pressure and held at a temperature of 21°C for over 200 hours for conditioning. After which, the cylinder shall be subjected to 5000 pressure cycles using a fluid medium between 10% of the service pressure and the 125% of the service pressure at a rate not exceeding 12 cycles per minute. Following fatigue testing, the cylinder shall be pressurized until burst. Samples of both the liner material and the metal end-boss shall be analyzed following the burst test for evidence of material embrittlement/degradation due to the aging/exposure to hydrogen fuel.

#### A.5.2.2 Pressure Relief Device Test at Elevated Temperatures

The pressure relief device shall be fixed to a hydrogen gas supply which is pressurized to the maximum design fill pressure (section A.3.2). In addition to the pressure loading, the pressure relief device shall be raised to a temperature equivalent to the maximum temperature which the cylinder is permitted to experience during a fast-fill loading condition (section A.3.4) and held for a period of 500 hours. At the end of the test, there shall be no leakage, no visible signs of metal extrusion, or no evidence of material embrittlement/degradation due to accelerated aging and exposure to hydrogen fuel.

### REFERENCES

[a] CGA G-5.3, “Commodity Specifications for Hydrogen”

[b] CSA B51-95 Part II, “High Pressure Cylinders for the Storage of Natural Gas as a Fuel for Automotive Vehicles”, January 1995.

[c] ISO/TC 58/SC 3/WG 17, “High Pressure Cylinders for the On-board Storage of Natural Gas as a Fuel for Automotive Vehicles”, July 1995.

[d] “Proposed Revision to American National Standard for Basic Requirements for Compressed Natural Gas Vehicle (NGV) Fuel Containers”, May 30, 1995.