STP/PT-003

HYDROGEN STANDARDIZATION INTERIM REPORT

For Tanks, Piping, and Pipelines

ASME STANDARDS TECHNOLOGY, LLC

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FOREWORD

Commercialization of fuel cells, in particular fuel cell vehicles, will require development of an extensive hydrogen infrastructure comparable to that which exists today for petroleum. This infrastructure must include the means to safely and efficiently generate, transport, distribute, store, and use hydrogen as a fuel. Standardization of pressure retaining components, such as tanks, piping, and pipelines, will enable hydrogen infrastructure development by establishing confidence in the technical integrity of products.

Since 1884, the American Society of Mechanical Engineers (ASME) has been developing codes and standards (C&S) that protect public health and safety. The traditional approach to standards development involved writing prescriptive standards only after technology has been established and commercialized. With the push toward a hydrogen economy, government and industry have realized that they cannot afford a hydrogen-related safety incident that may undermine consumer confidence. As a result, ASME has adopted a more anticipatory approach to standardization for hydrogen infrastructure which involves writing standards with more performance based requirements in parallel with technology development and before commercialization has begun.

Today, ASME codes and standards are used for hydrogen storage, transmission, and distribution. The anticipated requirements of the hydrogen economy will require local refueling stations with the capability to fill gaseous hydrogen vehicle tanks rapidly, to pressures as high as 10,000 psig. Although current standards could be used to build pressure vessels, piping, and pipelines meeting these operating requirements, it is likely that the resulting components would not, as a practical matter, enable commercialization of the technology.

ASME has worked closely with the Department of Energy (DOE), national laboratories, and other standards developing organizations (SDOs) to identify lead organizations to address the need for standards for hydrogen applications. ASME was selected to lead the efforts for pressure vessels, piping, and pipelines for storage, transportation, and distribution of hydrogen. Initial work of the ASME's Hydrogen Steering Committee led to the formation of volunteer task forces under the ASME Board on Pressure Technology Codes and Standards (BPTCS) to explore the standardization requirements for storage tanks, transportation tanks, portable tanks, piping, and pipelines for hydrogen-specific applications. The task forces submitted their recommendations at the end of 2003, and these recommendations led to initiation of standards actions, formation of project teams, and commencement of supporting research.

The ASME Boiler and Pressure Vessel (BPV) Standards Committee appointed a project team to develop new Code rules in the Boiler and Pressure Vessel Code Section VIII (pressure vessels) and Section XII (transport tanks) for hydrogen storage and transport tanks to be used in the storage and transport of liquid and gaseous hydrogen and metal hydrides. Rules for gaseous storage vessels with maximum allowable working pressures (MAWPs) up to 15,000 psig will be needed. Research activities are being coordinated to develop data and technical reports concurrent with standards development and have been prioritized per Project Team needs. The Project Team may identify additional needs and gaps as drafts are developed.

The Technical Reports to be developed will establish data and other information to be used to support and facilitate separate initiatives to develop ASME standards for the hydrogen infrastructure. These reports will target specific disciplines and fill the gaps identified by ASME's hydrogen task forces. This report is the first in a series of technical reports to be developed under sponsorship from the National Renewable Energy Laboratory (NREL) and addressing the following priority hydrogen infrastructure applications:

(a) H_2 Storage Tanks

(b) H_2 Transport Tanks

(c) H_2 Piping and Pipelines

(d) Portable H_2 Tanks

The H_2 Standardization Interim Report is intended to address priority topical areas within each of the four pressure technology applications for hydrogen infrastructure development. The planned application-specific reports will adopt the applicable sections of the interim report and further address key standardization issues including, as applicable, materials, design, fabrication, testing, examination, inspection, operation, maintenance, and installation. The application-specific reports are expected to serve as a primary reference for standards committees for review and approval of the draft standards.

Established in 1880, the American Society of Mechanical Engineers (ASME) is a 120,000 member professional not-for-profit organization focused on technical, educational, and research issues of the engineering and technology community. ASME conducts one of the world's largest technical publishing operations, holds numerous technical conferences worldwide, and offers hundreds of professional development courses each year. ASME maintains and distributes 600 codes and standards used around the world for the design, manufacturing and installation of mechanical devices. Visit www.asme.org for more information.

The ASME Standards Technology, LLC (ASME ST-LLC) is a not-for-profit Limited Liability Company (LLC), with ASME as the sole member, formed in 2004 to carry out work related to newly commercialized technology, expanding upon the former role of ASME's Codes and Standards Technology Institute (CSTI). The ASME ST-LLC mission includes meeting the needs of industry and government by providing new standards-related products and services, which advance the application of emerging and newly commercialized science and technology and providing the research and technology development needed to establish and maintain the technical relevance of codes and standards. Visit www.stllc.asme.org for more information.

ABSTRACT

This interim report is intended to address priority topical areas within pressure technology applications for hydrogen infrastructure development. The scope of this interim report includes addressing standardization issues related storage tanks, transportation tanks, portable tanks, and piping and pipelines. It is anticipated that the contents and recommendation of this report may be revised as further research and development becomes available.

The scope for the tank portions of this report (Parts I and II) includes review of existing standards, comparison with ASME Boiler and Pressure Vessel Code (BPVC) Section VIII, and recommendations for appropriate design requirements applicable to small and large vessels for high strength applications up to 15,000 psi. This report also includes identification of design, manufacturing, and testing issues related to use of existing pressure vessel standards for high strength applications up to 15,000 psi, identification of commonly used materials, and developing data for successful service experience of vessels in H_2 service.

Similarly, the scope of piping and pipelines portion of this report (Part III) includes reviewing existing codes and standards, recommending appropriate design margins and rules for pressure design up to 15,000 psi, reviewing the effects of H_2 on commonly used materials, developing data for successful service experience, researching leak tightness performance, investigating effects of surface condition of piping components, and investigating piping/tubing bending issues.

Part I - H_2 Tanks: Review of Existing Reference Standards

The study provides a detailed overview of various compressed gas cylinder standards in comparison to ASME Section VIII rules with particular emphasis on the differing design burst margins and the modifications required to make the rules applicable to high-strength metal or composite vessels for both stationary and transport uses at pressures up to 15,000 psi.

The margins between burst and maximum operating pressure for common transport compressed gas cylinders and vehicle fuel containers were found to be very similar to one another and also very similar to the basic design margin of ASME Section VIII Division 3 vessels. The minimum margin found was for the U.S. Department of Transportation (DOT) DOT-3AA specification, and this margin is recommended as the minimum for future design rules. The various metal cylinder design formulas were found to deviate significantly from the burst prediction formula as pressures were increased to 15,000 psi and the ASME Section VIII Division 3 collapse formula is recommended for future rules at these high pressures. Low design margins for metal vessels were found to be dependent on associated periodic requalification and specific recommendations are included for all designs except the higher margin rules of ASME Section VIII Division 1 and ASME Section VIII Division 2. The standards do not presently provide adequate coverage of fatigue and fracture issues for 15,000 psi metal vessels in a hydrogen environment and the concerns are discussed in comparison to lower pressure experience. It should be noted that standards developed by different standards developing organizations utilize different consensus processes, may have different approaches, and are typically intended for different applications; therefore design margins and pressure definitions vary accordingly.

It was found that evaluation of composite gas cylinder margins must address time at various stress levels for time-dependent mechanisms such as stress rupture to control. The allowable stress for glass composites was determined to be very similar for all standards and the glass stress requirements of the DOT Fiber Reinforced Plastic (FRP) specifications are recommended as the initial basis for future rules. It should be noted that FRP-1, FRP-2, and CFFC are limited in scope, sizes, designs, and materials and these limitations, along with the operating experience of other standards, such as natural gas vehicle-2 (NGV-2), should also be considered for future rules. Generally, composite cylinders

were not found to be designed using consensus-based rules. A preliminary proposal was outlined whereby simplified design may be developed and verified for general application. The allowable stress and resulting burst margins for carbon composites were found to vary significantly among the standards, presenting no single value. The discussion includes the significant differences between the service conditions of stationary and transport vessels and this should facilitate study of the necessary allowable design stress for future carbon composite design rules. The various composite cylinder standards vary significantly with regard to required resistance to external damage from chemicals and impact, and significant gaps are identified. Specific recommendations are included for the development of nondestructive examination (NDE) techniques for composite requalification, and recommendations for a performance based approach for validation of new techniques for use on different designs are provided.

Part II - H_2 Tanks: Study of Existing Data, Standards, and Materials

This study evaluates the potential use of four metallic vessel standards [ASME VIII-1 Appendix 22, 49 Code of Federal Regulations (CFR) 178, American National Standards Institute (ANSI)/CSA NGV2-1], and International Organization for Standardization (ISO)/Draft International Standard (DIS) 15869-2, and six composite vessel standards (DOT FRP-1 and FRP-2, ANSI/CSA NGV2, ASME VIII-3 Code Case 2390, ISO 11119, and ISO/DIS 15869) for 15,000 psi hydrogen service.

The study identifies problems with using existing standards (1) for pressures well above current common practice and (2) for hydrogen with its material compatibility issues, flammability, and small molecular size. Design, manufacturing, and testing gaps are identified in existing standards, and recommendations are made for future standards dedicated to this challenging service.

Commonly used materials are rated for their resistance to hydrogen embrittlement and crack growth. Where test data are lacking, recommendations are made for future data collection. In-service inspections (ISIs) based on fracture mechanics, analyses are recommended, but cycle-to-failure tests (using hydrogen) and design life limits may be required until data are available.

Tables and figures are used to display successful service data for storage, transport, portable, and fuel tank service. All metal vessels have service histories of 60+ years, with composites gaining acceptance in the last 5 to 10 years (mostly in vehicle fuel tank applications). The successful service data support the reduction of design margins for some metallic vessels, and also support the "performance standard" concept for composite vessels.

Part III - H_2 Piping and Pipelines: Study of Existing Data, Standards, and Materials

This study evaluates the potential use of four piping and pipeline codes (ASME B31.1, 31.3, 31.8, and 49 CFR 192) for up to 15,000 psi hydrogen service.

The study compares the codes and determines the existing design margins. Tables and figures are provided to display the design margins, and also to display successful service data for piping systems and pipelines built in accordance with the codes. Some service data dates back to the 1940s.

Commonly used materials are rated for their resistance to hydrogen embrittlement and crack growth. A table is provided that lists recommended materials for high-pressure hydrogen service. For pipelines, reference to European Industrial Gases Association/Compressed Gas Association (EIGA/CGA) 121/04/E is recommended. For small piping systems, 316L stainless steel (SS) is recommended.

Several special topics related to hydrogen service are covered: performance of welded and mechanical joints, post-weld and post-formed heat treatment, effects of surface finish, and hot and cold pipe/tube bending.

Recommendations are provided for design margins for systems constructed of materials that are resistant to hydrogen embrittlement. Where less optimum materials are selected, the same design margins can be used with adequate initial and in-service inspections.

Recommendations are made for future standards dedicated to high-pressure hydrogen service. The design rule recommendations account for the challenges of (1) pressures well above current common practice and (2) hydrogen with its material compatibility issues, flammability, and small molecular size.

PART I -
Review of Existing Reference Standards to Support New Code Rules for High-Pressure Hydrogen Vessels

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1 INTRODUCTION

1.1 General Background of Code Work for 15,000 psi Hydrogen Vessels

The ASME Boiler and Pressure Vessel Committee Project Team on Hydrogen Tanks has been formed to develop Code vessel rules for storage and transport of gaseous hydrogen at pressures up to 15,000 psi. There are now a relatively small number of hydrogen vessels and transport tanks in use at pressures as high as 10,000 psi. These vessels may not be suitable models for high volume usage as is expected for hydrogen as an alternative fuel. This report compares the requirements and commonly known experience base of a variety of standards for gas cylinders and pressure vessels used in common operating pressures between 2,000 and 5,000 psi. The standards considered cover a spectrum from the more prescriptive design approach of the ASME Section VIII Code to the performance based requirements of NGV2 for full composite cylinders.

The scope of this work is very broad, but limited in depth. There are often several potential remedies proposed for a single issue. This is the result of drawing on the diverse existing standards. In addition, the critical work of characterizing materials performance in 15,000-psi hydrogen has yet to be completed.

The reference standards, listed below in Section 1.2, also incorporate a variety of assumptions about the service conditions and periodic requalification needed to ensure continuing operational integrity. These differences are appropriate, but make it difficult to simply copy a standard intended for one type of service to another, different, type of service. An example is the difference in application and requalification between conventional individual DOT gas cylinders and vehicle fuel tanks. In the first instance the cylinder is exposed to a very broad range of potential physical damage in shipment and use, but the number of fatigue cycles is small and there is effectively unlimited access for inspection at requalification. In the second instance, the tank is installed in a protective vehicle structure, limiting the potential for physical damage but also limiting access for requalification. There are also a large number of fatigue cycles for fuel tanks. These differences in service conditions, absent any significant differences in gas or pressure contained, contribute to significantly different approaches to assure integrity.

This report attempts to present a listing of potential issues, often with recommendations to be considered by the committee responsible for the new rules. The broad safety issues of margins, fatigue, material compatibility, resistance to failure due to damage in service, requalification, and efficient design for 15,000 psi must be addressed in new rules, but there are many solutions that may be based on available data, some valid for only certain types of vessels and not for others. This report should provide an extensive kit of basic background, references, and tools that can be used as input to a good consensus standard development process. This report does not attempt to address all technical issues related to standards for hydrogen infrastructure applications, and it is expected that areas requiring further investigation will be identified.

There are also issues identified where no solution is available from the reference standards and available data. Although it is acknowledged that not all existing data was reviewed within the scope of this evaluation, it is generally concluded that hydrogen compatibility and fracture safety, both for thick metal vessels in fatigue and composite vessels after impact damage, are two examples of concerns that are not easily addressed by reference to traditional design controls and available data. These issues require solutions that are based on developed technology, verified to be effective and peer reviewed.

The recommendations are embedded with the relevant text sections. It is believed that the recommendations must be considered in the detailed context and not treated as a checklist that can be separated from the background discussion.

1.2 Reference Standards

The standards listed below were reviewed and compared in the preparation of this report.

ASME VIII-1	DOT CFFC	ISO 11119
ASME VIII-2 App. 22	DOT-3AA	NGV2
ASME VIII-2	DOT-3AAX	ISO 11439
ASME VIII-3	IGC Document 100/03/E	ISO 15869
DOT FRP-1	ISO 9809-1	ASME Code Case 2390
DOT FRP-2	ISO 111120	

1.3 Steel Cylinder Designs

The typical transport tank is designed to DOT Specification DOT-3AAX with a water capacity of several thousand pounds and a fill pressure between 2,000 and 3,000 psi. The construction is from seamless low-alloy steel, typically quenched and tempered 4130x and has a relatively low margin. The common terminology for this tank is a trailer tube, and they are usually fixed to a frame on a semi trailer or in a separate ISO module configuration. Although the DOT-3AAX specification imposes no maximum pressure limit, it may not be practical to scale this design to the much higher pressures envisioned for hydrogen transport. The thickness of the sidewall must increase at least proportionally with the pressure increase, and the hardenability of the steel is believed inadequate for the resulting heavier sections.

Increasing the alloy content can improve the quench response but there is a second constraint, the provision of a leak-before-break (LBB) failure mode. The relatively low margins common to seamless gas cylinders are acceptable because the cylinders will typically not fail by rupture. The U.S. DOT has required consideration of LBB as part of all recent new high-pressure cylinder designs and this should be anticipated as a requirement for new hydrogen tanks. The existing exemptions and work performed in ISO TC58/SC3/WG14 and reported in ISO TR 12391-2 found that LBB could be achieved at thicknesses at least up to 14.4 mm (0.567 in.) in DOT-3AA design. LBB may be achieved at higher material thicknesses with high-strength material operating at high pressures. As the wall thickness is increased, it is expected that this may be compounded by the unfavorable effect of hydrogen exposure on the fracture toughness of the steel. It may be more difficult to achieve LBB performance due to materials limits on fracture toughness.

A third barrier to the use of the DOT-3AAX specification is the very high weight of these all-metal designs, compounded by the unfavorable wall thickness ratios due to thick wall effects and the unfavorable compressibility factor of hydrogen at 15,000 psi. Hydrogen transportation by truck is governed by the maximum gross weight regulations for highway use. Any change that increases the relative weight of vessels will reduce the payload. As an approximation, the weight of a given design type of vessel with fixed material properties is proportional to the product of water volume and design pressure. If the pressure or volume is doubled, the weight is also doubled.

A rough approximation of the effect on vessel weight resulting from increasing the operating pressure was calculated by extrapolation of the hydrogen compressibility factor based on a published chart [64] covering the range of 0 to 6,000 psia. The factor is not exactly linear, showing slight upward inflection, but the approximation will serve. The estimated compressibility factor is 1.10 at the conventional service pressure of current transport vessels, 2,640 psi. At 15,000 psi the approximate compressibility factor is at least 3.15 and probably somewhat greater; however, additional investigation may be required to confirm the extrapolation. The amount of gas stored in a vessel of given size is the product of the water volume times the pressure ratio, fill pressure divided by atmospheric and then divided by the compressibility factor. If the weight of a vessel is assumed to increase linearly with design pressure, the payload of a truck using DOT-3AAX 15,000-psi vessels would be reduced by the compressibility factor ratio, 1.1:3.15 or a 65% reduction in payload at the maximum weight limit. Looked at another way, the weight of the vessel design must be reduced by the same factor to maintain the current payload. This magnitude of weight reduction is unlikely using any metals but may be feasible with composites.

Usually DOT gas cylinders are not at risk for fatigue failure in service. With few exceptions such as breathing apparatus cylinders, these cylinders are used as shipping containers and the number of pressure cycles per year is low compared to the typical fatigue cycle life of at least 10,000 cycles up to an effectively infinite fatigue life. It is expected that exposure to hydrogen at high pressures will reduce the fatigue life by a significant margin [1].

DOT specifications apply limits to the sidewall thickness as a function of material strength, but do not contain design rules for the ends. DOT also restricts discontinuities such as openings in the sidewall but not in the ends. ISO 9809 does add design constraints for the ends, but these features must still be proven by prototype test. Since the burst margin depends on the sidewall in these cylinders, it is appropriate to consider these design standards for the purposes of margins between burst pressure and operating pressure.

The DOT specification also effectively prohibits the use of autofrettage to improve the stress distribution at operating pressure by prohibiting the application of high internal pressures prior to the hydrostatic expansion test. This requirement is inherent in the design strategy for DOT cylinders as discussed later, but is a disadvantage at very high pressures.

The combined effects of hydrogen degradation of steel materials and thick-wall effects of 15,000 psi vessels introduces issues requiring new material data and possibly new design or NDE techniques in the development of new design rules. The inherent high weight of metal designs, even with the lowest proven margins, is also likely to be a limiting factor in their use for transportation at 15,000 psi.

1.4 Composite Cylinder Designs

Composite reinforced designs offer more weight-efficient transportation tanks but there is currently no specification or standard for such tanks at 15,000 psi. The properties and manufacturing of composites can address the critical concerns for metal vessels because metal liner sections can be thinner, LBB is easier to achieve at high pressures, depending upon the details of construction, and fatigue is therefore less of a concern.

Smaller, lower pressure, composite tanks are produced under exemptions and to detailed designs proprietary to each manufacturer. The DOT, ISO and ANSI existing standards for smaller composite tanks are not harmonized and contain a variety of design margin requirements. The U.S. regulatory authority for cylinders used in the commercial transport of gases, DOT, has not accepted any standard as adequate for large composite vessels in high-pressure hydrogen, or any other industrial gas, service. The development of ASME Code rules specifically for such tanks using the ASME consensus process, presents the best case for a comprehensive and credible standard for such tanks.

1.5 Stationary Storage Vessels

Vehicle refueling infrastructures for gaseous fuels typically incorporate high-pressure storage vessels as receivers, buffer tanks, and cascade storage banks associated with compressor stations. In the absence of compressors, these vessels must operate at pressures greater than the refueling pressure of the vehicles, generally a minimum of 1.5 times the service pressure of the vehicle tank. With plans for 10,000-psi vehicle tanks, the storage vessels must be capable of 15,000 psi operating pressure.

Another consideration is the expansive heating effects of hydrogen, which would also require a higher tank fill pressure in order to achieve 10,000 psi upon cooling to ambient.

Using the CNG precedent, either ASME Section VIII vessels or DOT specification gas cylinders may be installed at compressor stations. This use is clearly within the scope of the ASME Code, but also clearly not within the scope of DOT regulations for the transportation of hazardous materials. Long and successful precedent in this and other non-transportation uses of DOT cylinders has resulted in references in other codes, notably National Fire Protection Association (NFPA) 52.

Code storage vessels for vehicle fuels are typically ASME Section VIII Division 1 forged vessels made in accordance with Appendix 22. The Appendix 22 vessels are identical in appearance to DOT trailer tubes and made from essentially the same alloy but with higher margins than required by DOT-3AAX. Scaling either of the present ASME designs to 15,000 psi encounters the same feasibility concerns as scaling the DOT trailer tubes except that weight is not as great an issue for the stationary ASME vessels and LBB may not be as firm a regulatory requirement. Additionally, ASME and DOT toughness rules differ.

ASME Section VIII Division 3 provides Code rules for efficient pressure vessels for higher pressures. The provision for prestressed designs, using autofrettage or other techniques, allows some of the thick wall adverse effects to be offset and the use of layered and prestressed designs allows for greater total wall thickness. LBB can also be achieved even in very thick vessels if they are layered and designed in accordance with KD-810 (f). These rules may be usable for ground storage vessels, but the resulting weight will probably still be too great for transport tanks. It should be noted that vessels could also be constructed to ASME Section VIII Divisions 1 and 2; however, Division 3 may be the most appropriate choice.

Code Case 2390 under Section VIII Division 3 allows a composite reinforced vessel to be constructed by hoop wrapping a steel liner with fiberglass composite but limits the design pressure to 3625 psi. Vessels of this type can be considered similar to wire wound vessels.

1.6 Performance Based vs. Prescriptive Standards

Generally, a performance based standard will state the goals and objectives along with methods (e.g., testing and inspection) to demonstrate whether the vessel meets these goals and objectives. A performance based standard will focus on the critical characteristics of the final vessel, rather than the specific processes used to produce it. In contrast, a prescriptive standard will typically specify materials, design, and construction rules, without stating the goals and objectives. It is anticipated that standards for hydrogen infrastructure will include a mixture of performance and prescriptive requirements.

ASME Code rules are predominantly engineering calculations based on thoroughly developed and accepted formulas or design by analysis for metal structures. These rules, though often complex, can be used, understood, discussed, and accepted by a large number of professionals. In contrast, the reference performance standards give little if any guidance in engineering calculation, relying entirely upon the engineer to devise a design that will reliably satisfy the stated performance requirements. Designers of composite vessels are particularly dependent on internally developed and proprietary design tools, as well as commercially available analysis programs. Finite element analysis is becoming more common, but there is no standardization required in the many assumptions made in the use of this technique.

1.7 Reference Performance Based Standards

The reference standards are predominantly performance based rather than design based in contrast to typical Code rules. These performance based standards have been largely successful in lowering the weight of transport tanks and fuel tanks while maintaining operational integrity. One assumption that is common to many of the reference standards is that fatigue and fracture performance test results in using fluids such as water or oil as the pressurizing media will be representative of actual gas service. This may not be true for high-pressure hydrogen vessels. The characterization of material performance in high-pressure hydrogen not within the scope of this report, but the discussion and recommendations will address the identified needs.

1.8 Potential for a New Performance Code

Composite pressure vessels for high pressures are traditionally designed to performance standards, not prescriptive design codes such as those provided for metal vessels. The properties of the composite structural reinforcement are highly dependent on the details of design and processing that are proprietary to each manufacturer. This is in contrast to the Code rules for pressure vessels that require standard metallic materials meeting uniform specifications operating at design stresses that are limited in the various code rules. Code empirical design is usually only permitted in the event that no definitive code rule applies to the geometry and then the stresses may be determined by test. As an example, KD-1260 provides for empirically determining the allowable number of fatigue cycles and can be considered to be a performance standard.

Performance standards are often preferred over prescriptive codes, especially when production quantities or innovation rates are high. Performance standards are also more common for transportation equipment such as vehicle safety standards. Performance standards are often the only option with new technology that is developing empirically. In the present case of composite pressure vessels, a performance standard is easier to formulate because there is no generally accepted design method for such vessels but there are various standards of safety in the variety of service conditions that may impact the vessel during its life.

1.9 Performance Standards Dependent on Design Calculations

A common requirement in all performance standards for composite cylinders and vessels (all DOT, CSA, NGV2, ISO standards) is the determination of composite strength by a sample burst test and a minimum stress ratio between the composite strength and the composite working stress. This is more complex than a simple burst to working pressure ratio due to load sharing among different laminates and the liner, but is necessary to safe performance given the stress rupture characteristics of composites. The standards typically do not give definitive guidance in the calculations or empirical testing necessary to determine either the composite strength or the working stress for a given design. The designer uses proprietary calculation methods to determine compliance with the critical design margin. A potential area of uncertainty is in determining that the stress ratios of samples subjected to design verification testing are representative of stress ratios in production samples; however, production units are required to be the same design and construction as qualification test units.

1.10 Potential Design Code for Hoop-Wrapped Vessels

There have been developments in the availability of public domain design calculation methods that are applicable to composite pressure vessels. One such development is the recent publication by ASME titled *Hoop-Wrapped, Composite, Internally Pressured Cylinders, Development and Application of a Design Theory* by John A. Walters. Others are advancements in the application of finite element analysis (FEA) to composite vessels. It may be possible that new Code rules can now include mandatory stress analyses for at least the simpler composite designs. This would be very desirable because the designs would then be transparent to regulators and users.

The optimum choice of balance between performance and design standards may also depend on economics. Performance standards are usually the preferred economic approach for higher production volumes, such as motor vehicle tanks. Quantity of production is roughly inversely related to the component size. This would mean that the quantity of storage and transport, large tanks, could be relatively low. The cost of performance testing for low-volume production can become an issue. The use of performance based standards allows for quicker adoption of new technology, which may be important for commercialization of hydrogen infrastructure, where standards development is proceeding in parallel with technology development.

1.11 Potential for a Full-Composite Cylinder Design Code

In reviewing the composite cylinder standards it was necessary to continuously recognize that there are no common design rules for these cylinders. This situation may be cumbersome for pressure vessels where there is no central design approval authority such as DOT. Composite cylinders have been produced in large quantity for at least 25 years and it may now be time to develop a design code that will also include full-wrapped designs. The following are suggestions about how this might parallel the development of ASME Code rules for metals.

As in the early years of metal cylinders, the sidewall portion of composites is simpler and more convenient to analyze. If a design code could be developed for only this area, it could be applied as the DOT-3AA sidewall formula and the National Aeronautics and Space Administration (NASA) code were originally applied in DOT FRP-1. The sidewall would be designed by calculation and the ends would not be allowed to fail in qualification or sample tests. If this is applied to all tests (burst, fatigue, environmental etc.) it may provide a large degree of confidence in the whole design by calculation of only the simplest part. This would be a good start and the metal gas cylinder standards have not found it necessary to go further. Design by analysis methods are presently used by ASME.

Composite materials can be characterized for strength in the same way as Division 2 metals. A given steel specification, SA-516 as an example, specifies a range of permissible alloy additions and some other controls of grain size as well as minimum strength properties. The steel mills are free to vary their processes to optimize their own operations as long as they meet the minimum requirements. This approach could be used to develop composite material specifications. Additionally, specific rules for composite procedures should be developed and qualified, much the same as a given steel specification. Many components of the composite are already largely standardized:

(a) Glass fibers are commonly specified against ASTM types, E, ECR, R, RH, or S.

(b) The properties of intermediate modulus carbon fibers from different manufacturers are similar.

(c) Many resin systems are based on epoxy resins.

(d) The ASTM test methods for determination of composite tensile strength (TS) and resistance to water boil are well established and already referenced in the cylinder standards.

(e) Liner materials of polyethylene, 6061 T6 aluminum, 4130X steel, and other materials are common and these materials are well characterized.

The initial standard could be developed for a scalable vessel configuration with defined winding angles for both helical and hoop plies as well as an interspersing pattern. This standard can be validated by test using the actual design as specified. The results could be subjected to peer review and adopted as an initial design code. A manufacturer could then use this code in much the same way as a forged metal vessel is manufactured. The design is carried out by the code and the specified materials are used with verification tests on properties. The single greatest difference may be a continued reliance on destructive vessel tests for process control, but this should result from the standard development. This would be patterned on the laminate procedure qualification of ASME Section X and Code Case 2390.

Once an initial design standard with material specification is in place, it will probably grow by the gradual addition of material options and design features similar to the development of Section VIII.

This approach may not allow the degree of optimization that manufacturers can achieve with a pure performance standard, but there are real benefits to a design code as evidenced by the success of ASME Codes for metals.

2 COMPARISON OF OPERATING MARGINS FOR EXISTING STANDARDS

This section will compare the operating margins (or design margins) for the various reference standards to the margins required for current ASME Code Vessels. For the purposes of comparison, this margin is expressed as a burst pressure, either calculated or determined by test, divided by the maximum pressure of the vessel in operation. Conclusions will be drawn from the comparison based on different groupings of vessels, by application or by materials. The compared margins can be used as potential precedents for new, lower margin ASME design rules, accounting for the differences in application and material.

The standards are evaluated and compared to the present ASME design rules to provide a context for the development of new rules. The comparison of margins is complicated by the differing standard definitions of the pressure in service and different stress calculation formulas. This comparison also identifies the more significant differences among standards and their applications in practice, and presents margin ratios normalized for these differences.

2.1 Operating Margin Definition

The first requirement common to all vessel performance standards is the operating margin defined as the ultimate burst or failure pressure of the vessel divided by the operating pressure. Considering all types of pressure vessels, these margins are as low as 1.732 or as great as 6 and there is no universal methodology to arrive at the correct value. New standards are typically developed in the context of older standards with a demonstrated safety record for a given margin. Any comparison of margins is complicated by the lack of a uniform definition of the operating pressure conditions. For the purposes of this report, the different definitions relevant to this discussion are as follows.

2.2 Maximum Normal Operating Pressure (MNOP)

The first element in the margin ratio to be defined is the maximum operating pressure of the vessel, or MNOP. Since it is intended to compare the range of different specifications over a pressure range up to 15,000 psi but the service experience is at much lower pressures it was necessary to choose a specific pressure for the comparison. 3,750 psi is selected as the operating pressure for comparison of margins because it is a reasonable compromise between the common DOT 3AA cylinder pressures and the common ASME Appendix 22 pressures that represent the most clearly identifiable experience bases. 3,750 psi is within the scope of ASME Section VIII Division 1 [2], but vessels designed in accordance with Appendix 22 [2] are commonly used for storage of natural gas at 5,000 psi. It should be noted that ASME uses maximum allowable working pressure (MAWP), as defined in ASME Section VIII-1, UG98. MNOP is used in this report for the purpose of comparison.

2.3 ASME Design Pressure and MNOP

The ASME Section VIII Division 1 [2] defines design pressure in UG-21 as follows.

"Vessels covered by this division of Section VIII shall be designed for at least the most severe condition of coincident pressure and temperature expected in normal operation" with a footnote "It is recommended that a suitable margin be provided above the pressure at which the vessel will be normally operated to allow for probable pressure surges in the vessel up to the setting of the pressure relieving devices (see UG-134)."

ASME Section VIII Divisions 2 [10] and 3 [11] are less concise in the definition of design pressure, but it is believed that the Division 1 definition is clearest and it is used here. The ASME design pressure must be at least equal to Maximum Normal Operating Pressure (MNOP).

2.4 MNOP for Non-Code Reference Standards

Since the other reference standards use other pressure definitions to define the design, the pressures of all these standards must be restated in terms of a common pressure definition in order to make valid comparisons of margin. The margins proposed here are based on the maximum pressure that a cylinder or vessel is expected to experience in normal operations, excluding unusual upset conditions or fire that result in actuation of the relief valve or pressure relief device (PRD). It should be noted that the term "normal operation" includes upset conditions. This definition is consistent with ASME Code usage but is termed maximum normal operating pressure (MNOP). MNOP is used as a continual reminder that a common term has been used and that the other design conditions of the various standards are not intended.

2.5 MNOP by Vessel Usage

The definition and control of the maximum vessel pressure in normal operation varies considerably for the different vessel applications and to a lesser degree, on the detailed regulations for use, US DOT or UN/ISO.

2.5.1 ASME Storage Vessel MNOP

ASME Section VIII Division 1 design pressure is related to the Code requirement for maximum set pressure of a Code relief valve to prevent over pressurization of the vessel. In practical terms the operating pressure must be controlled at a slightly lower value to prevent frequent opening of the relief valve and the loss of the contents. In the case of Code vessels, the design pressure should never be reached during operating conditions of the vessel, excluding upset conditions, and is about 10% higher than the intended nominal operating pressure. Using the example of fuel storage vessels at vehicle refueling stations, this allowance provides for the pressure surge due to heating of a vessel during normal daily temperature fluctuations without actuation of the relief valve. The compressor control will be set at a value slightly less than the design pressure, but the actual operating pressure may increase routinely to the design pressure. MNOP for an ASME vessel is therefore equal to the design pressure.

2.5.2 DOT Compressed Gas Cylinder MNOP

DOT hazardous materials transportation regulations require the design of gas cylinders in terms of service pressure defined as the pressure in a full cylinder at a temperature of 21°C (70°F) [3]. This definition of service pressure is selected for the convenient use of cylinders, not because of any particular relevance to the design requirements. Since the cylinder is a closed pressure system when in transportation, the pressure will exceed service pressure whenever the temperature exceeds 21°C. The reverse is also true and the pressure at low temperatures will be less than the service pressure. The DOT service pressure is obviously not equivalent to the design or operating pressure of ASME vessels and some common basis for comparison is needed. The DOT regulations do limit the maximum pressure that may result from environmental heating of a filled cylinder. 49CFR173.301(a)(8)DOT [4] imposes a maximum increase of 25% above the fill pressure at the reference maximum temperature of 55°C. The MNOP for DOT cylinders is therefore 125% of the fill pressure at 21°C.

The concept of a maximum operating pressure for DOT cylinders is further complicated by the special provisions [5] to allow most steel cylinders to be filled 10% in excess of the service pressure at 70°F. This special filling limit [5] was applied as a wartime emergency measure to alleviate a cylinder shortage more than 60 years ago and was then made permanent based on the good safety record in wartime. This special filling limit is commonly allowed for hydrogen cylinders under DOT Exemption E 6530 [23]. For most steel DOT cylinders the maximum pressure expected in normal operation is therefore 137.5% of the service pressure. This applies only to seamless steel cylinders. A very common service pressure for DOT-3AA and 3AAX cylinders is 2,400 psi. The MNOP for these cylinders is 3,300 psi.

2.5.3 MNOP for ISO Gas Cylinders

The scope for this comparison includes a standard published by the European Industrial Gases Association (EIGA) and titled "Hydrogen Cylinders and Transport Vessels," IGC Document 100/03/E [6]. This standard does not include comprehensive design specifications but supplemental requirements intended to be added to a basic cylinder design specification. Four different cylinder standards are referred to in different parts of this document. Two of the references are for European specifications and two, ISO 9809 and ISO 11120, are for international standards. ISO 9809-1, for cylinders with water capacity up to 150 liters, was chosen as a basis for the margin comparison. ISO 11120 is for trailer tubes with water capacity in excess of 150 liters, but the rules for design margin are identical to those in ISO 9809-1. The ISO standards do not contain detailed rules for filling of cylinders. Individual countries provide these rules but there is one international document, the UN "Recommendations on the Transport of Dangerous Goods Model Regulations" (UNTDG). These rules are used to determine the detailed filling conditions for ISO cylinders.

For ISO standard gas cylinders the UN TDG P200 [7], defines a working pressure as 2/3 of the proof test pressure. This working pressure is the maximum pressure of the gas at a temperature of 15°C (59°F). Since the definition for this pressure condition is similar to the DOT definition of fill pressure, working pressure was selected over test pressure as the design pressure of ISO cylinders in this comparison. This is a simplification in presentation, but it must be noted that all design requirements in ISO standards are stated in terms of the proof test pressure. The pressure in an ISO cylinder will increase on heating just as in a DOT cylinder, but the UN TDG is intended to be applied in countries with hotter climates than exist in the US. The UN TDG P200 allows the pressure of the contents to increase to equal the proof test pressure at a maximum temperature of 65°C (149°F). Since this condition does not apply in the United States, and the number of permanent gases for which this is a limiting factor is quite small, the comparison is based on the expected service of ISO/UNTDG cylinders in the US and the maximum expected pressure in the cylinder is the pressure of the contents when heated to 55°C, the same limits applied to DOT cylinders. The fill pressure of ISO cylinders adjusted to the DOT filling temperature of 21°C is 1.02 times the ISO working pressure. MNOP for ISO cylinders is therefore 127.5% of the working pressure. A common working pressure for ISO cylinders is 200 bar (2,900 psi) and the MNOP for these cylinders is 3,698 psi.

ISO 11119 [8] is the standard for composite reinforced gas cylinders. It is new and the first gas cylinder standard to introduce the concept of varying some of the design requirements according to the nature of the gas contained and the resulting maximum developed pressure at 65°C. It is expected that ISO 11119 will be referenced in future editions of the UN TDG with the same pressure requirements as now apply to monolithic metal cylinders.

2.5.4 MNOP for Vehicle Fuel Containers

Vehicle fuel containers for permanent gases, predominantly compressed natural gas (CNG) use definitions of service pressure (NGV2 [52]) or working pressure (ISO 11439 [9]) that are analogous to the respective compressed gas cylinder standards. One significant difference between vehicle service and hazardous materials transportation lies in the common vehicle filling method. Vehicle cylinders are most commonly filled at a very high flow rate and compression heating of the gas in the cylinder is significant. For this reason, the maximum filling pressure is fixed in addition to the maximum settled pressure at the reference temperature defining service or working pressure. This maximum fill pressure is therefore the maximum pressure expected in normal operations.

NGV2 limits the maximum fill pressure to 1.25 times service pressure at 21°C (70°F) and ISO 11439 limits the maximum fill pressure to 1.30 times working pressure at 15°C (59°F). While gas cylinders used in transportation of compressed gases will experience MNOP only in hot ambient conditions, or while filling in moderately hot conditions, vehicle fuel containers are expected to experience MNOP at the end of many if not most fills. MNOP for NGV2 is 125% of service pressure and MNOP for ISO 11439 is 130% of working pressure. NGV2 cylinders with service pressures of either 3,000 psi or 3,600 psi are common, resulting in MNOP of 3,750 and 4,500 psi, respectively. Common working pressures for ISO 11439 cylinders are 200 and 240 bar resulting in MNOP of 3,770 and 4,524 psi, respectively.

2.6 Normal Operating Pressure (NOP)

When vessels are constructed of composite materials that may fail due to stress rupture as a result of continuous or long-term loads, it is desirable to consider a normal or perhaps approximate mean operating pressure. This is equivalent to the DOT definition of fill pressure at 21°C or the ISO definition at 15°C. Pressure excursions above NOP to as much as MNOP occur for gas cylinders but are assumed to be of relatively short duration. These excursions are ignored for purposes of composite stress limits in all DOT and ISO composite cylinder standards. The extensive safety record of DOT FRP-1 supports this approach and it is used later in addressing composite stress margins. For this purpose, the NOP of all gas cylinders and vehicle fuel cylinders is equal to the pressure at the DOT reference pressure of 21°C.

For composite pressure vessels used in the same way as ASME vessels, the concept of a fill pressure at a reference temperature does not apply. ASME vessels may operate continuously at pressures very near to the design pressure, MNOP. For such applications, NOP should be assumed to be equal to MNOP. This will assure that the mean operating stress of the composite material does not exceed the levels that have been demonstrated safe by DOT FRP-1.

2.7 Maximum Pressure During Upsets or Fire Exposure

The ASME Code also relates the design pressure to the maximum pressure developed in a fire, but this is a much more complex issue for portable cylinders. There is a large difference between the various designs in practice with respect to overpressure protection.

ASME Section VIII Division 1 and ASME Section VIII Division 2 [10] are the most conservative and limit the maximum pressure to 1.10 times design pressure or as much as 1.21 times design pressure if exposed to a fire. ASME Section VIII Division 3 [11] contains no explicit requirements for pressure relief in a fire.

DOT [12] requires the use of PRDs in accordance with CGA S-1.1 [13] with a maximum pressure rating equal to the test pressure for metal specification cylinders. ISO/UN TDG does not require a pressure relief device and the country of use will apply national requirements. It is likely that the U.S. DOT will require the same PRD provisions for both DOT and ISO/UN TDG cylinders.

CGA S-1.1 was developed for all metal cylinders, but is also used for PRD selection for composite cylinders. Composite gas cylinder specifications contain qualification fire tests to verify the effectiveness of the PRDs that are specified by the designer. It is common to use PRDs activated by the high temperature of the fire rather than by the pressure increase of the contained gas. This is due to the fact that compared to steel, composites have much lower conductivity and also lose strength more quickly when exposed to fire. Experience also indicates that thick composite layers may provide a thermal barrier making it difficult to raise the pressure of the gas inside the vessel and set off the PRD.

Code Case 2390-1 [14] is based on the requirements of ASME Section VIII Division 3 that contains no explicit requirements for pressure relief in a fire. The supplementary manufacturer's responsibilities include "provision for protection due to…fire…under the service conditions…" The Case gives no guidance to determining the effectiveness of such provisions. CGA S1.1, 5.1 General Requirements, includes a warning that "…Pressure relief devices may not prevent rupture under all conditions of fire exposure. When the heat transferred to the cylinder is localized, intense and remote from the relief device; or where the fire builds rapidly such as in an explosion and is of very high intensity, the cylinder may weaken sufficiently to rupture before the relief device operates, or while it is operating."

Given the wide variety of PRD requirements in the reference standards, this analysis does not attempt any comparison based on margin in a fire exposure or consider such pressures in relationship to MNOP. Performance in a fire should be addressed by adopting the requirements similar to those for metal cylinders in accordance with CGA S-1.1 [13] and for composites with performance tests similar to those used to develop CGA S-1.1.

2.8 Burst Pressure

Determining a margin requires that the burst pressure be known. This pressure should be the minimum expected value for a given design. The standards establish minimum burst pressure requirements either with a direct explicit test requirement or by requiring that calculated stress in operation be less that the material strength.

2.8.1 Burst Pressure of Composite Cylinders and Vessels

All of the composite cylinder reference standards require that a representative sample be periodically burst tested. All of these standards also contain no definitive method to calculate a minimum vessel thickness. The burst pressure used in the margin calculation for composite cylinders and vessels is the minimum required in the periodic burst test. It must be emphasized that the susceptibility of composites to stress rupture or creep requires a maximum fiber stress at normal operating pressure (either service pressure for DOT or working pressure for ISO) and this fiber stress is not simply related to the burst ratio.

Where standards include both composite and monolithic metal designs as in the case of ISO 11439 and NGV2, the empirical minimum burst is also applied to the metal cylinders and design formulas are omitted. While the minimum burst pressures are explicit in these standards, they are not completely comparable. The standards contain different requirements for a hold time at the minimum burst pressure, from zero to 60 seconds as well as different limits on pressurization rate in the test. Both of these factors can affect the measured burst pressure to a small degree, but these effects can be accounted for in practice and are ignored in this comparison.

ASME Code Case 2390 is an exception to the normal practice in composite cylinders in that it contains requirements for design calculations based on a composite coupon test rather than a strictly empirical burst test. This design calculation is far more complex than those for metal ASME vessels and is not attempted here. There is also an empirical burst test requirement for the laminate procedure qualification. The minimum burst pressure for Code Case 2390 is 2.0 times the design pressure, but higher pressures may result after taking into account all of the design requirements. The value of 2.0 times design pressure is used in the comparison.

Since all of the reference composite standards require periodic sample burst tests, the minimum burst pressure applies only to the sample vessel, not necessarily all vessels produced. In volume production the manufacturer must provide some margin in addition to the minimum burst pressure to allow for scatter. The minimum sample burst requirement is therefore assumed to be the minimum burst pressure for all cylinders produced.

2.8.2 Burst Pressure of Metal Cylinders and Vessels

This subject is not straightforward in that while the composite gas cylinder specifications require an actual burst test for each design and batch, metal specifications usually do not require an actual periodic test and rely on stress formulas to establish the required wall thickness. Using the design stress formulas to estimate the burst pressure of metal cylinders may be inaccurate, especially in the case of the DOT (Bach) [15] and ISO Lame-Mises [20] formulas used in DOT and ISO specifications and intended to accurately predict only elastic stresses, not representative of burst in a ductile metal cylinder. A preliminary evaluation of the differences between the standards in the way they calculate the margin indicated that a single method of calculating burst pressure was needed to obtain comparable results.

Similar to the sample requirements for composite designs, the strength of metals must be periodically verified during production and the thickness of cylinders verified against the design minimums. The manufacturer must meet these minimums or risk high rework and scarp rates. The minimum calculated burst requirement is therefore assumed to be the minimum burst pressure for all cylinders produced.

The standards for metal vehicle fuel cylinders, starting with NGV2, apply the same performance test to burst margin as is necessary for composites. No design formulas are provided, but the manufacturer must still establish limits on material strength for the design and perform sample material tests as well as sample burst and cycle tests. The required burst margins are very similar to the calculated margins for DOT and ISO metal gas cylinders.

2.8.2.1 Selection of a Single Formula for Calculating Burst Pressure

In order to estimate a comparable burst pressure for the metal designs it is necessary to adopt some common burst calculation formula. In the development of the ISO 9809-1 [20] standard the mean diameter formula derived from Tresca has been used with some modifications to provide results in agreement with empirical tests. In his section on liner burst pressure, Walters [51] discusses this formula and also proposes a formula based on triaxial von Mises yield criteria that is theoretically more rigorous and provides results in agreement with the empirical tests and the modified mean diameter formula at pressures common for current gas cylinders. The Faupel [16] formula was suggested for consideration. A detailed comparison of the various design formulas from the reference standards to the Tresca, Walters, and Faupel burst formulas was carried out over a wide pressure range of MNOP from 625 to 18,750 psi.

The results for a representative design, ASME Section VIII Division 1, Appendix 22, are shown in Figure 1. The ASME Division 3 formula for plastic collapse is intended to predict the pressure at which the entire wall thickness will yield, a reasonable definition of the first stage of bursting in a ductile metal vessel. For the purposes of this comparison the flow stress (mean of yield and tensile strength) was used in the ASME formula to account for some strain hardening and bulging before burst. The Faupel formula is very similar to the ASME but uses the ultimate tensile strength with an added term relating to the yield to tensile ratio. These two formulas and the modified Tresca give linear and very similar results over the complete pressure range. It can be seen that the Bach (DOT) and Lame-Mises (ISO) deviate considerably and predict progressively lower burst pressures as the MNOP is increased. The Barlow and Walters formulas deviate in the opposite direction.

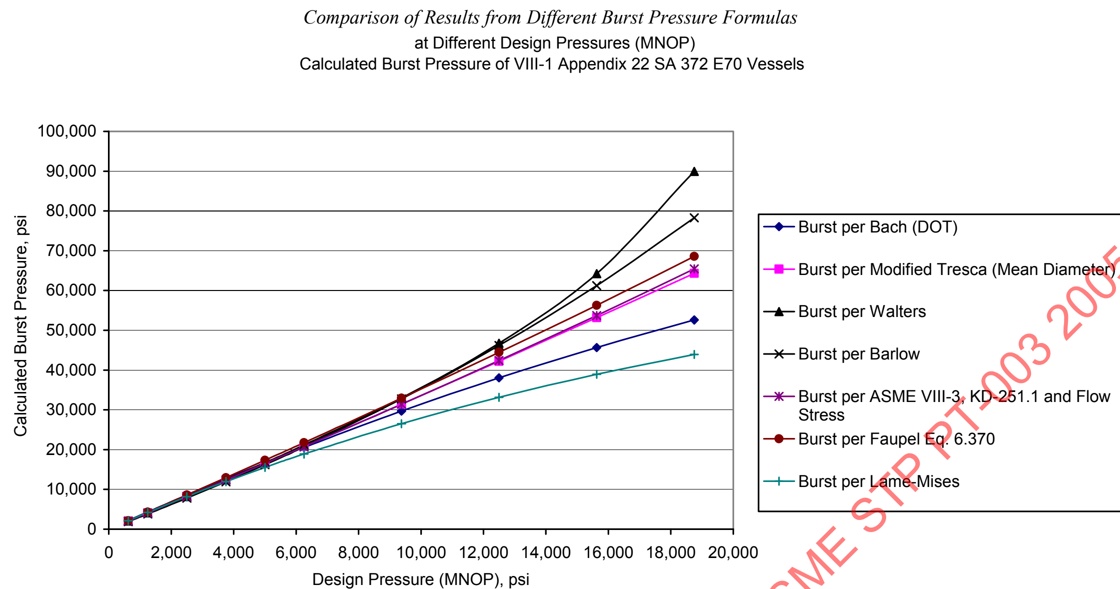

Figure 1 - Comparison of Results from Different Burst Pressure Formulas at Different Design Pressures

It is concluded that the Bach, Lame-Mises, Barlow, and Walters formulas are intended for conventional gas cylinder pressures of a few thousand psi, and should not be used for the comparison of margins at higher pressures. The ASME formula was chosen for the margin comparison because it predicts a burst pressure margin slightly lower than the design margin for DOT-3AA cylinders and because it is inherently familiar to users of the ASME Code. The Faupel formula gives a somewhat higher result, one that is not supported by actual experience in burst testing of DOT-3AA cylinders and is not used for that reason. Based on extensive experience in actual burst tests, minor variables such as the rate of pressure increase or hold time at pressure can account for greater differences in actual burst pressure than are represented by the three different linear burst formulas. Since the intent here is a comparison of burst margins, the critical requirement is that the chosen burst formula gives consistent results across a variety of designs, unlike the various specification design formulas.

Since it is likely that any new rules for metal vessels will be design based rather than strictly performance, the formula used to calculate the burst margin should be validated empirically for the high pressure range.

2.8.2.2 Burst Pressure of ASME Vessels

The burst pressures for ASME Section VIII Division 1 [2] and ASME Section VIII Division 2 [10] vessels in this comparison are calculated based on the minimum design thickness in the cylindrical wall. For ASME Section VIII Division 3 [11], the burst calculation is based on the minimum wall thickness in the cylindrical portion to meet the minimum collapse requirement of 1.732 times design pressure per KD-240. This is the simplest requirement in Division 3, but all of the other requirements are based on detailed assumptions about layering and autofrettage and cannot be addressed without detailed knowledge of a particular design.

(a) ASME Material Properties Assumption

All design thickness and materials properties for ASME vessels are dependent on the specific material of construction. High-pressure ASME vessels are commonly designed using SA-372 quenched and tempered forgings. SA-372 E70 [17] is used as the reference material specification for all ASME vessel calculations in this analysis. This minimizes material differences with the gas cylinder standards because SA-372 E70 is very similar in composition and heat treatment to the common 4130X alloy steel used in DOT cylinders and the 34 CrMo 4 steels that are common for ISO cylinders. SA-372 E70 represents a reasonable choice for compliance with the hydrogen compatibility requirements of IGC Document 100/03/E.

(b) ASME Design Margins

The ASME Section VIII Code does not use a consistent approach to establishing design margins across all three divisions. Neither Division 1, with the exception of Appendix 22, nor Division 2 contains an explicit design margin. Instead the margins are provided by defining the allowable design stresses in Section II Part D as some fraction of ultimate or tensile strength. These margins are 3.5 for Division 1 and 3.0 for both Appendix 22 and Division 2. Division 3, KD-240 (a) does have an explicit requirement for design margin in burst, 1.732 times design pressure for plastic collapse. This calculation is based on the minimum specified yield strength from ASME Section II Part D.

There is one significant issue with using the material properties listed in ASME Section II Part D [18] for SA 372 E70 in calculating burst pressures or in calculating collapse pressures as required in VIII Division 3. The minimum tensile strength is specified at 120,000 psi, but the minimum yield strength is specified at 70,000 psi. This allows a yield to tensile (Y:T) ratio as low as 58.3%. This is not realistic for quenched and tempered 4130. As a general approximation, the yield to tensile ratio of 4130 gas cylinders and pressure vessels is estimated at 88% for a tensile strength of 120,000 psi. The unrealistically low yield strength value in Section II does not affect the wall thickness in Divisions 1 and 2 where the design stress is a function of tensile strength, but it does affect the wall thickness in Division 3 where yield strength is used. An accurate estimate of yield strength is also important for the calculation of the burst pressure. Both yield and tensile strength are used in the burst calculation. If the actual yield strength is 88% of tensile instead of the 58.3% value in Section II, the mean stress at burst will be 18.7% higher than that calculated from Section II values. This analysis uses yield strength equal to 88% of the tensile strength for calculating burst pressures of all steel cylinders and vessels.

A second issue relating to ASME burst pressures is the potential to revise the minimum yield strength in Section II or to allow the use of actual yield strength in the design of new Code vessels. Either of these approaches is technically more valid than the present requirement. Since a new steel alloy can be added at any time and the minimum yield strength of that alloy may be accurately estimated in Section II, a design designated VIII-3 372 NEW is included in the analysis. This design assumes the use of actual yield strength, estimated at 88% of the tensile strength in the design calculations as well as the burst pressure calculations.

2.8.3 Burst Pressure for DOT Metal Gas Cylinders

DOT does not require a burst test for DOT-3AA or 3AAX [19] cylinders and the burst pressure must be calculated from the design minimum wall thickness as determined in accordance with the specification for the maximum allowable wall stress. The minimum tensile strength (104,478 psi) for that thickness is used and the yield strength is estimated at 88% of the tensile strength. Although there are several steel compositions permitted under DOT-3AA, 4130X is by far the most common and as discussed previously is very similar to both the common ASME and common ISO alloys.

The DOT-3AA or 3AAX specifications are the only standards in the comparison that do not permit a minimum design tensile strength of 120,000 psi. This is probably a result of the age of the specification, and the basic design approach should be valid with a higher tensile strength as long as the safe limit for hydrogen compatibility is not exceeded.

2.9 Burst Pressure of ISO Metal Gas Cylinders

A design qualification burst test is required for ISO 9809-1 [20]/UN TDG [7] portable metal gas cylinders, but this may not be defined as a minimum design value since it is a one-time test of a representative, not minimum, sample. Composite specifications typically require a burst test for each lot of 200 cylinders and this will force the manufacturer to treat the burst requirement as a minimum design value or risk lot failures. ISO 11120 [21] for trailer tubes does not require a burst test but has basic thickness requirements identical to those of ISO 9809-1 and is therefore not treated separately. The design thickness is a function of the ultimate tensile strength. Material compatibility is required in accordance with ISO 11114-1 [22]. The maximum tensile strength of the 34 CrMo 4 steel that is very similar to SA 372 E70 and 4130X is 950 Mpa (137,775 psi) for cylinders used in hydrogen service. A minimum tensile strength of 120,000 psi is used in calculating the thickness of ISO cylinders and the yield strength is estimated at 88% of the tensile strength.

2.10 Summary of Margin Definitions

The comparison is based on the following definitions:

(a) The margin is defined as the ratio of the minimum burst pressure to the maximum pressure in normal operations, MNOP.

(b) For metal cylinders, the minimum burst pressure is calculated from the minimum thickness and minimum material strength using the ASME Section VIII Division 3 collapse formula and flow stress as the mean of yield and tensile strength for metal cylinders and vessels.

(c) Burst pressure for composite cylinders and vessels is equal to the minimum value required by the standard for periodic production burst tests.

(d) Margins are compared at a pressure equivalent to MNOP of 3,750 psi.

(e) The Maximum Normal Operating Pressure (MNOP) is equal to design pressure for ASME vessels.

(f) MNOP for transport vessels is equal to the DOT required maximum pressure in a full cylinder at 55°C for all gas cylinder standards.

(g) MNOP for vehicle fuel cylinders is equal to the maximum pressure permitted at fill.

2.11 Composite Stress Ratio Margins for Composites

Composite stress ratios are defined in terms of calculated stress at burst pressure compared to calculated stress in service. DOT FRP-1, FRP-2, and CFFC define the allowable service stress as a percentage of the stress at burst pressure, 30% for FRP-1 as an example. NGV2 and the ISO standards express the margin as stress at burst pressure divided by stress in service, 3.5 for glass Type 3 designs as an example. The ANSI/ISO definition of stress ratio was selected here because it relates more easily to the simpler but similar burst margin. These stress ratios are calculated against normal operating pressure, NOP, defined as follows.

(a) For gas cylinders NOP is the pressure of the contents at 21°C.

(b) For stationary pressure vessels subject to continuous control over operating pressure, NOP is equal to MNOP.

2.11.1 DOT-3AA Specification Margin

DOT-3AA contains no requirement for verification of design margin by burst testing. As a result there is no need for any added margin in either thickness or strength in addition to the minimum calculated numbers and manufacturers routinely ship cylinders down to and at the minimum design values. Additionally it must be recognized that the minimum tensile strength is only the lowest measured in two specimens from one cylinder out of each 200-piece lot. Lots are acceptable at the minimum, but it is readily understood that normal variation within the lot, or even within the piece, make it virtually certain that some members of a lot accepted with minimum properties will have actual properties below the minimum.

2.11.2 DOT-3AA Margins Further Reduced

Emergency provisions were put into effect during World War II to allow DOT 3A and 3AA cylinders to be filled to 110% of their marked service pressure. This wartime expedient was successful and is still in effect [5]. Hydrogen is permitted by exemption [23] under these provisions for DOT 3A, 3AX, 3AA, and 3AAX.

2.12 Findings from Comparison of Margins between Different Standards

Table 1 summarizes the results of the margin analysis of ASME Section VIII Divisions 1, 2 and 3 vessels in comparison with the other reference standards for gas cylinders and pressure vessels. The following explanatory notes will help in interpreting the information.

The ISO practice in fuel tank standards of establishing a unique burst margin requirement dependent on the type of reinforcing fiber results in a large number of ISO design entries. It appears that both fiber stress ratios and burst margins were adopted, probably to reflect different forms of construction, satisfy regulators, or to satisfy diverse opinions. This is a complication but reflects the actual complexity of design for materials that are susceptible to stress rupture.

The columns and assumptions used in Table 1 are now presented in more detail:

(a) Column 1, Standard of Construction

The various standards for comparison are listed in the first column. ISO 11439 and ISO DIS 15869 contain minimum burst pressures that vary with reinforcing fiber type as noted in the suffix added after the standard designation: g = glass, a = aramid, c = carbon.

The composite vessel type follows the convention established in NGV2. The type is shown as a suffix to the various ANSI and ISO standard designations and is combined with an alpha code to designate the fiber type; glass, aramid or carbon, for Types 2, 3, and 4:

(1) Type 1 cylinders are all metal designs.

(2) Type 2 are metal-lined composite reinforced designs with load sharing liners that can alone resist the operating pressure, normally termed hoop-wrapped.

(3) Type 3 are metal-lined composite reinforced designs with load sharing liners that alone cannot resist the operating pressure, normally termed full-wrapped.

(4) Type 4 cylinders are plastic lined full-wrapped designs.

(b) Column 2, DP Design Pressure Ratio to Design Burst Pressure BPD:DP

The design pressure definition varies with the type of standard as previously discussed. For ASME vessels it is the ASME design pressure. For DOT cylinders it is the service pressure. For ISO cylinders it is the working pressure defined as 2/3 of the hydraulic proof test pressure. For composite designs and metal fuel tanks all of which depend on a periodic burst test to establish the burst pressure, the margin specified in the standard is entered. For metal designs not fuel tanks, the margin is based on the particular wall stress calculation formulas that are included in each standard.

Table 1 - Margin Comparison for Various Gas Cylinder and Vessel Standards

1	2	3	4	5	6	7	8	9
Standard of Construction	**DP Design Pressure Ratio to Design Burst Pressure BPD:DP**	**MNOP Pressure Ratio to Design Pressure MNOP:DP**	**Margin Burst Design Burst Pressure to MNOP BPD:MNOP**	**Margin Calculated Burst Pressure to MNOP BPC:MNOP**	**Difference between Design and Calculated Margins**	**Glass Stress Ratio Burst to Design**	**Aramid Stress Ratio Burst to Design**	**Carbon Stress Ratio Burst to Design**
DOT FRP 1	3.000	1.250	2.400	N/A	N/A	3.33	N/A	N/A
DOT FRP 2	2.500	1.250	2.000	N/A	N/A	2.50	N/A	N/A
DOT CFFC	3.400	1.250	2.720	N/A	N/A	N/A	N/A	3.33
DOT 3AA	2.488	1.375	1.809	1.721	5.1%	N/A	N/A	N/A
IGC/ISO 9809-1	2.308	1.275	1.810	1.791	1.1%	N/A	N/A	N/A
ISO 11119-1	2.500	1.275	1.961	N/A	N/A	2.50	2.40	2.40
ISO 11119-2	3.000	1.275	2.353	N/A	N/A	3.40	3.10	2.40
ISO 11119-3	3.000	1.275	2.353	N/A	N/A	3.40	3.10	2.40
NGV2-1	2.250	1.250	1.800	N/A	N/A	N/A	N/A	N/A
NGV2-2	2.250	1.250	1.800	N/A	N/A	2.65	2.25	2.25
NGV2-3	2.250	1.250	1.800	N/A	N/A	3.50	3.00	2.25
NGV2-4	2.250	1.250	1.800	N/A	N/A	3.50	3.00	2.25
ISO 11439-1	2.250	1.326	1.697	N/A	N/A	N/A	N/A	N/A
ISO 11439-2g	2.500	1.326	1.885	N/A	N/A	2.75	N/A	N/A
ISO 11439-2ac	2.350	1.326	1.772	N/A	N/A	N/A	2.35	2.35
ISO 11439-3g	3.500	1.326	2.640	N/A	N/A	3.65	N/A	N/A
ISO 11439-3a	3.000	1.326	2.262	N/A	N/A	N/A	3.10	N/A
ISO 11439-3c	2.350	1.326	1.772	N/A	N/A	N/A	N/A	2.35
ISO 11439-4g	3.500	1.326	2.640	N/A	N/A	3.65	N/A	N/A
ISO 11439-4a	3.000	1.326	2.262	N/A	N/A	N/A	3.10	N/A
ISO 11439-4c	2.350	1.326	1.772	N/A	N/A	N/A	N/A	2.35
VIII-1	3.499	1.000	3.499	3.843	-9.0%	N/A	N/A	N/A
VIII-1, APP 22	3.000	1.000	3.000	3.290	-8.8%	N/A	N/A	N/A
VIII-2	3.000	1.000	3.000	3.259	-7.9%	N/A	N/A	N/A
VIII-3, 372 E70	1.732	1.000	1.732	2.791	-37.9%	N/A	N/A	N/A
VIII-3 New 372a	1.732	1.000	1.732	1.850	-6.4%	N/A	N/A	N/A
CC2390, VIII-3	2.000	1.000	2.000	N/A	N/A	2.78	N/A	N/A

Note: ISO/DIS 15869 is not presented in the table above since the results would be nearly identical to those for ISO 11439.

N/A = not applicable.

(c) Columns 3, MNOP Pressure Ratio to Design Pressure MNOP:DP

The relationship between MNOP, maximum normal operating pressure, is defined in relation to DP or design pressure for the different standards.

(d) Column 4, Margin Burst Design Burst Pressure to MNOP BPD:MNOP

This column contains the margin between design burst and MNOP obtained by dividing the values in Column 2 by the factors in Column 3.

(e) Column 5, Margin, Calculated Burst Pressure to MNOP BPC:MNOP

This column contains margins between MNOP and burst pressures that have been calculated using either the minimum periodic burst test pressure if such is specified in the standard or a calculated burst pressure using a single formula regardless of the standard of construction. This method eliminates the variations in design margin that result from the different standard design formulas but are not true differences between designs. The formula used to calculate the burst pressures is the plastic collapse formula from ASME Section VIII Division 3.

(f) Column 6, Difference between Calculated and Design Margins

This column shows the difference in percent between the burst margin calculated with a single common formula and the burst margins calculated using the design formulas of each individual standard.

(g) Columns 7, 8, and 9

Columns 7, 8, and 9 show the fiber stress ratios required in the various composite cylinder standards. As discussed elsewhere, these ratios are not simply related to the burst margins but result from the interpretation of burst test results using proprietary stress analyses, commercially available finite element analysis, or by using strain gages. They are included here as convenient reference for that discussion.

The U.S. DOT establishes and enforces detailed requirements for the periodic retest or inspection of all gas cylinder used for transportation in the US. For ISO cylinders DOT is expected to incorporate the UN TDG requirements by reference.

2.13 Conclusions from Comparison of Margins

2.13.1 DOT FRP-1 Anomaly

The margin for DOT FRP-1 is not representative of actual feasible designs. In addition to the minimum requirement for a burst pressure of 3.0 times service pressure (NOP) with a 1-minute hold, DOT FRP-1 also requires that the composite fiber stress at service pressure be no more than 30% of the stress at actual burst pressure. This results in an approximate minimum design burst pressure of 3.5 times service pressure. NGV2 and ISO 11119 glass designs are similarly affected as discussed later.

2.13.2 Selection of Calculated over Design Margins for Metal Designs

Using DOT-3AA as an example, the margin of burst over MNOP calculated using the Bach (DOT) stress formula is 1.809 compared to a calculated margin using the ASME Division 3 collapse formula of 1.732 It is well established that the Bach formula will predict a slightly higher burst pressure for DOT-3AA cylinders than will be obtained in actual tests of cylinders with minimum thickness and minimum tensile strength. The ASME formula is considered more accurate in this regard. In this case, the design burst ratio is at least 5.1% higher than would be expected in a test.

Using ASME Section VIII Division 1 Appendix 22 as a second example, the margin using the design sidewall calculation is 8.8% less than the margin resulting from the Division 3 collapse formula.

If the standards were compared simply using the margins inherent in the different design calculations, the deviation between ASME Appendix 22 and DOT-3AA margins as actually expected in burst tests would be more than 14%. For this reason, the calculated margins that are independent of the variations in design formulas are used in all subsequent discussions of margins in this report. This approach allows a more accurate comparison with the burst test margins of the various composite cylinder standards. Figure 2 shows the varying differences between design margins and calculated margins for the different metal vessels.

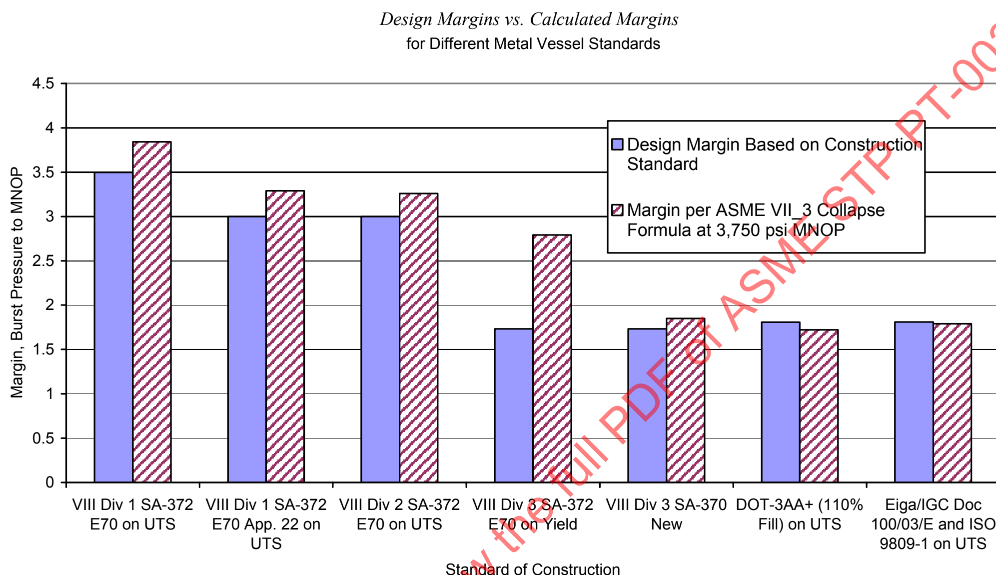

Figure 2 - Design Margins vs. Calculated Margins for Different Metal Vessels

2.13.3 Primary Factors Affecting Margins

The margins in the various standards appear to depend primarily on two factors, the category of use, including periodic examinations and tests, for which the standard vessel is intended and the properties of the vessel primary structural materials, particularly with respect to time-dependent failure modes such as stress rupture and creep, and also susceptibility to fracture failure. Additional factors, including level of maturity of the standards, allowable materials, and the size of the cylinders, may also play a role, but are not discussed further within this report.

2.13.3.1 Margins by Use Category

For all existing gas cylinders intended as containers for compressed gases in transportation, the minimum margin between burst and MNOP is 1.721 for the DOT-3AA/3AAX specification.

For Type 2 Composite reinforced gas cylinders intended as containers for compressed gases in transportation, the minimum margin between burst and MNOP is 1.961 for the ISO 11119-1 standard. The margin for the DOT FRP-2 standard is very similar at 2.000.

For Type 3 Composite reinforced gas cylinders intended as containers for compressed gases in transportation, the minimum margin between burst and MNOP is 2.353 for the ISO 11119-2 standard.

The margin for the DOT FRP-1 standard is very similar at 2.400. The DOT CFFC margin is significantly higher at 2.720. It should be noted that as discussed previously, the fiber stress ratio requirements of FRP-1 drive the required burst pressure above 3.0 times service pressure to about 3.5 times service pressure. This value translates to a margin at MNOP of 2.80.

For Type 4 Composite reinforced gas cylinders intended as containers for compressed gases in transportation, the only margin between burst and MNOP is 2.353 for the ISO 11119-3 standard.

For all gas cylinders intended to be installed on motor vehicles as fuel tanks the minimum margin between burst and MNOP is 1.697 for ISO 11439 Type 1.

For Type 2, 3, and 4 gas cylinders intended to be installed on motor vehicles as fuel tanks the minimum margin between burst and MNOP is 1.772 for ISO 11439 Type 2, 3, and 4 gas cylinders with carbon composite.

For ASME Code vessels of SA-372 E70 material intended for stationary installation as storage vessels, the minimum margin between burst and MNOP is 2.791 for Division 3. The Division 1 margins are 3.843 and 3.290 (Appendix 22). Division 2 margin is 3.259.

For ASME Type 2 Code Case 2390 vessels intended for transportation of compressed gases aboard vessels and barges the margin between burst and MNOP is 2.00. This should be taken as a rough estimate because there are many design details that in combination with the maximum composite stress limitation may result in significantly higher margins in a particular actual design.

2.13.3.2 Margins by Materials Category

Viewing the margins from the standpoint of structural material properties categories addresses the second major independent variable. Since the category of stationary storage vessels is entirely represented by all metal ASME Section VIII vessels, they are not included in this comparison of material affects on margin.

Metal vessels constructed entirely of material that is not susceptible to stress rupture or creep have the lowest margins in each category of use.

Composite vessels dependent on glass fiber composites for a large portion of their strength, Types 3 and 4, have the largest margins in each category of use. NGV2 and ISO 11119 do not yield any directly comparable values for Type 3 and Type 4 glass vessels. The minimum burst pressure requirements for ISO 11119 and NGV2 cylinders can be considered highly accurate estimates only for Type 1 and carbon wrapped Type 4. The composite stress ratio requirements that apply in parallel with the absolute minimum burst requirement will generally require design minimum burst pressures above the minimum burst pressures stated in the standards for designs with load-sharing metal liners. The effect is relatively small for Type 2 designs and carbon-reinforced designs but quite large for glass wrapped designs. Hybrids using a mix of carbon and glass will be affected in proportion to the fiber mix. The only standard now in effect with a reasonably accurate burst pressure specification for these cylinders is ISO 11439 with margins of 2.64. This is probably quite close to the actual margin required to meet the fiber stress limit in DOT FRP-1. The margin for glass reinforced Type 3 and 4 cylinders is controlled by the stress ratio requirement and appears to be independent of the category of use, being about 2.64 for either transportation or vehicles.

Carbon fiber designs that depend on the composite for most of the vessel strength vary the most depending on the category of use. All carbon fiber vehicle fuel cylinder designs of both Types 3 and 4 have low margins from 1.772 for ISO 11439 to 1.800 for NGV2. For transport cylinders, the margin varies from 2.252 for ISO 11119 Types 3 and 4 to 2.720 for DOT CFFC Type 3. The mean ISO/ANSI fuel cylinder margin is 40% less that the mean ISO/DOT transport cylinder margin. This difference may be the result of the difference in physical protection provided in service to fuel cylinders and gas cylinders [49].

2.14 Summary of Comparative Margins

A significant factor affecting the margin appears to be the intended usage and life of the vessel.

2.14.1 ASME Code Vessels

ASME code vessels for stationary installations have by far the largest margins but three other factors must be considered.

The weight of a stationary vessel is typically of minimal concern once it is installed and this provides little impetus for more weight-efficient Code designs. However, new hydrogen infrastructure applications may require weight efficiency, even for stationary installation (e.g., refueling station roof installations).

ASME Code vessels should operate without any life limit and without any uniformly applied periodic examination or retest requirement. However, ASME Section VIII Division 2 and 3 vessels have a design fatigue life that is specified by the user, and it is expected that the vessel will be examined or retired at the end of this life. While some jurisdictions require periodic vessel inspections, this is not a uniform practice.

ASME design rules allow complicating and stress concentrating features that are not permitted in gas cylinders. The common provision of a drain opening in the dome near the sidewall in Appendix 22 vessels is an example.

2.14.2 Gas Cylinders for Transportation

Gas cylinders for transportation of compressed gases have margins much lower, about one half of the current ASME Section VIII margins.

Gas cylinders for transportation of compressed gases are used under strict U.S. federal regulations [24] governing inspection, charging, retest and protection in shipment. Additionally, there are use limits on the product that can be carried in the cylinder, while ASME Section VIII leaves the application to the designer and user.

Gas cylinders for the transportation of compressed gases have also been designed with weight as a consideration.

Gas cylinders for the transportation of compressed gases must withstand casual damage in handling and shipping without failure.

2.14.3 Gas Cylinders for Vehicle Fuel Tanks

Gas cylinders for vehicle fuel cylinders have margins that vary from slightly lower than those for gas cylinders used in transportation to 30% lower for composite designs incorporating carbon fiber.

Gas cylinders for vehicle fuel are incorporated into the vehicle structure with the additional requirement that they be protected from vehicle cargo, mechanical damage, and collision impact [56]. This is a significant departure from the shipping conditions for transport gas cylinders and trailer tubes that must resist these factors without external protection barriers.

NGV2 gas cylinders for vehicle fuel have also typically been designed to supplementary original equipment manufacturer (OEM) vehicle specifications that sometimes add to or make more stringent the requirements of the base standard. In the common light-duty vehicles and school buses, the entire vehicle is subject to federal fuel system integrity requirements that include a variety of crash tests for resistance to, or protection from, impact [55].

Weight efficiency is also a concern for vehicle fuel tanks.

3 MANUFACTURING AND IN-SERVICE INSPECTION AND TEST PRACTICES IMPACTING MARGINS

This section includes a discussion of current and potential inspection and test practices with recommendations by vessel type and material of construction. Requalification methods including proof testing, visual inspection, and other more advanced forms of NDE are discussed in the context of specific design types. Failure modes are also taken into account in recommending inspection methods. A basic methodology for approval of NDE methods on the basis of performance tests is presented to help validate new techniques for specific vessel types.

This information was also used in considering the later recommendations for margins. The scope for this study includes recommended margins with and without periodic requalification. The recommended margins are based on the inspection and test capability for a given design and material combination.

3.1 Review of Existing Inspection

The ASME Boiler and Pressure Vessel Code committee has formed a project team to develop code rules for pressure vessels used to store hydrogen, with pressures ranging from 3,600 to 15,000 psi. Periodic requalification is a major way of limiting that degradation and inspection is therefore relevant to the standard margins. As input to these standards, guidance and recommendations on the testing and retesting of cylinders is required. These recommendations should address inspection in service and also at manufacture. ASME also plans to address, as part of a parallel effort, the issue of in-service inspection of these vessels.

3.2 Review of Existing Inspection Techniques for Metal Cylinders

Required retesting of DOT metal high-pressure cylinders in service has been performed by a combination of visual inspection, hydrostatic pressure testing and volumetric expansion during pressurization. The cylinders were rejected due to leaking, bursting, excessive volumetric expansion or flaws detected with the visual inspection [25][26].

Although the appropriateness of the hydrostatic test for cylinder retesting has been questioned, it is an excellent quality control test at manufacture. Small changes in the volumetric expansion can indicate manufacturing problems either in the heat treatment or autofrettage of metal-lined cylinder or problems in the fabrication or filament winding of composite cylinders.

The hydrostatic and visual test methods for retesting cylinders are widely used in many of the cylinder standards. It is required as part of most of the U.S. Department of Transportation (DOT) standards [27] and the inspection interval and test pressure are set according to the service history and design margins. A summary of the hydrostatic retest provisions for DOT cylinders is given in the following table.

The DOT 3AA cylinder is often used to store hydrogen, and provided that it has a water capacity less than 125 lb, it may be requalified every 10 years. The hydrostatic test has worked well for cylinders in this type of service, where general corrosion and/or exposure to heat are often the critical forms of damage. This type of damage produces wall thinning or weakening, which will be readily detected with the hydrostatic test, particularly if it is performed at stresses close to the yield strength. The value of this approach is apparent from the excellent safety record of DOT cylinders - not a single failure has been reported, due to gas pressure and cyclic fatigue, in over 60 years of service [28].

Table 2 - Requalification of Cylinders According to 48 CFR 180.209

Specifications Under Which Cylinder Was Made	Minimum Test Pressure	Requalification Period
DOT 3	3,000 psig	5 years
DOT 3A, 3AA	5/3 times service pressure	5, 10, or 12 years depending on service
DOT 3AL	5/3 times service pressure	5 or 12 years
DOT 3AX, 3AAX	5/3 times service pressure	5 years
3B, 3BN	2 times service pressure	5 or 10 years
3E	Test not required	
3HT	5/3 times service pressure	3 years
3T	5/3 times service pressure	3 years
4B, 4BA, 4BW, 4B-240ET	2 times service pressure	5, 10, or 12 years depending on service

The value of the hydrostatic test for screening subcritical cracks is not as straightforward. It is dependent on the crack size and geometry, the material properties and the test pressure. This has never been a major concern for most DOT type cylinders since for these applications the number of pressure cycles is normally low, and the material property limitations will prevent stress corrosion cracking. However, for cylinders in higher cycle hydrogen service (such as refueling station storage) subcritical crack growth could be an important consideration.

Cylinders that have low fracture toughness may be good candidates for the hydrostatic test to detect subcritical cracks. In fact, service history in the pipeline industry shows the value of the hydrostatic test in screening older pipe materials for subcritical cracks. In one case [29] the operator reported that before instituting hydrostatic testing on older pipe materials they experienced over 30 failures in one year. Since the hydrostatic test program was instituted in 1972 there has not been an in-service failure.

For newer steels, with higher fracture toughness, the hydrostatic test may be a much poorer screening tool for subcritical flaws. Deep semi-circular cracks in tough materials will not fail in the hydrostatic test. In particular, cracks in thin-walled vessels, where the fracture toughness is high, (since the crack is in predominately plane stress), will not fail under a hydrostatic test. Therefore the hydrostatic test is a poor test for screening cracks in thin-walled vessels, made from tough steels. However for thicker walled vessels, with higher strength steels, and lower fracture toughness values the hydrostatic test may be a valuable screening test for cylinder integrity.

For cylinders with high fracture toughness, which cannot be adequately screened with hydrostatic test, the failure mode is likely to be Leak-Before-Break (LBB). Therefore the inadequacy of the hydrostatic test is alleviated by the benign failure mode. For these cylinders, a catastrophic failure is only possible for long shallow flaws (typically with a length to depth ratio greater than 10). This discussion on the merits of the hydrostatic test highlights that a one-size fits all approach may not be appropriate for these cylinders and that the actual use of the hydrostatic test will depend on a fitness for service analysis that considers the material properties, the service conditions, the test frequency and pressure and also the role of inspection at manufacture.

These newer cylinders with higher strength and minimum toughness should be designed to fail due to fatigue in the sidewall. If this is not the case, fracture analysis, LBB and NDE all become much more complex.

To detect cracks in these vessels other techniques can be used. In particular, methods for retesting metal cylinders by ultrasonic testing (UT) have been developed and have been granted exemptions by the U.S. DOT [30]. These techniques were originally developed for wall thickness measurements but they are also capable of detecting subcritical cracks in these vessels. The results from these tests showed that UT is a sensitive technique for the detection of most forms of damage in these cylinders, including localized thin areas, pitting, corrosion, and also preexisting defects. The advantage of this technique is that it is also capable of detecting small subcritical cracks that may not be detectable with the hydrostatic test.

The other inspection technique that has been used for metal cylinders is Acoustic Emission (AE) in combination with UT. Acoustic Emission has been used in place of the hydrostatic test for retesting tube trailers [31]. These tests have been performed since the mid-1980s under a number of exemptions granted by the DOT. AE is used to locate the site of the emission and a follow up UT examination is performed on this region of the vessel. This approach works well for long tube trailers since this geometry makes it relatively straightforward to locate the source of the emissions using AE.

For other standards, such as the ANSI/CSA NGV2 [32] standard for compressed natural gas vehicle fuel containers, the requirement for all-metal cylinders is that a visual inspection be performed every 3 years. This visual inspection must be performed using the Compressed Gas Association (CGA) standard CGA C-6.4 [33]. In this standard the visual inspection must detect corrosion and other surface damage to the cylinder. The internal surfaces of the cylinders are not inspected and therefore internal fatigue cracks will not be detected.

Although no internal inspection is performed, there have been no known failures of metal cylinders in NGV service that can be attributed to cyclic fatigue. Fatigue failures have occurred in metal cylinders [34] but these have always involved the presence of large preexisting flaws that would be screened with an ultrasonic inspection at manufacture, or poor designs that did not account for the transitions between the metal sidewall and the domes. The low number of failures may also be a consequence of very low number of actual refueling cycles that most of these cylinders have experienced in NGV service. The standards are designed for a maximum of three refueling cycles per day, whereas in reality CNG cylinders in NGV service rarely experience more than one refueling cycle per day. In fact a review of CNG cylinder after 10 years of service found the internal condition of the cylinders to be excellent [35] with no evidence of fatigue cracking or corrosion.

For cylinders in hydrogen service that may experience high numbers of actual filling cycles, internal fatigue cracking may be a concern. Although definitive data is yet to be developed, it must be anticipated that exposure to high-pressure hydrogen will adversely affect the fatigue life of many metals used in cylinders. Any inspection technique must detect this critical form of damage or the design must accommodate this mode of failure. For all-metal cylinders the following table gives a summary of the inspection methods used in the different standards.

The above discussion has considered the retest requirements. At manufacture a hydrostatic test must be performed on every cylinder since this is part of the cylinder quality control. The requirements for UT at manufacture are a little more complex and depend on the type of service and jurisdiction; and these requirements are summarized in Table 3.

Table 3 - Inspection Standards for All-Metal Cylinders Used in Hydrogen Service

Standard	Recommended Inspection Method	Recommended Inspection Interval	Comments
DOT 3A, 3AA	Hydrostatic and visual or ultrasonic	10 year	User can choose hydrostatic or UT
CSA NGV2	Visual inspection	3 years	
DOT Tube Trailers	Hydrostatic or AE/UT under exemption	5 years	

As can be seen in Table 4, in the United States, only higher strength steel cylinders are required to undergo a UT examination and hydrogen cylinders have strength levels below the 135 Ksi cutoff for mandatory UT at manufacture. Therefore, cylinders in hydrogen service in the United States do not require a UT examination. In contrast all new European cylinders in hydrogen service are required to undergo a UT inspection at manufacture.

Table 4 - UT Inspection Requirements at Manufacture for Metal Cylinders

Standard Authority	Standard	Recommended Inspection
DOT [28]	49 CFR Part 107	UT only required for cylinders with strength in excess of 135 Ksi
ISO	Standard 9809-1	UT required on all cylinders
EIGA (European Industrial Gases Association) [36]	IGC Document 100/03/E	UT required on all cylinders

3.3 Review of Existing Inspection Techniques for Composite Cylinders

For composite cylinders, reviewing the inspection requirements is more difficult. This is due to the fact that in some cases the composite cylinders designs and materials are relatively new and the actual failure modes may not be comprehensively understood. Furthermore, damage to composites may be more difficult to detect with NDE techniques. In view of these difficulties the U.S. DOT is currently investigating a range of NDE techniques for requalifying high-pressure composite gas cylinders [37].

For composite tanks the hydrostatic and visual test are currently the primary inspection methods that are required by the U.S. DOT according to FRP-1 and FRP-2 and the individual exemptions. A visual inspection standard has also been developed [38] by the Compressed Gas Association in order to support these inspections. For these cylinders the retest provision has traditionally been every 3 years although in some cases this has been extended to 5 years under individual exemptions. Furthermore, the U.S. DOT requires that an inspection by performed on a composite cylinder prior to every refill.

This approach to composite cylinder integrity has, in general, provided good outcomes, with few failures. This is because for composite cylinders the critical damage is external and this damage will be detected with a visual inspection. Furthermore the hydrostatic test can detect some other forms of damage such as stress rupture as a result of long-term degradation of fiber strength, a well-known failure mode in glass composites.

The visual inspection has also been used for inspection of composite cylinders in Natural Gas Vehicle service. In this case a visual inspection is performed on the cylinders using the Compressed Gas Association standard CGA C6.4 [33]. The results from this inspection have also been positive. The visual inspection has been shown to be capable of detecting most forms of damage to the cylinders and this is also highlighted from the failure data for these cylinders as shown in Figure 3. Figure 3 shows the number of NGV cylinder failures in the United States. The failure in 2002 was a steel cylinder whereas most of the failures in the 1990's were composite cylinders. As a result of these failures, in 1998 a national cylinder inspection program was implemented that provided standards and training for cylinder inspectors. As shown in the figure there have been no cases of composite cylinder failures since this program has been implemented.

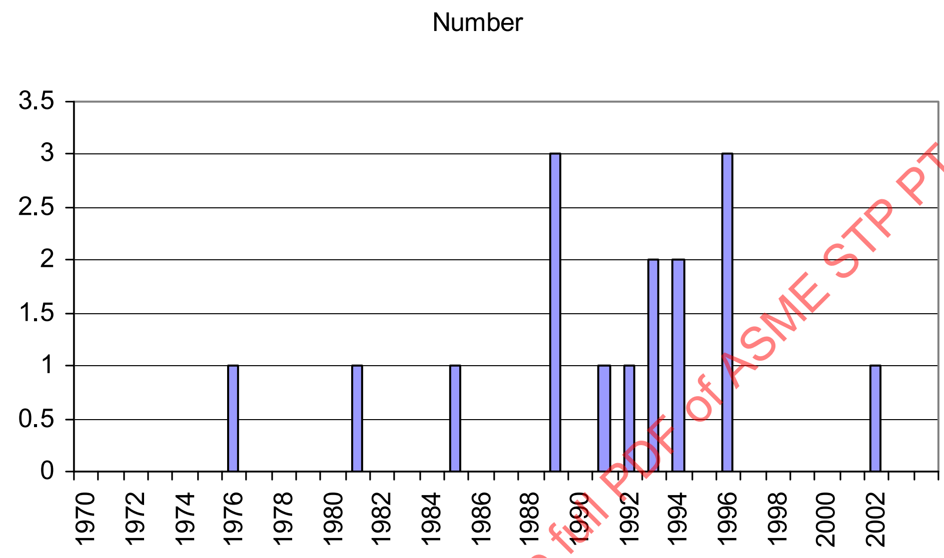

Figure 3 - Chart Of CNG Cylinder Failures in the United States Since 1970

Although Figure 3 shows the substantial improvement in the service experience of composite cylinders since the implementation of the visual inspection program, not all of service experience is as a result of the improvements in the construction standards and installation requirements for cylinders used in NGV service.

Although these results attest to the value of a visual inspection, it is possible that the number of composite cylinder failures may increase as these cylinders reach the end of their design life. In particular, visual inspection cannot detect some of the critical forms of damage in these composite cylinders. For example, stress-rupture or impact damage to internal laminate plies may not be detectable with a visual inspection, and these effects may cause failures of these cylinders in the longer term.

It is clear that for the composite cylinder inspection a reliable inspection approach may be required to supplement the visual inspection and to detect some of the critical, nonvisible, forms of damage in these cylinders. Although the experience with the visual inspection of NGV cylinders has been good, the limited service experience of these composite cylinders in NGV service has not been extrapolated to predict the behavior of these composite cylinders in hydrogen infrastructure service.

3.4 Applicability and Limitations of Various NDE Techniques to Specific Vessels

The various NDE techniques described above will be discussed with reference to the following vessel types:

(a) Metal monobloc or layered vessels of steel or nonmagnetic alloys.

(b) Composite hoop-wrapped vessels with seamless or welded liners of steel or nonmagnetic alloys.

(c) Composite full-wrapped vessels with seamless or welded liners of steel or nonmagnetic alloys.

(d) Composite full-wrapped vessels with seamless or welded nonmetallic liners and metal bosses of steel or nonmagnetic alloys.

3.5 Metal Monobloc or Layered Vessels of Steel or Nonmagnetic Alloys

For this cylinder type, termed here all metal, many of the inspection techniques have been developed and validated as part of the DOT and international cylinder standards. Furthermore the failure modes are well understood and the inspection technique can be tailored to the specific type of damage. For example, if crack growth is life limiting then UT can be used to detect these subcritical cracks before catastrophic failure occurs.

For metal cylinders there are four primary inspection techniques that have been used and these are visual, hydrostatic, UT and AE. The benefits and limitations of each of these techniques for the inspection of all-metal cylinders are given in Table 5.

Table 5 - Summary of Advantages and Limitations of Inspection Techniques for All-Metal Cylinders

Inspection Method	Advantage	Limitation
Visual	Can detect most external damage	Cannot detect wall thinning
Hydrostatic	Can detect wall thinning or metal weakening.	Cannot detect subcritical cracks in tough materials. May initiate or accelerate crack growth.
Ultrasonics (UT)	Capable of detecting wall thinning and subcritical cracks	Equipment is expensive, and inspection is difficult to perform on larger stationary cylinders.
Acoustic Emission (AE)	Least expensive, capable of whole volume inspection without raster type scanning	Should only be used with UT follow-up to size flaws. Limitations with smaller cylinders.

The hydrostatic test is an effective test to detect wall thinning or weakening and in combination with the visual inspection can detect most forms of damage in these metal cylinders. The limitation of the hydrostatic test is that it cannot detect deep cracks in tough steels, particularly thin-walled vessels. In addition, the test can actually initiate cracks or cause existing cracks to grow. However, a hydrostatic test should be able to detect cracks in thicker vessels, if the test pressure is sufficiently high. The exact size of the crack that could be detected can be determined from an elastic-plastic fracture mechanics analysis or from simple tests performed on cracked cylinders. The conclusion is that the hydrostatic test has value for screening metal cylinders. However it must be considered on a case-by-case basis that accounts for the factors such as the material strength and toughness, the design margins, the likely failure modes and also the likelihood of a benign LBB-type failure.

Other inspection techniques such as ultrasonics (UT) can be used for cylinder inspection. Ultrasonics can detect internal cracks, and can also detect a loss of wall thickness. However, UT is insensitive to loss of material properties, for example as a result of fire damage. Therefore UT, if used, must be combined with a visual inspection.

Acoustic emission (AE) is another technique that can be used for inspection of metal cylinders; however, follow-up UT is also required. For the DOT tube trailer inspection [31], the purpose of AE is to locate the source of the emissions produced by cracking, and a follow-up UT is used to confirm the finding. Therefore the ability to locate the source of the emission is an important consideration when using this technique. AE works well for long tube trailers since the length to diameter ratio produces a plane wave that makes the linear location technique accurate. For smaller cylinders, with shorter length to diameter ratios, it is much more difficult to locate the source of the emissions.

The second consideration in using AE to inspect metal cylinders is to understand the cause of the emissions. Most emissions from cracks occur as a result of a phenomena known as crack face rubbing [39]. A rough crack surface, with corrosion products between the crack faces, will produce the greatest number of emissions. For hydrogen service, where there may be little or no corrosion, the acoustic emission signature must be obtained on cracks without the presence of corrosion debris.

3.6 Composite Hoop-Wrapped Vessels with Seamless or Welded Liners of Steel or Nonmagnetic Alloys

The composite wrap is a critical component for this cylinder type and should be the focus of the inspection. Failure of the metal liner as a result of subcritical crack growth is likely to result in a more benign LBB failure. Service failures of these cylinders in NGV service has been characterized by failure of the composite wrap [40], primarily due to environmental degradation or damage, followed by an overpressurization failure of the metal liner.

Table 6 summarizes some of the different techniques that have been applied to the inspection of composite cylinders. The four well-known techniques are given, together with other techniques such as thermography that have shown promise in a recent review by the Aerospace Corporation [41].

Visual inspection can detect damage to the composite wrap as a result of impact or service damage and is therefore valuable in preventing failures of this cylinder type. The hydrostatic test can also be used to reinspect these cylinders. However, since the metal liner is under compression as a result of autofrettage, the test results need careful interpretation. If the hydrostatic test pressure is close to the autofrettage pressure then the hydrostatic test can detect loss of prestress to the wrap. The disadvantage is that some of the fibers may be damaged if the test pressure is too high.

Ultrasonics is difficult to perform for this cylinder type due to the rough composite surfaces that will make coupling with the sensors difficult. Furthermore the metal liner cannot be interrogated through the composite wrap. UT can be used to inspect the composite wrap for evidence of impact or other damage. However in most cases this is a difficult inspection to perform since the damage will be distributed. UT relies on reflections from well-defined sources, such as cracks, whereas distributed damage in a composite is a poor acoustic reflector. Furthermore the fiber layer for these cylinder types will complicate the ultrasonic inspection and make interpretation of the results very difficult [37].

Acoustic emission (AE) can also be used to detect damage in these cylinders. Most of the experience with AE is from petrochemical pressure vessels where AE has been approved for use in ASME Section V, Article 11 [42] and more recently as part of Code Case 2390, Section VIII, Division 3 for composite reinforced pressure vessels in transportation service.

Table 6 - Summary of Advantages and Limitations of Inspection Techniques for Hoop-Wrapped Cylinders

Inspection Method	Advantages	Limitation
Visual	Can detect most external damage to composites	Cannot detect damage to metal liner
Hydrostatic	Can detect problems with prestress	Possibility of fiber damage if test pressure is too high
Ultrasonics (UT)	Can detect composite damage	Difficult to perform on composite due to sensor coupling problems and winding patterns
Acoustic emission (AE)	Least expensive, can potentially detect loss of fiber strength and impact damage, and fatigue cracks in metal liner	Calibration data required
Thermography	Can detect near-surface impact damage, rapid and low-cost inspection	Cannot detect damage far from the surface

Acoustic emission could be used to detect the damage to the fibers in these hoop-wrapped cylinders and in particular may be capable of detecting a loss of fiber strength due to stress rupture damage to glass fibers. Unfortunately the accept/reject criteria have not been established for these cylinder types, and the criteria used in Section V for Section VIII vessels cannot be applied here. However AE could be used as a reinspection technique provided reliable accept/reject criteria can be established for these vessel types. These accept/reject criteria must account for the typical types of damage found in composites, such as stress-rupture and impact damage.

3.7 Composite Full-Wrapped Vessels with Seamless or Welded Liners of Steel or Nonmagnetic Alloys

For the composite full-wrapped vessels the analysis is very similar to the hoop-wrapped case. The critical component is the composite wrap. As before, visual inspection is an effective inspection technique for detecting most forms of damage to the wrap. The hydrostatic test can also be used to detect problems with the prestress but care must be taken not to damage the wrap. Ultrasonics are difficult to apply due to sensor coupling problems and also the difficulty of inspecting distributed damage. Finally, AE can be applied but again accept/reject criteria must be developed for this cylinder type.

3.8 Composite Full-Wrapped Vessels with Seamless or Welded Nonmetallic Liners and Metal Bosses of Steel or Nonmagnetic Alloys

For this cylinder type (termed here all-composite), the composite wrap handles 100% of the pressure load. Although the visual inspection technique can detect most forms of damage, the critical form of damage in these vessels is impact damage, and this can be difficult to detect with a visual inspection. For this cylinder type internal impact damage can occur that will not be detected with the visual inspection [43].

This type of damage can be detected with the hydrostatic test, but only if the reduction in the burst pressure is significant compared to the ratio of test stress to burst stress. Ultrasonics can also detect impact damage in these cylinders. Acoustic emission (AE) and thermography are two other techniques that can be employed. The results for AE are mixed [41] and validation of the technique is required for this particular cylinder type. Thermography is another technique that is being evaluated [37]; it uses changes in the surface temperature, after a thermal pulse, to detect the presence of internal damage. The technique can detect near-surface damage, but it is very sensitive to the depth of the damage beneath the surface, and the detectability falls off rapidly with distance from the surface [44]. Therefore subsurface impact damage may not be detectable with this technique.

The following table describes the advantages and disadvantages of the different techniques for the inspection of these cylinder types.

Table 7 - Summary of Advantages and Limitations of Inspection Techniques for All-Composite Cylinders

Inspection Method	Advantage	Limitation
Visual	Can detect most external damage to composites	Cannot detect internal impact damage
Hydrostatic	May detect significant damage that reduces the burst pressure.	Possibility of fiber damage if test pressure too high
Ultrasonics (UT)		Difficult to perform on composite due to sensor coupling problems and winding patterns
Acoustic emission (AE)	Least expensive, can potentially detect loss of fiber strength and impact damage	Calibration data required
Thermography	Can detect near-surface impact damage, rapid and low-cost inspection	Cannot detect damage far from the surface

3.9 Overall Recommendations

In providing recommendations for cylinder inspection, the approach adopted here is to use performance guidelines, whenever possible. These performance guidelines should be dictated by the failure modes. Although this is a desirable, it can be difficult to achieve in practice because of the difficulty of obtaining vendor-independent data.

Therefore, in cases where the failure modes are well understood and where there is a history of inspection with known techniques, then these techniques should be used. This is the case for the all-metal cylinders where the hydrostatic/visual inspection has been used to successfully screen most forms of damage in these cylinders. Ultrasonic and AE inspection techniques have also been developed and are also capable of detecting damage in these cylinders. Because the failure modes in all-metal cylinders are well understood, there is also the option of using a high design margin and eliminating any retest requirements. It should be noted that the scope of ASME Section VIII applies to new construction; therefore, in-service inspection (ISI) and in-service testing (IST) requirements are outside of the scope.

In cases where the inspection techniques are not available and/or are currently under development, performance requirements should be used. This approach will spur the development of improved inspection techniques and also will also provide the impetus for vendors to validate their inspection techniques. Therefore the recommendations given here are divided into steel and composites. Each is now considered in turn:

3.10 Recommendations for Inspection of All-Metal Cylinders at Manufacture

At manufacture, all-metal cylinders used in hydrogen service should be inspected using an ultrasonic inspection. This is in addition to any other quality checks such as hydrostatic and visual inspection. This inspection is recommended as part of the ISO standards and also the European standards [36] and is included as part of the DOT requirements for cylinders with strengths in excess of 135 Ksi [28]. It should be required here for all metal cylinders, used in hydrogen service, irrespective of the strength levels.

3.11 Recommendations for In-service Inspection of All-Metal Cylinders

For the in-service inspection the requirements for periodic inspection are dictated by the design margins and also by the service. The design margins of these hydrogen cylinders will be closer to the requirements of DOT cylinders rather than ASME Section VIII Division 3 requirements. Therefore periodic re-inspection will be required. However the inspection techniques and also the inspection frequency are not mandated here. However, here is some guidance that can be used:

(a) Visual inspection should be performed at every filling. This is the procedure that is required as part of the DOT standards and has contributed to the excellent safety record of the DOT cylinders. The visual inspection should follow the recommendations in the DOT standards [28].

(b) A thorough external visual inspection should be required as part of any re-inspection techniques. This visual inspection should follow the CGA guidelines for inspection of metal cylinders [26].

(c) The inspection technique and frequency of the inspection should be based on a Fitness-For-Service analysis. In this Fitness-For-Service analysis it is likely that there will be three classes of cylinders, namely cylinders used in stationary storage, cylinders used in transportation and also portable cylinders.

(d) Any of the inspection methods given in Table 3 can be used for the reinspection of these vessels. The inspection technique should be capable of detecting the critical forms of damage, determined as part of the Fitness-For-Service analysis. For example, if the cylinders experience a high number of pressure cycles then subcritical cracks must be detected. In this case the hydrostatic test may not be appropriate and UT or AE may be required. Conversely, for stationary cylinders, which will operate at higher pressure, the hydrostatic test may be capable of screening cracks or other forms of damage in these thicker walled cylinders. For these cylinders the need for in-service inspection may also be dictated by the lack of an LBB type failure.

(e) The inspection interval is again dictated by the service that these cylinders will experience. Since the cylinders may experience very differing service if used in stationary applications, or if used in transportation then this service experience dictates the inspection interval. A Fitness-for-Service analysis can be used to define this inspection interval. If this is difficult to perform or if no data are available then the inspection should default to the DOT retest requirements.

(f) The probability and consequence of failure should also be factored into the in-service inspection. Consequence calculations should account for a number of factors such as the severity of the failure (that is primarily the amount of stored energy), the presence of LBB and also a consideration of a public or industrial type failure. Although these calculations are routinely performed for probabilistic calculations of failure in Nuclear and Petrochemical installations [45], a simplified approach could be adopted here based on the total energy released. For example, small portable cylinders could have a baseline of 1, and for larger cylinders the energy released could be calculated and used to provide consequence factors. These consequence factors could be used to increase the inspection interval in cases of higher consequence failures.

3.12 Recommendations for Inspection of Composite Cylinders at Manufacture

At manufacture, the inspection of all-composite cylinders should follow similar requirements to DOT FRP-1 and FRP-2. These standards have been successfully used for composite cylinders in DOT service. At manufacture these cylinders undergo a visual inspection in combination with a hydrostatic test. No other NDE technique is used. The recommendation here is to use these DOT FRP-1/FPR-2 requirements for the inspection of these cylinders at manufacture.

For metal-lined cylinders, ultrasonic testing of the metal liners should be performed, similar to the recommendations given for the all-metal cylinders.

3.13 Recommendations for In-service Inspection of Composite Cylinders

Currently visual inspection and the hydrostatic test is the primary inspection method used for DOT cylinders manufactured to FRP-1 and FRP-2, and the visual inspection should continue to be used to inspect these composite cylinders since the costs of inspection are low. However recent studies on all-composite cylinders conducted by NASA have shown that the visual inspection is only capable of detecting impact damage that exceeds 20% of the cylinder strength [46]. It should be noted that these all-composite cylinders were of different design and application than NGV2, and some experience with NGV2 cylinders has demonstrated adequate post-accident burst strength even with visual damage indications. Visual inspection is not capable of detecting internal impact damage in these all-composite cylinders. Furthermore the visual inspection will not detect stress-rupture damage in composites, a well-known failure mode in glass fibers. In-service inspection is also advisable since these cylinders may not have defined life and consequently progressive long-term damage, which is often not visible, must be detected.

For composite cylinders there is no generally accepted and reliable method for inspection and recertification of these cylinders. A recent review conducted by the DOT [37] showed that the most promising techniques are acoustic emission and thermography. However these results were preliminary and further studies are needed in order to properly validate the results. In view of these difficulties here are some recommendations:

(a) A hydrostatic proof test should be performed on these cylinders after installation. This should be a requirement particularly for composite cylinders used for stationary and transportation applications where there is the potential for damage during the installation of these cylinders.

(b) Visual inspection should be performed at every filling. This is the procedure that is required as part of the DOT standards and has contributed to the excellent safety record of the DOT cylinders. The visual inspection should follow the recommendations in the DOT standards [28].

(c) A thorough external visual inspection should be required as part of any reinspection techniques. This visual inspection should follow the CGA guidelines for inspection of composite cylinders [38].

(d) An inspection performance standard should be developed that would require any inspection technique to detect the critical forms of damage in these cylinders. Types of damage that must be detected are impact damage, and stress rupture damage. A critical consideration is the levels of impact and stress-rupture damage. The damage should be sufficient such that it will result in failure of the cylinders, yet it should not be detectable with a visual inspection. This is similar to the Fitness-For-Service approach adopted for metal cylinders.

(e) In this Fitness-For-Service approach for composite cylinders, the critical forms of damage must be determined and the inspection technique must be developed that can detect this damage before it results in rupture of the cylinders. For composite cylinders this critical damage is likely to be

impact damage that is non-detectable with the visual inspection. The exact impact event that will produce this damage is not known but can be determined from simple testing performed on these cylinders. However, the impact damage should be a realistic representation of the types of damage that these cylinders are likely to experience in service.

(f) The probability and consequence of failure should also be factored into the in-service inspection similar to the approach used for metal cylinders. Consequence calculations should account for a number of factors such as the severity of the failure (that is primarily the amount of stored energy), and also a consideration of a public or industrial type failure. For example, small portable cylinders could have a baseline of 1 and for larger cylinders the energy released could be calculated and used to provide consequence factors. These consequence factors could be used to increase the inspection interval in cases of higher consequence failures.

4 RECOMMENDED MARGINS FOR NEW CODE RULES

This section contains specific recommendations for margins to be applied to new vessel design rules. The recommendations are based on the margin comparison in Section 2, the use history of the various reference standards and the design type and materials. Some of the recommended margins also vary based on the vessel application, stationary or a transportation vessel such as a DOT cylinder or trailer tube. Metal vessels are assumed to be manufactured from materials that are not susceptible to creep or stress rupture at the operating pressures and temperatures. This assumption is based on the metals allowed in the reference standards and commonly used for ASME Code vessels.

Vessel materials that are subject to creep and stress rupture, all composites, are treated separately from metal vessels. The margins for these should be based on lower allowable stress ratios depending on the degree of susceptibility to stress rupture of the fiber type. Issues such as cyclic fatigue that cannot be effectively managed with a simple design margin in burst are identified as needing independent design controls.

Cylinders, like any structure, are likely to fail when exposed to the highest operating loads. For this reason the margin should be measured against the maximum developed pressure or maximum fill pressure. On the rare occasions when cylinders containing permanent gases fail, the cylinder is usually being filled, being proof tested or has been exposed to temperatures in excess of the design, driving the gas pressure close to or above the maximum normal operating pressure for the design. Since cylinders do not typically fail at service pressure and at room temperature, this pressure should not be used to determine margins. All margins are based on the maximum normal operating pressure, MNOP.

All recommended margins are subject to the provision of effective inspection and testing of vessels for deterioration in service. These minimum requirements are given in Section 3, above. Periodic requalification has been an integral part of the integrity controls applied to gas cylinders [47] and this practice is necessary for the vessels and cylinders addressed here. If it is not possible to require such inspection and test on a consistent basis, the margins now applied in ASME Section VIII Division 1 should be applied to metal vessels; however, service life limits may be necessary without an appropriate inspection program. Composite vessels should not be used at any margin without consistent inspection and test requirements.

Before recommending margins for new Code rules it is necessary to identify some issues that are not directly dependent on the margin of burst pressure to operating pressure, inspection, and testing, and therefore must be subject to other design controls.

4.1 Factors Not Addressed by Margin to Burst

The burst to operating pressure margin allows for some level of unpredictable magnitude of the service loads without resulting in rupture of the cylinder. However, a simple finite margin does not provide significant protection in the following circumstances.

4.1.1 Pressure Control

Margin does not protect against loss of pressure control on fill. Filling compressors are typically positive displacement piston units and will continue to pressurize the cylinder until either a pressure control interrupts the flow or a backup relief valve in the system vents the gas faster than it is being supplied to the cylinder by the compressor. Gas cylinder ruptures occur in those instances where both the pressure control and pressure relief systems fail simultaneously or are deactivated. It is not feasible to increase the margin to reduce the probability of failure to an acceptable level if there is no effective control over fill pressure.

4.1.2 Material Degradation

Margin does not protect against loss of wall thickness due to corrosion or wear unless there is a stringent periodic inspection of wall thickness and the rate of corrosion is both low and reasonably uniform. A corrosion allowance is part of many ASME Code vessel designs, but these allowances are based on previous experience with similar vessels in similar service conditions and it is still necessary to detect the corrosive wall loss at a critical value and remove the vessel from service to prevent failure. Hydrogen is not a corrosive gas and no corrosion allowance is required for the internal surfaces. However, the external surfaces may be exposed to corrosion from the environment unless properly coated or protected.

4.1.3 Cyclic Fatigue

Burst margin alone does not protect against fatigue failures in service. Fatigue cracks initiate and grow in locations where the surface condition, local geometry resulting in stress concentrations or bending stresses or residual stresses provide a favorable environment for fatigue crack initiation and growth. None of these causes of fatigue failure are particularly significant to the burst pressure of a vessel. The ductile metals required for all general-purpose pressure vessels are not subject to brittle fracture due to surface condition, and local stress concentrations can be relieved by plastic deformation as the pressure approaches the ultimate burst pressure. The plastic deformation redistributes the stresses more uniformly to the surrounding metal without a large reduction in burst pressure. A vessel design may have ample burst margin but unacceptable fatigue performance if it is poorly shaped and finished. Fatigue margins are considered a significant issue for these vessels and are addressed later.

4.1.4 Fire Exposure

Margin does not protect against failure of cylinders exposed to fire. The failure of a cylinder in a fire results from two factors, the increased gas pressure and loss of strength in the material of the cylinder, both caused by the heating effect of the fire. Regulations in the United States require the use of one or more pressure relief devices (PRDs) to vent the contents of a cylinder before the combined pressure increase and physical weakening result in cylinder failure. Since flame temperatures in a fire can cause the gas pressure in the cylinder to more than treble and can reduce the strength of a steel cylinder by an even greater degree, preventing rupture in a fire by margin is not feasible. As a general rule, any cylinder at design conditions that is not protected with a PRD will fail in an intense fire.

The most common PRD for metal cylinders is a simple rupture disc that is activated by the increasing gas pressure. The heat of the fire also reduces the rupture pressure of the disc material, but this factor is not taken into account in the PRD standards. This simplest device is adequate because the strength of alloy steel cylinders is not as affected by increasing temperatures as is the gas pressure, and the increasing gas pressure causes the rupture disc to fail before the cylinder. It is generally accepted that these devices will not adequately protect a partially charged cylinder because the gas pressure must increase from a lower initial value and the steel cylinder may be softened by the fire before the gas pressure builds sufficiently to rupture the disc.

Any PRD can be defeated if the flame impingement on the cylinder is intense and localized.

4.1.5 Impact Damage to Composites

As discussed in Section 6, composites may suffer very significant loss of strength due to impact and this has been the cause of vessel failures. The potential loss of strength can be so great that increasing the original margin to allow for it would be prohibitive in both weight and cost, and would still not be assuredly adequate because some level of impact must be first estimated. Separating impact resistance from burst margin will allow design to be optimized for both characteristics independently.

Rupture failure due to impact is not a concern for metal high-pressure vessels. Typical metal specifications or welding procedure qualifications require severe flattening or bend tests without cracking of the metal.

Since a simple margin of burst pressure in excess of maximum normal operating pressure is not adequate to protect against the failures listed above, the design or performance specification or installation codes must address these failures modes.

4.2 Minimum Recommended Gas Cylinder Margins for Materials Not Susceptible to Creep, Stress Rupture, or External Impact Induced Fracture (Metals)

The margins between MNOP and the cylinder burst pressure do not vary greatly among the different metal cylinder types or specifications included in this comparison. There is also no significant amount of failure data for cylinders that may be considered to have failed due to an insufficient margin between burst pressure and maximum normal operating pressure. The standards for vehicle fuel cylinders permit slightly lower margins than the standards for compressed gas cylinders used in transportation. These vehicle standards include life limitations, protected installation locations, and other limitations on use that are not appropriate for portable gas cylinders, trailer tubes and stationary pressure vessels. In this situation, a conservative approach is to require a margin for new metal cylinders to be equal to the lowest successful margin now in compressed gas cylinder service. This is the margin for DOT 3AA cylinders with allowance for filling to 10% in excess of the marked service pressure. The maximum normal operating pressure at 55°C is 137.5% of the marked service pressure. The margin of burst pressure to maximum normal operating pressure is calculated to be 1.721:1. Using this as a benchmark, any new metal specification cylinder should have a ratio of burst pressure to maximum normal operating pressure of at least 1.721:1. It is coincidental that the DOT-3AA specification cylinder has been used in large quantities over the longest time span of any reference cylinder standard. Since none of the newer standards apply a lower margin, the choice of DOT-3AA is very straightforward.

The recommended margin between burst pressure and MNOP for any new ductile metal cylinder is 1.721.

4.3 Minimum Gas Cylinder Margins for Materials Susceptible to Creep, Stress Rupture, or Impact Induced Fracture (Composite Reinforced Cylinders)

Margins for composite cylinders are fundamentally different from those of monolithic metal cylinders. The different material characteristics and susceptibilities to failure preclude the simple adoption of proven metal margins for composite cylinders. Before considering composite cylinder margins it is necessary to review the design characteristics of these cylinders.

4.3.1 Design of Composite Cylinders

The margins of composite cylinders must account for stress rupture by limiting the maximum allowable composite stress at normal or average pressure loads. For this reason, the composite cylinder margins are recommended against NOP rather than MNOP where only short-term exposure is expected. This continues the proven practice in DOT FRP-1 and FRP-2 without requiring added material to meet the allowable stress rupture stress limits at the higher MNOP.

4.3.1.1 Composite Margins Driven by Stress Rupture Concerns

The margins of all composite gas cylinder standards are driven primarily by concerns for the susceptibility of the composite to stress rupture resulting from long-term cumulative damage occurring while the vessel is stressed in normal operations. Composite stress levels, unlike metal stress levels, are not simply related to pressure with a single factor. Establishing a composite stress ratio (margin) at MNOP does not allow the margin at NOP to be extrapolated without detailed knowledge of the actual design being compared. For this reason, it is necessary to define the margins of composite materials at the normal operating pressure NOP equivalent to DOT service pressure and not at MNOP as recommended for all metal vessels.

When determining the margins for composite designs it is necessary to consider the lack of consensus on design analysis method for composite cylinders. Many of the reference composite cylinder standards allow reliance on proprietary design methods. This is in marked contrast to the standards for metal cylinders and pressure vessels that, with the exception of NGV2 and ISO 11439, contain thoroughly verified design analysis rules. For the metal designs, the analysis is performed and then is verified by a completely independent empirical test. The critical composite and liner operating and ultimate stresses are not determined directly but must be estimated based on the proprietary design model and the empirical test results. At the end of this empirical design process the design may then be verified with the exact same tools of analysis and test as were used in the empirical design stage. This approach is inevitably susceptible to common causes of error in both the design and verification steps due to the complete interdependence of the two steps. The discrete steps in this original design process are usually as follows:

(a) A preliminary design calculation is made with an assumed composite strength.

(b) A vessel is manufactured in accordance with the design and subjected to a burst test.

(c) The design calculation method is used to determine the composite strength that is calculated to result in the actual measured burst pressure.

(d) The calculated composite strength is lower than the theoretical strength of the aggregate fiber strands and the difference is termed "translation."

(e) The calculated composite strength with empirical translation is established as the ultimate strength of the composite for the design.

(f) When the calculated composite strength is used in the design calculation method, the burst pressure is predicted with no apparent error. The method is perfectly precise, but the accuracy must be unknown.

Since the reference standards do not require empirical verification of the design calculations regarding the stress ratio, this important characteristic is controlled neither by a true design standard nor a true performance standard, but a somewhat undefined combination. This ambiguity could be clarified in future code rules by requiring either design according to consensus calculation methods or by an explicit performance test such as comprehensive strain gauging.

Any practical design calculation method incorporates simplifying assumptions. This is true in ASME VIII Divisions 1, 2, and 3, and these simplifying assumptions are limited and consensus-based. If no such assumptions were made, the calculation of composite vessel designs would be massively complex. Although none of the reference standards except Code Case 2390 give explicit limitations on these assumptions, some of the actual assumptions that I have seen used include the following.

(a) *Thin wall theory*. This was the basic assumption in the NASA design calculation originally referenced in DOT FRP standards. It is probably nonconservative when applied to thick-walled composite designs for up to 15,000 psi because the stress on the inner wall will exceed the assumed thin-wall stress.

(b) *Assumptions that principal stresses may equal the yield strength of the liner*. This very simple approach may be used successfully for DOT FRP-2 designs due to the mandated design minimum liner thickness and modest performance requirements. Since von Mises yield criteria effects are ignored, this method overstates the contribution of the liner to burst strength and the composite strength determined by deduction is less that the actual value. The result is to err on the conservative side with respect to stress ratio.

(c) *Assumptions that the radial stress component is negligible and that two-dimensional (2-D) von Mises criteria may be used*. This assumption makes non-FEA calculations much simpler and introduces a small error by overstating the contribution of the liner to burst strength, again resulting in a conservative stress ratio. The magnitude of error is greater at higher burst pressures.

(d) *Neglect of the Bauschinger effect*. This is significant for Type 3 designs and results in calculated compressive stress in the liner after autofrettage of as much as 95% of the minimum yield strength. DOT FRP-1 sets 95% as the maximum compressive stress after autofrettage. Consideration of the Bauschinger effect makes actual achievement of this level very questionable, but the effect is to overstate the load transfer to the composite during operation and is again conservative with regard to calculated stress ratio.

(e) *Liner properties are assumed to be isotropic* but the forming processes used to manufacture metal liners are generally considered to produce directionality.

(f) *The composite is simplified and not treated as discrete elements*. The average directional properties of layers are used. The transfer of loads by shear is affected by the assumed level of matrix cracking. This is probably most significant in the dome portions.

(g) *FEA provides answers in terms of strain* and the stress is then calculated based on the modulus. With any composite structure the modulus is highly directional and somewhat variable based on the consistency of the fiber and resin composite. This is different from the situation in solid single-component materials such metals. If this is determined to be a potentially significant source of error, a strain ratio may be more accurate than a stress ratio, and would be more direct to verify using strain gauges, or volumetric or diametral expansion measurements. A parallel is probably the ASME Section VIII Division 3 KD-3 fatigue evaluation that requires correction for any modulus different from that used to generate the design S-N curves, recognizing that strain is the most significant value.

The net effect of the specific assumptions chosen by a particular manufacturer is that while the numerical methods of FEA are very sophisticated, the results are still highly dependent on the initial assumptions, and these are entirely separate from the numerical methods.

All of this is of concern because we recognize a critical failure mode, stress rupture that may only be controlled using design calculations that are not defined in detail or in accuracy by the standards. Since the soundest precedent for the acceptable stress ratios is the safe performance of DOT FRP designs, any design calculation method should be consistent.

As an example, it may be possible to utilize the design theory by Walters [51] to develop completely verified and consensus design analysis rules for Type 2 cylinders, but no such complete theoretical treatment has been offered for the more complex Type 3 and Type 4 designs. A simplified approach to a new design code for full-wrapped vessels was presented in the introduction.

4.3.1.2 Design Pressure for Composite Cylinders

The susceptibility of all fiber-reinforced composites to stress rupture required a reexamination of the designation of MNOP as the design pressure that was originally adopted and then applied in the previous section on metal vessels. The maximum operating stress is critical in metal vessel design but for composites a major limiting design factor is stress rupture.

In metal-lined composite cylinders the composite stress is not a simple factor times pressure due to the prestressing applied in autofrettage. Without detailed design information about the cylinders in successful service it is not possible to extrapolate the margin at service pressure or service pressure to a margin at MNOP. Since fiber stress is the principal concern in reliability of composite cylinders, it is necessary to define the margin in these designs at service pressure rather than at MNOP.

This margin based on service pressure can be considered adequate only for gas cylinders and similar applications where MNOP is reached for only short portions of a cylinder's total life. The stress rupture characteristics of glass fiber require this limitation. It is known that glass fiber is susceptible to stress rupture and E-glass and S-glass have been extensively studied [49].

In gas cylinders, whether for transportation or vehicle fuel tanks, the excursions to MNOP are brief and do not represent a significant portion of the service life of the cylinder. If the design is driven by stress rupture concerns, the service pressure condition is most significant.

For metal-lined composite cylinders the wrap stress from NOP to MNOP is not a simple factor and is dependent on the details of the actual design. Walters [51] illustrates this quite clearly and his presentation is not duplicated here. The effect is that while the burst ratio at MNOP for these cylinders can be determined from the standards, the stress ratio at MNOP cannot. If dependence is placed on the successful history of DOT FRP-1 and FRP-2 cylinders in determining safe margins for new rules, the comparison must be done at service pressure, not MNOP. This is unfortunately inconsistent with the Code definition of design pressure, but is necessary unless actual fiber stress ratios at MNOP can be obtained for the usage base of DOT composite cylinders. All subsequent discussion of composite cylinder margins is in terms of burst to service pressure or normal operating pressure ratio.

4.3.2 Recommended Margins for Types 3 and 4 Full-Wrapped Metal-Lined Designs Using Glass or Aramid Composite

The experience base in composite gas cylinders is limited with the exception of the DOT FRP-1 and FRP-2 [48] designs. The margins required for glass composite cylinders in the other standards are little different from the DOT and the DOT experience base is best. Recommended margins for glass composite vessels should be based solely on the margins that have been successful when applied to large numbers of DOT FRP gas cylinders. The initial determination of margins for DOT FRP-1 was dominated by concerns for stress rupture and the resulting margins are large in comparison to metal designs. DOT FRP-1 designs are dependent on the glass fiber for most of their strength. If the composite fails due to stress rupture, the cylinder will fail. Using the Glass Composite Strand Stress Rupture Design Chart [49] results in a 1:1,000,000 probability of strand failure within the 15-year service life of FRP-1 cylinders at NOP with a service stress of 30% of the ultimate composite strength.

Failure of 1:1,000,000 strands is not equivalent to failure of 1:1,000,000 cylinders because there are many strands in the structure. Conversely the strand data was from tests in dry air at ambient temperature, and stress rupture is accelerated by both high temperatures and moisture. The results of stress rupture tests on glass composite CNG cylinders at Powertech [40] confirms the sensitivity of glass composites to accelerated deterioration when exposed to elevated temperatures or water. Since the design chart by Robinson did not consider these effects, the predictions may not be very conservative when applied to gas cylinders. With these basic questions about the stress rupture of glass fiber, it is fortunate that we have actual use experience from large numbers of FRP-1 cylinders in service during the last 25 years. This experience has been favorable and supports the continued use of the fiber design stress limit in FRP-1.

DOT FRP-1 requires a minimum design margin at service pressure of 3.0. This is not an accurate estimate of the actual minimum design margin because FRP-1 also requires a maximum fiber stress of

30%, defined as the calculated stress in the reinforcing fiber at actual service pressure divided by the calculated stress in the fiber at the actual burst pressure. Inverting this value gives a ratio of ultimate to service stress of 3.33. Since composites are susceptible to stress rupture with the ultimate stress being lower as the composite is held for longer times at high stresses, any burst pressure requirement for composite cylinders should probably specify a certain hold time at the minimum design burst pressure. This hold is specified at 1 minute for DOT FRP-1. Considering the effect of the metal liner and the required autofrettage prestress, the actual minimum burst pressure must be greater than 3.33 and probably 3.5 times service pressure to satisfy the composite stress ratio of 3.33. With no consensus design stress calculation methods, it is prudent to require a design margin in burst that will tend to produce a glass stress ratio of around 30% regardless of the accuracy of the proprietary calculations. Accounting for some prestressing of the metal liner, this burst to service pressure ratio is about 3.5. This is the recommended design margin at service pressure, NOP in the case of DOT FRP-1 cylinders and all other glass composite full-wrapped metal-lined cylinders. DOT FRP-1 cylinders typically have thin aluminum liners that contribute little to the burst strength. The fiber stress ratio is therefore very similar to the burst pressure margin. The minimum burst margin and fiber stress ratios can be approximately equated for such full-wrapped cylinders. The same is also obviously true for cylinders with non-load-sharing liners, Type 4 plastic lined composite cylinders.

The various ISO and ANSI standards for full-composite gas cylinders and fuel containers considered elsewhere in this report are all derivative of DOT FRP-1 and have slightly different stress ratio requirements for glass as a result of different definitions of service pressure or different hold times in the burst test. Since there is relatively little available experience base with these newer standards and the composite stress ratio requirements are all reasonably equivalent, the DOT FRP-1 model is used exclusively as a recommendation.

The aramid stress rupture strand data used in the development of DOT FRP-2 [49] indicates that the margin required for stress rupture reliability could be substantially reduced compared to glass. The curves also show a pronounced down turn and there is also no experience base of DOT exemption cylinders at a lower design margin for aramid. These reasons, when compared to glass or carbon result in a recommendation to retain the margins recommended for glass if aramid fiber is used. With the lack of use history and the small probability of aramid use in commercial vessels, the same margins are recommended for aramid full-wrapped cylinders as for glass.

4.3.3 Recommended Margins for Type 2 Hoop-Wrapped Designs

DOT FRP-2 [48] cylinders and other hoop-wrapped designs require a relatively thick metal liner that can typically resist a pressure of 1.25 times the service pressure without bursting. This factor is not explicitly defined and may be lower for Code Case 2390-1. With the yield to tensile ratio of most liner materials being about 0.90, the liner without reinforcement will be in the elastic range at service pressure and stress rupture of the wrap may not result in immediate rupture of the cylinder. DOT FRP-2 cylinders are typically filled individually and are subject to an external visual inspection prior to each fill in accordance with DOT regulations [50]. The composite wrap on DOT FRP-2 cylinders is relatively thin because it carries only a portion of the pressure load in the hoop direction and the fibers are aligned in a unidirectional, not intersecting pattern.

4.3.3.1 Glass or Carbon Composite Reinforced Type 2 Hoop-Wrapped Cylinders

The lower design margin for the glass composite on DOT FRP-2 cylinders was justified because of the redundant load carrying capacity of the metal liner at NOP or MNOP. Failure of the composite wrap may not lead immediately to failure of the cylinder in these designs. The difference in cylinder failure mode resulting from composite stress rupture provides the rationale for a higher composite service stress in hoop-wrapped cylinders. Subsequent standards have been based on the original DOT

FRP standards with small adjustments to the stress ratios to account for small detail differences in the required burst test procedure and small differences in the definition of service or working pressure.

4.3.3.2 Future Applicability of the DOT FRP-2 Composite Stress Limit

The stiffness of the metal liner and the prestressing from autofrettage also allow the burst margin and the fiber stress ratio to be quite independent, more so than for FRP-1, but DOT FRP-2 imposes an arbitrary maximum on the autofrettage pressure that effectively prevents a high level of prestress. FRP-2 allows a glass fiber stress ratio of 2.5 at service pressure, NOP, the fiber stress being as high as 40% of the short term tensile strength.

The limitation on autofrettage pressure that is unique to DOT FRP-2 is not included in derivative standards such as NGV2. It is probable that existing FRP-2 glass-wrapped cylinders actually possess a stress ratio substantially in excess of 2.5, most possibly three or more. This is due to the limited autofrettage and to the ease of empirical design to meet the performance requirements of FRP-2, but Walters [51] shows how such designs can easily have very conservative stress ratios by overestimating the contribution of the liner to hoop strength and by deduction, underestimating the strength of the composite at burst. With the design methods described by Walters, it is now convenient for engineers to use design by analysis and produce cylinders with stress ratios near the minimum required. Two actions are recommended before the glass stress ratio of 2.5 is adopted into new ASME standards for hoop-wrapped pressure vessels.

(a) Survey the FRP-2 designs in use and determine the actual stress ratios. This can be done by empirical sampling of cylinders taken from service or by analysis of manufacturer's design data if such data can be obtained.

(b) The Walters design calculations should be validated empirically with more test data and carefully characterized test articles. It accounts for the theory well, but the available test data for validation was limited and some assumptions about the test articles were necessary.

Another consideration that may account for the lack of stress rupture failures in FRP-2 cylinders may be the stiffness of the thick liner and the resultant reduced increase in wrap stress as the temperature increases above 21°C and the internal pressure exceeds NOP. This increase in wrap stress was calculated for one actual nominal steel-lined hoop-wrapped (DOT-E8965) design as a 10% increase in wrap stress when the pressure is increased from service pressure to 125% of service pressure. At the other extreme, the wrap stress would be expected to be proportional to pressure in a Type 4 design where the pressure increase of 25% would be expected to result in a wrap stress increase of 25%. It should be noted that other factors affecting wrap stress include preload due to autofrettage and thermal stresses during operation. Since stress rupture is highly sensitive to stress level, this may prevent or reduce the accelerated damage that must occur to DOT FRP-1 cylinders in similar conditions.

The study of actual stress ratios recommended above is probably relevant only to glass hoop-wrapped designs. Carbon resistance to stress rupture is superior to glass and therefore not a concern on Type 2 cylinders. The low impact resistance of thin carbon composites is an area of concern on Type 2 cylinders; however, the stiffness and ductility of the inner metal liner will prevent "oil-canning" upon impact and rupture due to composite impact damage.

The recommended design margin for glass reinforced Type 2 cylinders is 2.5 at service pressure with the additional requirement that the composite stress ratio not exceed 2.5 or a higher number that may be determined from the survey recommended above.

4.3.4 Recommended Margins for Type 3 and 4 Carbon Composite Vessels

In the case of carbon composites we do not have long-term history of significant numbers of carbon composite gas cylinders in service. There is sufficient field experience, combined with research data, to support the current stress ratios in NGV2. It is believed that there are tens of thousands of carbon and carbon/glass hybrid NGV2 CNG cylinders, some in service since 1993. These cylinders are designed in accordance with NGV2 [52], and this standard requires a minimum design margin of 2.25 at service pressure for carbon fiber composites. Carbon/glass hybrids must either have both types of fibers meet their stress ratio requirements, or one must meet its stress ratio requirements if the other fiber is removed. There are a number of different designs represented, from carbon/glass hybrids with plastic liners to pure carbon with plastic liners to carbon and carbon glass hybrid Type 3 on aluminum liners to carbon and carbon/glass hybrid Type 2 on steel liners.

A larger number of carbon composite gas cylinders have been produced in later years in accordance with DOT-CFFC [53]. This standard requires a margin of 3.4 at service pressure but the time in use is very short. The relatively high margin is necessary since small cylinders manufactured only with carbon fiber have trouble passing gunfire tests at lower margins, and cylinders with aluminum liners have trouble passing cyclic fatigue tests at lower margins. There is a small amount of anecdotal data for both sets of cylinders. There have been two instances of rupture failure in service of NGV2 Type 4 (plastic lined) cylinders in the United States [74], as well as a number of leaks related to plastic liner problems. If the recommended installation codes are followed, the severity of a leak failure is low and this failure will probably be addressed with improvements in liner materials and processes without any need for new design controls.

The NGV2 Type 4 design with pure carbon composite was withdrawn from production shortly after failures and it is believed that no significant quantity of other NGV2 Type 4 cylinders using only carbon fiber have since been produced. There has also been a failure of a carbon/steel Type 2 that was mistakenly filled with an explosive mixture [54]. The recommended installation codes should address this particular failure. There have been no failures reported of the DOT-CFFC cylinders. The NGV2 Type 4 rupture failures may or may not be relevant for current production NGV2 designs because the NGV2 standard was changed in 1998 to increase the impact test requirements and the failure analysis for the ruptures was not made available to determine whether the changes addressed the actual root failure cause.

The significant experience base with low margin designs is limited to metal cylinders, but low margins may also be justifiable for carbon composites. The high resistance of carbon fiber to common environmental factors such as corrosives, heat, and moisture is promising for the use of low margins, but there are other balancing considerations as well. Since the experience base is so small for carbon composite gas cylinders, any margin for new Code rules should take into account the fundamental nature of carbon composites used in pressure vessels. This should be done in comparison with the materials for which we do have significant use experience, ductile metals with low margins and glass composites with high margins. Section 7 contains an expanded discussion of composites and carbon in particular as related to the use of metal margin experience for these newer vessel materials. It is necessary to understand the characteristics of composites in comparison to ductile metals in order to understand whether metal cylinder experience may be applied to composite designs with low margins that take advantage of the lower susceptibility of carbon fiber to stress rupture in comparison to glass.

4.3.5 Burst Design Margins for Carbon Composite Designs

Sufficient information is not available to permit the recommendation of a single design margin based on data from use history for carbon composite cylinders with the confidence possible for ductile metal cylinders or for glass composite cylinders similar to DOT FRP-1 and DOT FRP-2. The options for margins at NOP fall between a lower bound of 2.25 from NGV2 and an upper bound of 3.4 from

DOT CFFC. The service condition limitations for these two standards are compared below to provide a context for the standard margins.

4.3.5.1 Summary of Service Conditions for NGV2 Containers

(a) NGV2 requires containers to be mounted in protected positions within the motor vehicle. 4.8 states "This standard contains no requirements for container integrity in a vehicle collision. Container locations and mountings should be designed to provide adequate impact protection to prevent container failure in a collision."

(b) Light-duty vehicles and school buses must be certified to Federal Motor Vehicle Safety Standard 303 [55]. This standard subjects the vehicle to very high impact loads to verify that the fuel system, including the container, maintain integrity in a simulated accident impact.

(c) Other CNG vehicles are designed in accordance with NFPA 52 [56] that contains detailed requirements for mounting and protection of CNG containers.

(d) NGV2 containers are tested for resistance to what Robinson terms casual damage by a drop test impacting on a plane surface. This simulates an accidental drop onto a flat floor. NGV2 also requires both low-energy and high-energy point impacts. Other types of casual damage such as impact with a curb are not simulated.

(e) NGV2 containers are not depressurized during normal operations. Fuel systems component regulators and fuel injectors require a significant supply pressure from the fuel tank. The range of minimum operating pressures may be slightly less than 100 psi for some vehicles and as high as 300 psi in other cases. Dedicated NGVs with no other fuel source also must have enough remaining fuel margin to return to the fueling station. NGV2 containers are limited to a maximum life of 20 years with triennial inspections.

(f) NGV2 containers may be installed in closed compartments with little or no ventilation. Permeation of the flammable gas is therefore a critical concern to prevent the accumulation of a flammable mixture in the compartment around the container and effective design controls are included.

(g) NGV2 containers must be inspected every 3 years according to the manufacturer's criteria.

4.3.5.2 Summary of Service Conditions for DOT CFFC Gas Cylinders

(a) CFFC cylinders are used with surfaces exposed to all forms of casual damage.

(b) CFFC cylinders are not built into larger protective systems.

(c) CFFC cylinders are tested for resistance to both point impacts and nonplane surface impacts representative of curbs and other obstructions.

(d) CFFC, and any other DOT gas cylinders, are intended as shipping packages for compressed gas and may be completely depressurized by the user before being returned empty for refilling. Empty DOT CFFC cylinders being transported back to the filling location are not stiffened by internal pressure to better resist blunt impact. Since most CFFC cylinders are used for emergency life support, it is likely that "empty" cylinders usually contain a significant pressure because they were exchanged while still functional, but this is not necessarily true of DOT cylinders in general.

(e) CFFC cylinders must be hydrostatically tested and inspected every three years.

4.3.5.3 Service Conditions for New Code Vessels

The new Code rules are intended for application to both stationary and transport vessels. These conditions are addressed separately.

(a) Cylinders for Transportation

For the purposes of gas transportation cylinders and trailer tubes, the service conditions of NGV2 are not necessarily valid. The margin of 2.25 should not be used for cylinders in these applications without the addition of verified design controls against rupture failure due to impact, up to and including sympathetic failure caused by rupture of an adjacent similar cylinder.

Impact failure that may cause delayed failure is also a consideration. Using the NASA conclusions discussed in Section 3 regarding capability of visual inspection to detect damage to composites, a cylinder with impact damage that reduces the burst strength by up to 20% may be accepted at the required prefill inspection and be filled for shipment. It should that some experience with NGV2 cylinders has demonstrated adequate post-accident burst strength even with visual damage indications. The margin of this particular cylinder at service pressure, NOP, would be reduced from 2.25 to 1.8. The margin at MNOP would be further reduced to 1.44, quite significantly less than the proven margin for metal cylinders. The periodic pressure test could be expected to reject this cylinder, but the hazard of impact damage is always present and does not accumulate slowly over time as in the case of metal fatigue. Undetected impact damage is a hazard at each fill.

The transportation cylinders may be returned empty without any benefit of stiffening due to internal pressure to help resist impact damage. It is important that the vessel not sustain significant damage while empty that will not be reliably detected in the normal prefill inspection.

Cylinders will be subject to inspection prior to each fill and periodic requalification by test and inspection will be required.

Cylinders will probably not be shipped in strong outside packaging as is required for DOT-3HT and other more fragile designs.

Additionally, the stress rupture strength of carbon fiber composite pressure vessels should be studied and updated to provide confidence that the margin of the vessel will not fall below 2.25 at the end of the vessel design life. This study should include a conservative estimate of the potential error in calculating the ultimate and service stress in the fiber since these may not be directly related to burst and pressure. Since the stress rupture data used by Robinson was so limited, additional data could eliminate stress rupture entirely as a consideration for carbon composites. If this can be determined, it would probably revert to the use of margin at MNOP as is recommended for metal cylinders that are not subject to stress rupture or creep.

Translation, the empirical design/material factor, is discussed later in Section 7 but it must be considered here as a factor of uncertainty regarding the design stress calculations for composite cylinders. The margin at MNOP for FRP-1 glass cylinders is 3.5, 1.55 times the NGV2 margin for carbon cylinders. The significance of any uncertainty in calculation of design stresses by proprietary methods is therefore likely greater for carbon NGV2 cylinders than for the glass DOT FRP-1 cylinders in the experience base.

The margin can be applied simply to burst pressure, not composite stress at burst, a significant simplification. In this case the recommended margin may be as simple as dividing the minimum margin by the percentage of burst strength assured based on visual inspection. Using 2.25/0.80 gives a margin of 2.813 based on the NASA estimate of nondetectable strength loss. This example may be overly conservative after actual test data is obtained and evaluated for the thicker, higher pressure, designs being planned for the new rules.

(b) Stationary Storage Vessels

For the purposes of stationary storage vessels it may be feasible to provide service conditions analogous to those for NGV2 containers. The margin of 2.25 could be used for such applications providing the developed Code rules account for potential sources of damage to the carbon composite and that some form of adequate periodic inspection and retest is implemented. This recommendation is subject to the same controls against stress rupture as outlined above.

Stationary storage vessels in refueling station cascades typically experience minimum operating pressures slightly less than 50% of NOP [57]. This high internal pressure will stiffen the vessel against external impact, reducing concerns about impact damage while the vessel is in use.

As recommended in Section 3, composite vessels should be proof tested after installation as protection against casual but critical damage during handling and installation. This practice or other NDE may eliminate the need to increase the margin of new vessels to compensate for the limited capability of visual inspection to detect damage as discussed for transportation cylinders.

The new Code should provide rules that are not dependent on empirical design or else require some other form of peer review equivalent for composite pressure vessel designs with low margins. This replaces the design review and approval of the exemption process that is now the responsibility of DOT for composite cylinders.

The potential for sympathetic failure should also be investigated and secondary containment required if necessary. This is expected to be easier to provide in a stationary installation.

4.3.5.4 Capability of Periodic Inspection of Carbon Composite Cylinders

Visual detection of impact damage in composite laminates is limited because in some cases the inner plies are most susceptible to damage that will not be detected by a visual inspection. This is in contrast to the typical single-wall metal vessels where damage occurs at the visible surfaces. As discussed in Section 3, a NASA study concludes that such damage must be extensive enough to result in a 20% reduction in burst pressure to be detected visually. It should again be noted some experience with NGV2 cylinders has demonstrated adequate postaccident burst strength even with visual damage indications. Visual inspection of gas cylinders at fill is an important control against damage that may result reduced burst strength. This control will continue to be important for carbon composites with sensitivity to impact damage, but the limited inspection capability should be considered.

4.3.5.5 Prevention of Rupture Failure Due to Impact

The minimum design margin for carbon gas cylinders should not be relied on to assure safe performance after impact. This is consistent with the approach in DOT specifications for metal cylinders that specify some absolute minimum wall thickness to assure adequate resistance to external impact. This exact approach may not be appropriate for the variety of composite materials, but the general approach of separating the need for resistance to physical impact from the pressure margin should be followed.

Studies of the effect of impact on composite cylinder burst pressure [69] showed that the burst pressure is reduced by more than 60% with an impact energy less than three times the threshold value for which no reduction in burst pressure results. This demonstrates that it is very important to accurately and conservatively estimate the amount of impact energy that a design must resist in service. DOT CFFC is limited to relatively small cylinders and it is not known what the scale effects will be when the size is extended to trailer tubes. The relatively small energy impact in the CFFC drop test may signify little in the context of a tube trailer traffic accident.

One such tube trailer accident on May 5, 2001 resulted in fracture of the neck on a steel DOT-3AAX trailer tube but did not result in rupture of the tube [58]. This example of the severity of real-world impacts that must be expected in large compressed gas cylinder service is not consistent with the limited impact test in CFFC or the even lower drop test requirement in NGV2. Any impact requirement for new composite compressed gas cylinders and tubes of the sizes contemplated in this report should not be incorporated by simple reference to NGV2 but should be the result of a thorough study of the service environment of gas cylinders and the inherent characteristics of carbon composites. This study should result in either a design margin that is adequate to provide protection against service-induced failures or an absolute minimum wall thickness as required in DOT-3AA or comprehensive performance tests and periodic retests that are tailored to the service hazards. This is conceptually similar to the recommendations for stationary storage vessels, but the scope of possible damaging service incidents is much greater for cylinders in transportation and issues of public safety are generally treated more conservatively than those of industrial safety where other secondary safety controls are easier to implement.

It is likely that Robinson was correct when he predicted that the critical design issue for carbon composite vessels would be resistance to impact and casual damage, not simple resistance to rupture. This has already proven true in NGV2 cylinders with relatively little exposure to heavy impacts. When the existing impact test requirements of NGV2 or DOT-CFFC are considered in the context of the impact energy in a heavy truck accident or the rupture of an adjacent high-pressure cylinder it is clear that additional requirements are necessary for large and general-purpose carbon composite gas cylinders.

The experience base for NGV2 containers also includes several instances of heavy impact without container rupture. It is possible that variations in the details of design, and/or the conditions at the time of impact account for the different outcomes. Designs with thicker composite, hybrids using both glass and carbon fiber, as well as designs with a significant metal liner may be more inherently resistant to impact that the all-carbon Type 4 that has been absent from the U.S. market for about 8 years. Future all-carbon designs permitted in the standards may be significantly more susceptible to impact than those currently in production.

The existing experience base of accident results involves vehicle fuel containers that were in use and therefore partially charged. It is generally accepted that any significant internal pressure reduces the potential for impact damage to fiber reinforced vessels. The service conditions of fuel containers require that they not be empty during actual use. Vehicles are not intended to run out of gas, and most systems incorporate a low-pressure shutoff when the pressure in the fuel container drops below the level required by the regulator and injectors. Empty industrial cylinders, trailer tubes, and pressure vessels in transit to installation sites are not pressurized and the new Code rules for these should carefully address this difference in service conditions with regard to potential impact damage.

The scope of this report includes portable cylinders with pressures as low as 3,600 psi. Using common current industrial cylinder sizes for comparison this means a diameter of about 8 to 9 inches and a relatively thin wall. The research on impact resistance of carbon fiber vessels indicates that thickness has a major influence on the threshold energy level for damage. The small all-carbon portable cylinders included in the scope will be much thinner that the larger hybrid Type 4 CNG containers that represent nearly all of the actual use experience base for Type 4 NGV2 containers. This difference in thickness should be recognized, and the NASA and other studies of impact resistance should not be disregarded on the basis of service experience with a narrow class of vessels that does not represent the broad scope of the intended Code rules.

Impact resistance, particularly against immediate failure, should not be an insurmountable issue. There is anecdotal evidence that some large NGV2 cylinders have withstood impacts much greater than those required in the NGV2 standard test without rupture failure. This is encouraging and very fortunate since the impacts occurred on the public highway, not in a controlled test environment. Any new design code rules should require verification of a realistic level of impact resistance before the vessels are placed in service.

Impact damage that may result in delayed failure and is limited by reliable inspection capability can probably be factored into the required margin at manufacture to give an operating margin after impact that is still adequate.

The thickness increase that will accompany the increase in operating pressure to 15,000 psi will also likely increase the impact resistance in comparison to the two 3,600 psi designs that ruptured in service. After suitable impact tests are defined and performed with carbon Type 3 and 4 designs, this increase may prove sufficient, eliminating the need for additional design controls for future 15,000-psi vessels.

5 REQUIREMENT FOR SEPARATE DESIGN MARGINS FOR FATIGUE

This section includes a discussion of fatigue margins, how they are established in the Code and reference standards and how they may be addressed in new Code rules. As discussed in Section 4, when low margins are used on pressure vessels the resulting service stresses may cause fatigue failure at normal operating pressure. This concern is not addressed by the burst margin and is addressed separately here. Each of the different reference standards has provisions that have resulted in successful management of the fatigue issue and these are described and discussed. The differences between the service conditions of the reference standards and the new proposed code vessels are also discussed along with the significance for fatigue.

The low burst margins permitted in ASME Section VIII Division 3 are contingent on an independent requirement for fatigue design. There are various different approaches to the design fatigue margin in the non-ASME reference standards, but in all cases except DOT-3AA and ISO 11120, fatigue is addressed as a separate concern from the design margin. In the case of DOT-3AA, fatigue failure is a remote possibility and the standard simply predates the development of more sophisticated approaches to cylinder fatigue design. In the case of ISO 11120 fatigue is addressed indirectly by excluding unfavorable geometries such as inverted end shapes and by requiring NDE to detect significant manufacturing flaws. Fatigue may become a critical concern due to the degradation of properties by exposure to hydrogen and the larger strains occurring in metal liners of composite vessels.

5.1 ASME Code Fatigue Rules

Fatigue failure is not addressed in Section VIII Division 1 rules. The design margins are relatively large and only extraordinary fatigue design requirements are addressed and then with controls outside the scope of Division 1. Section VIII Division 2 and to a greater extent, Section VIII Division 3 do have mandatory fatigue design rules. Division 3 is selected as the most likely model for design rules because it offers two different analytical design approaches and a reasonably comprehensive empirical approach. Code Case 2390 is an exception with a fatigue requirement of 33,000 cycles to design pressure and a margin of at least 20 applied to the number of cycles expected during the vessel's 20-year life.

5.2 DOT Composite Fatigue Margins

DOT exemptions authorizing FRP-1 and FRP-2 make reference to the periodic retest requirements for DOT-3HT cylinders. DOT-3HT cylinders are lightweight, high-tensile strength steel cylinders authorized for use aboard aircraft. This specification introduced the limited-life DOT cylinder with both design and lot qualification fatigue test requirements. The number of test cycles to service pressure is 10,000 and 49CFR 205(v)(c) sets the maximum number of use cycles at 4,380 or every second day for the 24-year life of a DOT-3HT cylinder. This is a fatigue design factor of 2.283 on the number of cycles. It should be noted that this margin is applied against service pressure, not the maximum developed pressure.

DOT-3HT cylinders are used predominantly for breathing oxygen or a mixture of carbon dioxide and nitrogen to be used for inflation of emergency slides or flotation devices. Inflation cylinders are very unlikely to experience many fill cycles during the 24 year limited life of a DOT-3HT cylinder. Oxygen cylinders supplying the flight deck are used in routine, not just emergency conditions. These may be removed from service after the maximum number of cycles. Since the regulations do not contain an explicit maximum normal operating pressure, the actual maximum pressure on each fill cycle is in excess of service pressure and as high as 125% of service pressure. Some of the fatigue design margin against service pressure must account for this higher-pressure range for actual service cycles.

The DOT-3HT requirements are not directly applicable to hydrogen cylinders since they are not permitted for flammable gases, but the DOT exemptions for FRP-1, FRP-2, and CFFC composite cylinders refer to the retest requirements for 3HT cylinders. It is not clear whether this means that composites are also limited to 4,380 filling cycles, or whether the number should be 2,728 for one every second day of the 15 year limited life of composite cylinders, or whether there is no limit of cycles for FRP and CFFC cylinders. Given the low number of cycles in the required fatigue tests, a limit is needed and the best estimate is that the design fatigue margin for DOT composites is intended to be between 2.283 and 2.90.

These fatigue margins appear quite low as design values but they apply not only to the initial design but also to on-going production as a lot test. The practical impact of this requirement is that while a manufacturer could qualify a design with little excess fatigue resistance by performing the required three fatigue test samples, continuous production requires a reasonable assurance that each lot sample will satisfy the requirement for 10,000 cycles. Lot fatigue test requirements have the effect of forcing the manufacturer to be conservative with respect to the minimum design fatigue margin or else risk repeated lot test failures. If a 10% probability of lot failure is acceptable, probably not true economically, the design should have a Weibul B-10 life of 10,000 cycles and a fatigue design margin in the range of 2 to 3 is probably appropriate when coupled with the B-10 life.

ASME Section VIII Division 3 correctly considers the failure mode in fatigue to be a first consideration in determining the fatigue design. If the design will fail in fatigue by leaking instead of bursting (LBB), the fatigue analysis requirements may be less rigorous. This is appropriate given the relatively benign LBB failure mode. The DOT requirements can also be viewed in this light. Although no DOT specifications explicitly require LBB, it is commonly present in DOT-3HT and composite cylinders. DOT-3HT cylinders are limited to hemispherical or 2:1 ellipsoidal end shapes. This eliminates the fatigue-prone region of the common inverted bottom on industrial cylinders and effectively forces the location of the fatigue failure into the cylindrical sidewall where bending stresses are low. The specification also requires a surface finish no worse than 250 RMS. The effect of these limits is a design that historically fails LBB in fatigue tests.

FRP-1, FRP-2, and CFFC designs satisfy the general requirements of KD-931 (b) and can be considered to be inherently LBB where the liner is covered with composite. The exposed end domes of FRP-2 cylinders may not be LBB if a fatigue failure there originates due to bending as opposed to membrane stresses.

This discussion of fatigue margins assumes that requirements similar to those of KG-311.10 are met. This means that the LBB failure mode is taken into account if it is supported by vessel history or analysis and also that a leak failure is acceptable. There are a number of approaches to establishing that a design will fail LBB. The question of the acceptability of a leak failure is up to the customer, but in general usage a leak in a fuel system is not treated as a catastrophic event.

5.3 DOT-3AA Metal Fatigue Margins

DOT-3AA and 3AAX cylinders are not required to meet any explicit fatigue test requirements. Some commercial purchase specifications require that DOT-3AA cylinder designs be qualified with 10,000 cycles to the hydrostatic test pressure, 1.515 times the maximum fill pressure, NOP, at 70°F and 1.21 times the maximum developed pressure at 55°C pressure, MNOP. The limiting design element in these tests is usually the inverted bottom of industrial cylinders. DOT 3AA gives no design limits for this bottom, and the only practical limit on stress is that the stress at the hydrostatic test not significantly exceed the yield strength and result in unacceptable permanent expansion.

For the sidewall, the stress at test pressure is limited to 67% of the actual ultimate tensile strength by thickness formula, but with a Y: T ratio of about 88%, the stress in the bottom portion could be as high as 88% of the tensile strength. This potential 30%+ increase in fatigue stress can result in a failure in the bottom at a number of cycles well below the life of the sidewall. It is also important to consider that a fatigue failure in this area will very often not be LBB. The bending stresses in this area promotes the growth cracks with a very long ratio of length to depth, postponing penetration and leakage until the crack extent is so great as to result in collapse and rupture. The result is analogous to fatigue failure in a thread or blind end as discussed in KD 141(b). All such features in a Division 3 vessel must have a fracture mechanics analysis, not an assumption of LBB.

Actual fatigue cycle tests of DOT-3AA and DOT-3AL designs from seven different manufacturers performed by Pressed Steel Tank Co., Inc and submitted in support of their application for DOT exemption E 9791 [59] gave results for sidewall failure up to more than 60,000 cycles at test pressure but some bottoms failed at less than 3,000 cycles, only 5% of the best result for sidewall failure locations. The failures in the sidewalls were LBB, but not in all inverted bottoms. Since bending stresses drove the bottom failures, it should not be assumed that the mode would change to leak at the lower MNOP of about 80% of test pressure.

The fatigue performance of the larger DOT-3AAX "trailer tubes" can be inferred from similarity to smaller DOT-3AA cylinders. The materials of both are equivalent in composition and heat treat. The sidewall finish should often be similar since both tubes and cylinders are often made from hot finished pipe or equivalent forgings. Although DOT permits inverted bottoms on both, no one wants a trailer tube to stand upright, and tubes typically have hemispherical ends and are not subject to the high bending stresses typical of many industrial cylinder designs. It can therefore be estimated that the fatigue life of DOT-3AAX tubes will exceed 10,000 cycles to test pressure in a prototype test.

LBB performance of DOT-3AAX cylinders is less clear. A common trailer tube diameter is 22 inches outside diameter (OD). A DOT-3AAX 4545+ tube for filling to 5,000 psi will have a minimum design sidewall of 0.909 inches. If it is assumed that this thickness can be optimally heat treated, there is still the question of determining LBB in a vessel of about twice the thickness of any reasonably common DOT 3AA cylinder. The greater thickness has the effect of altering the conditions at the fatigue crack from approximately plain stress to more in the direction of plain strain. LBB for such a tube is still an open question.

The commercial specifications applied to many DOT-3AA industrial cylinders do not require cycling to failure with LBB failure mode at test pressure, and test results showed that not all 3AA cylinders are LBB at test pressure.

5.4 NGV2 Fatigue Design Rules

The design fatigue margin in other reference standards is not derived from DOT requirements. For NGV2, the design qualification and lot qualification fatigue requirements are the same as the intended use cycles, a fatigue design margin of 1.0 on cycles. The test fatigue pressure is, however, the same as the maximum permitted fill pressure (MNOP), not the nominal service pressure. Conservatism in the NGV2 design fatigue margin comes from the manufacturer's self interest in being able to pass almost all lot tests, coupled with some conservatism in allowing for 750 full refuelings per year of design calendar life. NGV2 also requires demonstration of LBB or the fatigue design margin is increased by a factor of 2.25 to 3.0. DOT FRP/CFFC and NGV2 take similar approaches; combining a low fatigue design margin and also requiring a lot test to require the manufacturer to manage scatter in fatigue results, but do not require LBB for either DOT FRP or CFFC cylinders.

5.5 ISO Fuel Cylinder Fatigue Design Rules

ISO 11439 and ISO DIS 15869 adopted the NGV2 fatigue approach but increased the design refueling cycles to 1,000 per year of design life.

5.6 ISO Metal Gas Cylinder Design Rules

For unlimited cylinder life, ISO 9809-1 requires either 12,000 cycles to the hydrostatic test pressure, 1.5 times the working pressure, or 80,000 cycles to working pressure as prototype tests. For this analysis, the equivalent "DOT" service pressure is 102% of the ISO working pressure and the maximum normal operating pressure is 120% of that service pressure or 122% of the ISO working pressure. The pressure margin for fatigue in ISO 9809-1 is therefore either 1.50/1.22 or 1.23 against MNOP for 12,000 cycles or 1/1.22 or 0.82 for 80,000 cycles.

It is important to note that these results are required only on initial prototypes and there is no on-going lot testing for fatigue. A substantial portion of any theoretical design fatigue margin must therefore be dedicated to scatter. An illustration of fatigue scatter may be taken from the previously mentioned test data presented in support of the Pressed Steel Tank Exemption E9791. In these tests eight nearly identical high-strength steel cylinders were cycled to failure at 1.5 times the maximum fill pressure. The sidewalls of all cylinders were ground to remove all perceptible surface imperfections and subjected to wet magnetic particle examination prior to and after closing. The cylinders were produced from a single steel heat and in a single heat treat lot. All of these measures are expected to reduce the scatter in fatigue test results.

Two cylinders failed in the sidewall-bottom-transition (SBT) due to circumferential grinding marks on the inside. One withstood 34,772 cycles and failed LBB while the other withstood 17,469 cycles and burst. The process controls were subsequently adjusted to eliminate grind marks in the transition.

Six cylinders failed in the sidewall after cycles ranging from 21,326 to 30,648. All sidewall failures were LBB.

The fatigue life of the sidewalls ranged from 21,326 to more than 34,772 cycles, a ratio of 1:1.63. This scatter resulted even after every feasible measure to eliminate variation was taken on the prototype units. Other estimates of fatigue scatter may vary from 4:1 to 10:1. As a general rule, all of the detail improvements in uniformity and surface condition that are used to increase fatigue life also have the affect of reducing scatter by making all samples more similar to one another.

ISO 9809-1 contains design limits on the thickness and shape to reduce the high stresses in the SBT that are present in many older DOT-3AA designs. Walters [60] presents stress analysis results for an ISO compliant design, but it is clear that the SBT remains more susceptible to fatigue than the sidewall. The peak meridional tensile stress at the inside of the knuckle is about 1.45 times the hoop stress in the sidewall. The meridional stress on the outside of the knuckle is compressive, 0.68 times the sidewall hoop stress. This type of bending stress with steep gradient in a blind vessel end is recognized in Division 3 as inherently questionable for LBB. This area is also more difficult than the sidewall to examine with common NDE techniques. The ISO design requirements for the bottom probably result in improved fatigue performance over the minimum DOT requirements, but fall short of ensuring a sidewall failure location and resultant assurance of LBB.

ISO TR 13763 [61] does not give any derivation for the number of actual cycles intended in service. There is also no requirement that the ISO 9809-1 designs demonstrate LBB.

ISO 11120, the standard for trailer tubes that are equivalent to DOT-3AAX specification tubes in the United States, does not contain any specific design controls against fatigue. The design margin on burst is somewhat higher than DOT-3AAX, there is a special control on the Y:T ratio for tubes to be used for hydrogen, and ISO 11120-7.2 requires that the ends be hemispherical. Taken together, these requirements probably result in a tube with fatigue cycle and LBB performance equivalent to the DOT-3AAX discussed earlier. The same caveat regarding the potential loss of LBB performance with higher pressures and thicker sections applies.

5.7 ISO Composite Gas Cylinder Fatigue Design Rules

ISO 11119 allows for limited life designs by requiring either 250 cycles to the hydrostatic test pressure or 500 cycles to the maximum developed pressure per year of design life, the latter only for cylinders dedicated to a specific gas service. This requirement is applied to both prototype and production lot tests. For hydrogen, the maximum developed pressure can be calculated. For a 5,000 psi working pressure, the maximum developed pressure at 65°C in hydrogen is approximately 5,950 psig or 121% of ISO working pressure or 119% of the equivalent DOT service pressure.

Applying the ISO 11119 fatigue margins in terms of the use in the United States, the pressure margin in fatigue is 1.5/1.22 or 1.23 against MNOP for 250 cycles per year of design life or, strictly for cylinders dedicated to hydrogen service, 1.19/1.12 or 1.06 against service pressure for 500 cycles per year of service.

ISO 11119 allows a nonlimited life for any cylinder meeting the number of cycles calculated for a 48 year life, 12,000 to the hydrostatic test pressure or 24,000 to the maximum developed pressure.

Any ISO 11119 design that survives two times the minimum numbers of cycles for a limited life design or the number of cycles for an unlimited life design need not demonstrate LBB.

It is apparent that the fatigue requirements for a nonlimited life design under ISO 11119 are more demanding than under ISO 9809-1 because of the fatigue lot test requirement in ISO 11119. The designer of an ISO 9809 cylinder must only pass the sample test once while ISO 11119 requires frequent retests.

5.8 ASME Code Case 2390-1 Fatigue Design Rules

Code Case 2390 is a hybrid of fatigue design and fatigue performance test. The design stress analysis must be performed in accordance with KD-240, accounting for plastic response. The fracture mechanics fatigue analysis must be done in accordance with KD-4 and LBB may not be assumed. The resulting design must then be verified in fatigue testing. At least 33,000 cycles to the design pressure are required with at least 3,000 at the minimum design temperature and the balance at the maximum design temperature. The temperature limits also apply to the test fluid, unlike the typical extreme temperature cycle test in the other reference standards for composite gas cylinders. The design in-service cycles may be no greater than 1/20th of the fatigue test cycles. This qualifying test is required for the design and must be repeated annually thereafter or after no more than 1,000 vessels. Since design pressure and maximum normal operating pressure are equal for ASME vessels, the pressure margin in fatigue is 1.0 times MNOP for 33,000 cycles, or 20 times the cycle design life, whichever is greater. Also, the margin in ASME Section VIII Division 3, Article KD-4 is based on limiting the crack to 1/4 of the critical crack size or limiting the number of cycles to 1/2 of those required to reach the critical crack size. This test requirement appears to be very conservative compared to the other reference standards, but other factors should be considered.

The fatigue test is required only annually or for each 1,000 vessels produced. This provides less assurance that the manufacturer will account for scatter in fatigue results to assure acceptable results in frequent lot tests as required in the other composite standards.

There is no requirement for LBB, and the details of the design requirements do not appear to make LBB an inherent characteristic. Unlike all other reference standards, there is no minimum strength requirement for the liner beyond supporting the burst factor of 2.0. It should be noted that margin on collapse was changed to 1.732 in the 2004 edition of ASME Section VIII Division 3, and it may be possible to change the Code Case as well. The autofrettage is combined with the proof test, but there are no particular limits on the stresses in the liner, either before or after autofrettage. It is possible that the resulting design will fail by fatigue due to the longitudinal stress in the liner and the hoop wrap will not prevent a rupture failure in this direction. The Case allows both circumferential and longitudinal welds in the liner, and there is no requirement for local reinforcement at the welds. Weld misalignment and peaking are addressed in the fracture mechanics analysis. The fatigue stresses in the welds will be as high as in the base metal, and the fatigue resistance of the weld must be assumed less, resulting in fatigue failure in the weld. If there is a fatigue failure in the longitudinal weld, the hoop wrap will provide sufficient reinforcement to prevent a burst failure mode.

Nearly all of the fatigue testing is performed at the maximum design temperature. The differential thermal expansion between the steel liner and glass composite will transfer more load to the wrap at this temperature and reduce the peak fatigue stresses in comparison to stresses at a more normal working temperature.

Of the two considerations, LBB is the most important. Any design that will not fail LBB must have a higher design margin in fatigue and/or be subject to stringent NDE for requalification as recommended in Section 3.

6 EVALUATION OF MARGINS FOR 15,000 PSI METAL AND COMPOSITE VESSELS

This section draws on the results of the margin comparison in Section 4 but focuses on margins for high-pressure vessels, up to 15,000 psi operating pressure. Since the reference standards and the experience base were for lower operating pressures, typically a few thousand psi, it is necessary to determine whether the margins that have been demonstrated to be safe in vessels at lower pressures can be adopted for 15,000-psi vessels. It was found that the issues related to all metal vessels are significantly different from those for composites and the two-material groups are treated separately as in Section 4.

6.1 Use of Reference Standards

All recommendations for margins are based on the general margins that were reviewed, normalized and reduced to specific recommendations in Section 4. This section will address those specific additional issues that must be considered when the pressure of the vessels is increased beyond the typical maximum pressure for general-purpose gas cylinders and pressure vessels. The ASME Code generally recognizes 3,000 psi as a level in Section VIII Division 1 above which special considerations are suggested for the manufacturer. Divisions 2 and 3 contain alternative rules and are more generally suited to higher design pressures. A common vessel design using Section VIII Division 1 for higher-pressure service is the forged, seamless vessel as described in Appendix 22. The features allowable in this design eliminate welds, stress concentrations, materials with low ductility and the other characteristics that would be increasingly undesirable in vessels as pressure is increased. These are also the undesirable features that are absent in metal gas cylinders with low margins. Appendix 22 vessels are commonly used for CNG fuel storage at normal operating pressures up to 5,000 psi. The actual pressure experience with gas cylinders is very similar. While there are very small numbers of DOT gas cylinders in use at higher pressures, 5,000 psi is a reasonable threshold for ordinary cylinders, whether metal or composite. DOT FRP-1, DOT FRP-2, and DOT-CFFC contain explicit limits to not more than 5,000 psi service pressure (6,000 psi MNOP).

6.2 Design Pressure Requirements

The context of discussion of new high-pressure vessel designs for hydrogen is predicated on providing storage at 15,000 psi to allow rapid filling of vehicles to 10,000 psi. 15,000 psi is therefore interpreted as normal operating pressure (NOP) or service pressure. This storage may be either portable or stationary. In the stationary case, the vessels will be pressurized from a compressor and the NOP will be 15,000 psi. Assuming that the new vessels will be installed and used in a way similar to the 5,000-psi fuel storage vessels at CNG refueling stations, NOP must be less than MNOP to allow for thermal expansion effects. For this reason MNOP is estimated at 110% of NOP for an above ground storage vessel. Since MNOP = design pressure in ASME nomenclature, the ASME design pressure of a "15,000 psi" cascade storage vessel is 16,500 psi.

6.3 Design for 15,000 psi Metal Vessels

6.3.1 ASME Minimum Burst Margin

ASME Section VIII Division 3 is the only reference standard that explicitly covers the design of pressure vessels for pressures to 15,000 or 17,000 psi; however, this pressure range is not excluded from ASME Section VIII Divisions 1 and 2. KD-240 (a) requires a calculated margin in collapse of 1.732. There are many additional design rules dependent on the details of the vessel design, loading and materials that are too complex to be generalized here, but the calculated margin on collapse may not be less than 1.732.

6.3.2 Critical Difference in High Pressure Design

The principal difference in design between conventional pressure vessels for 5,000 psi service and 16,500 psi vessels is the thick wall effects and the much higher radial compressive stress at the inside surface of the vessel. These effects will result in locally higher stress at the inside surface and possibly drive the margin due to fatigue concerns, not simply the margin against collapse. ASME Section VIII Division 3 contains express rules to allow techniques such as layering and prestressing to reduce the local high stress on the inside as separate from the issue of margin against collapse. This practice is recommended for any new code rules.

The same practice of separating the margin in collapse from the secondary issue of thick wall effects and high stress at the inside diameter (ID) should be carried over from Division 3 to any future versions of these other standards for 15,000 psi pressures.

6.3.3 Effect of Design Pressure on Recommended Minimum Margin

When margin is defined strictly as protection against collapse load as it is in KD-240 (a), there is no need to increase or decrease that margin with pressure.

6.3.4 Extrapolation of Reference Standards to 15,000 psi Operating Pressure

As shown in Section 1, the other standards for metal vessels typically include design rules for minimum thickness that are not intended to result in a constant margin against collapse with very high pressures. All such rules with the exception of KD-251.1 result in significant increases in margin against collapse as the design pressure is increased from the intended range of 5,000 psi to 15,000 psi as illustrated in Figure 4. This is believed to be due to the simplifying assumptions in the formulas that are reasonable at the lower pressures but result in progressively higher errors as the internal pressure increases as a percentage of the design material strength.

All of the reference standards for composite vessels incorporate provisions for layering and prestressing. None of these standards contain any useful design calculation rules and the standards treat all vessels as empirical designs that may only be deemed safe after performance tests that are intended to provide safe margins against different failure modes in service.

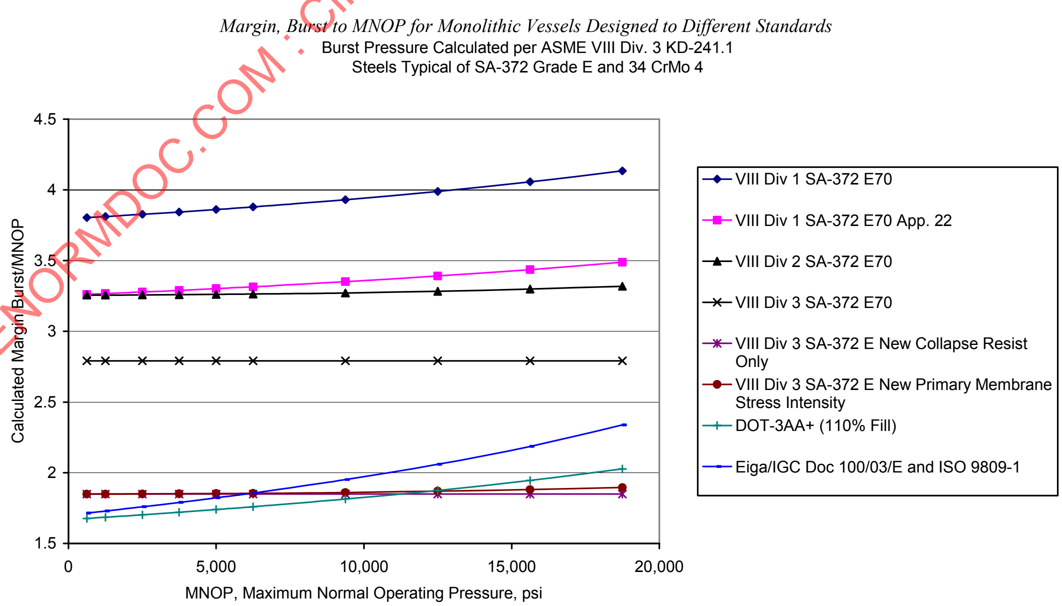

Figure 4 - Margin, Burst to MNOP for Various Standards

6.3.5 Wall Thickness of Ductile Metal Vessels for 15,000 psi Operating Pressure

This section compares the minimum wall thickness required by various metal vessel standards for an operating pressure of 15,000 psi. As introduced in Section 1.3, the required wall thickness is a major issue in both the design and manufacture of metal vessels for very high operating pressure. This is one reason to use the lowest design margin consistent with safety.

6.3.5.1 Assumptions

SA 372 E70 quenched and tempered low alloy steel was selected for this comparison because the chemistry, heat treatment and tensile strength limits are common and generally acceptable for all of the different standards. For the purposes of burst pressure calculation, the estimated actual minimum yield strength is 88% of the UTS. This issue was introduced in Section 2.8.2.2.(b) and is analogous to the guaranteed minimum yield strength concept used in ISO standards.

The maximum tensile strength of 140,000 psi for SA 372 E70 is higher than the 137,775 psi maximum for hydrogen service imposed by IGC Document 100/01/e, but it is believed feasible to heat treat reliably within the reduced range of 120,000 psi to 138,000 psi. This discussion assumes that the present maximum tensile strength limit will be applicable at 15,000 psi, but there is some chance this may not be true after material tests are complete.

The thicknesses are normalized to an MNOP equal to 110 % of NOP, typical for ASME storage vessels. The MNOP or ASME design pressure is therefore 16,500 psi. Applying the recommended minimum margin of 1.721 recommended in Section 4.2 results in a minimum burst pressure of 28,397 psi. The MNOP: Design pressure ratios used for the other standards are from Table 1, Column 3.

The burst pressure calculation is based on ASME Section VIII Division 3 KD-251.1 except that the stress is the minimum flow stress, mean of minimum UTS and estimated minimum yield strength. Designing for this margin and burst pressure results in a significant reduction in wall thickness in comparison to all three ASME Section VIII Divisions if used with the allowable stress values from ASME Section II Part D. In addition, all but one of the various design rules for determining minimum wall result in a calculated wall thickness at higher pressures that is greater than necessary to maintain a constant margin against plastic collapse burst. The exception is the collapse formula in ASME Section VIII, Div.3.

Figure 5 shows a comparison of the required minimum wall thickness for different metal vessel designs with 8-inch inside diameter over a wide range of MNOP values. The diameter selected is arbitrary and the results are scalable to other diameters. The thicknesses were calculated as follows.

(a) The calculations for ASME Divisions 1 and 2 use the standard design rules and design allowable stress from ASME Section II-D.

(b) The ASME Appendix 22 calculation uses an allowable stress of 1/3 of the specified minimum tensile strength.

(c) The Division 3 SA372 E70 calculation is based on the design allowable yield strength from Section II-D and the calculation for resistance to plastic collapse in KD-251.1

(d) The Division 3 SA372 New Collapse Resist Only is calculated with an allowable yield strength equal to the estimated minimum yield strength of 105,600 psi, not the minimum value from II-D. This is the thickness that would be required if a new SA372 material were adopted with a higher minimum yield strength.

(e) The DOT-3AA thickness is calculated with the standard stress formula and the DOT minimum tensile strength of 104,478 psi.

(f) The IGC/ISO 9809-1 thickness is calculated using the ISO formula and a minimum tensile strength of 120,000 psi, the same as SA 372 E70.

(g) The final DOT-3 with 120,000 min UTS line is calculated using the DOT-3AA stress formula but with a minimum tensile strength of 120,000 psi for direct comparison to the other standards with the same minimum tensile strength.

6.3.5.2 Calculated Minimum Thicknesses

(a) The minimum thickness for a calculated burst pressure of 28,397 psi is 0.974 inch. This is the thickness that would be necessary if the only requirement were the recommended burst to MNOP margin of 1.721 with minimum tensile strength of 120,000 psi and minimum yield strength of 105,600 psi and using a design calculation based on KD-251.1 but using the flow stress rather than the minimum yield strength.

(b) The minimum thicknesses calculated using the different Code and standard formulas shown in Figure 5 are as follows.

(1) The minimum design thickness for ASME Section VIII Div 1 SA372 E70 is 2.757 inch.

(2) The minimum design thickness for ASME Section VIII Appendix 22 SA372 E70 is 2.202 inch

(3) The minimum design thickness for ASME Section VIII Div 2 SA372 E70 is 2.045 inch.

(4) The minimum design thickness for ASME Section VIII Div 3 SA372 E70 is 1.697 inch.

(5) The minimum design thickness for ASME Section VII Div 3 using a realistic minimum yield strength of 105,600 psi is 1.056 inch.

(6) The minimum design thickness for DOT-3AA is 1.326 inch.

(7) The minimum design thickness for IGC/ISO 9809-1 using a minimum tensile strength of 120,000 psi is 1.269 inch.

(8) The minimum design thickness using the DOT stress formula and a realistic minimum tensile strength of 120,000 psi is 1.099 inch.

In the cases of ASME Section VIII Division 3 and DOT-3AA, the calculated minimum thickness is not only a function of the basic design rules but also of the additional stress limits. In the examples of ASME Division 3, the first calculation is based on the minimum yield strength for SA 372 E70. The very low specified minimum yield results in a thicker sidewall. The second calculation is included to show what the thickness requirement would be if a material specification with a higher, but realistic, minimum yield strength were adopted. This second example is a more accurate estimate of the wall thickness and margin inherent in Division 3 design rules.

In the case of DOT-3AA, stress limits outside of the basic design rule limit the maximum usable minimum tensile strength to 104,478 psi. As in the case of ASME Division 3, this results in a greater required wall thickness independent of the basic design rules. The second DOT-3 example excludes the limitation to 104,478 psi minimum UTS and uses the same minimum tensile strength as all of the other examples, 120,000 psi.

6.3.5.3 Recommendations

If a new Code is developed based on an accurately determined minimum burst margin, two requirements are recommended.

(a) The stress or thickness calculation rule should be selected and validated to give consistent results over the desired pressure range of 3,600 psi to 16,500 psi. KD-251.1 is suggested as a good

candidate for low-alloy steels and similar metals. A number of the other reference standard rules appear to become progressively less accurate at very high pressures.

(b) The stress used in the calculation should be a realistic estimate of the flow stress of the metal and based on minimum tensile and yield strengths for the actual vessels produced. For the particular case of SA 372 E material, this would require either the adoption of a new grade designation in Section II D or else the adoption of a guaranteed minimum value similar to ISO standards. If the vessels manufactured to the new Code are forgings or otherwise heat treated after fabrication, the yield strength will be controlled by the vessel manufacturer's process and the concept of guaranteed minimum yield strength may be easiest to implement.

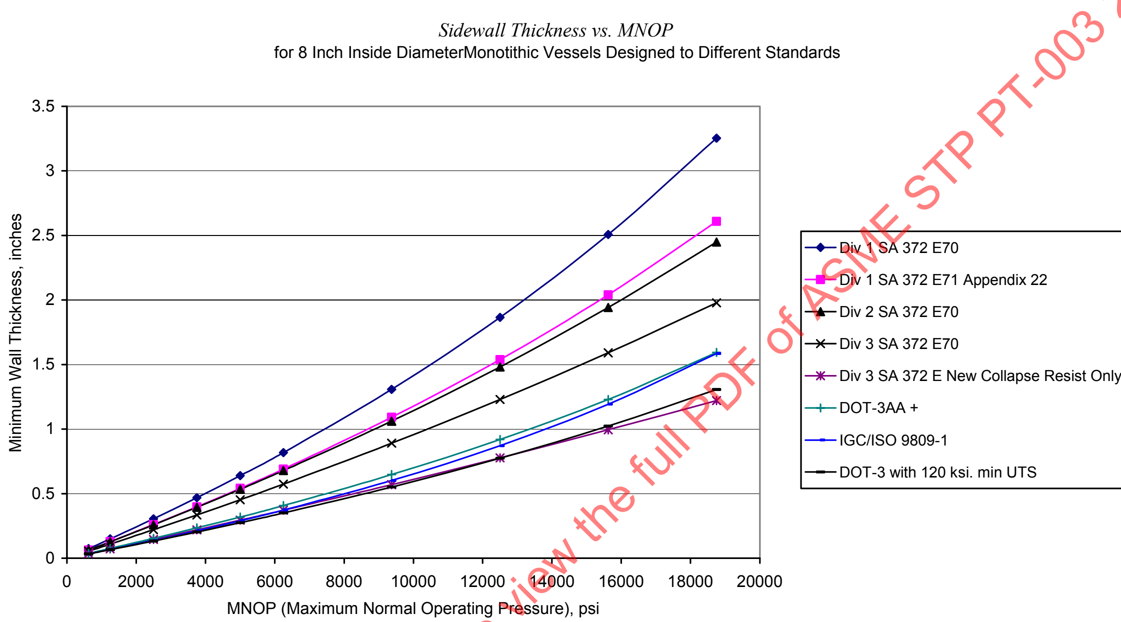

Figure 5 - Minimum Design Sidewall Thickness for Various Standards

6.3.6 Wall Thickness Concerns for Vessels Operating at 15,000 psi

Only one standard out of all those referenced for this report is explicitly applicable to vessels for 15,000 psi service, ASME Section VIII Division 3. This section applies only to storage vessels and is not referenced by DOT for transport cylinders or trailer tubes. As a result of the limitation to storage vessels, the design pressure may be considered equal to the maximum normal operating pressure (MNOP) except for the margin for a nominal relief valve setting. The primary difference between 15,000-psi vessels and those that are commonly produced in accordance with the various gas cylinder standards and ASME Section VIII Divisions 1 and 2 is in the thickness of the vessel wall in comparison to the diameter. This thickness effect does not in itself require different margins, but it does affect many of the assumptions that support the safe use of low margins. The thickness also has a disproportionately adverse impact on the cost and weight of vessels due to the inefficient distribution of operating stresses through the thickness of a conventional monolithic metal vessel. Reducing the negative effects of increased thickness on the design is the major benefit of optimizing the margin at lower values typical for compressed gas cylinders. The increase in design pressure and resultant wall thickness increase may affect the assumptions for metal vessels.

6.3.7 Critical Conditions for Safe Application of Low Margins at 15,000 psi

For the purpose of this discussion, the safe application of low margins in metal vessels is based on the approach of satisfying the same critical conditions that exist for DOT-3AA cylinders.

6.3.7.1 Limit Discontinuities

The vessel should be manufactured free abrupt section changes, stress raisers and other discontinuities. With the proper restrictions, welded construction can be used. The heads at each end must be integral, preferably concave to pressure and adequately thickened at the openings. ASME Section VIII Division 1 Appendix 22 is a good reference for these requirements. All of these limitations exist in the low margin experience base cylinders designed to DOT-3AA and DOT-3AAX. The vessel resulting size may be limited by available seamless stock sizes as well as the available capacity to form integral heads.

6.3.7.2 Ductile Behavior

The metal vessel should behave in a ductile manner in fatigue, not failing by brittle fracture. This may impose additional requirements on the vessel material, which may be subject to embrittlement due to exposure to hydrogen. Additionally, the added thickness required for 15,000 psi NOP vessels results in greater constraint and shifts the failure from elastic plastic in the direction of linear elastic, increasing the risk of a brittle fracture. The increased thickness in proportion to diameter reduces the amount of plastic bulging at the failure, further increasing the risk of brittle failure. Without verification, there is no assurance that the condition of ductile failure will be satisfied.

The metal of the vessel must not be embrittled by exposure to low-temperature environments. DOT-3AA cylinders are considered acceptable for use at -40°C but additional impact test requirements are considered necessary for arctic service at -50°C [62]. It may be unlikely that 15,000 psi hydrogen vessels will be used in the arctic and warmer requirements should not be difficult to meet as long as the added wall thickness does not compromise the quality of the heat treatment.

In the event that a ductile LBB failure mode cannot be provided, effective testing during service must be applied to detect subcritical cracks well before they grow to a size that could result in failure. See Section 3 for more detail on this.

6.3.7.3 External Loads Must be Small

The bending stresses in long vessels must not result in a margin below the minimum value of 1.721. This factor is dependent on the length of the vessel and the support points. It can be managed and need not be a major limiting factor.

6.3.7.4 Manufacturing and Retest Proof Test Must Be Discriminating

The individual proof pressure test at manufacture and at periodic requalification must subject the cylinder to high pressure and stresses sufficient to cause test failure if there is a significant deficiency in sidewall strength. This test is integral to the DOT-3AA specification that is the precedent for low-margin vessels. This test ensures against significant loss of margin at MNOP during the life of the vessel. The retest requirement assumes that flaw detection NDE is not performed. Given the size of the vessels, the large amount of energy stored in the test fluid compressed to a large factor in excess of 15,000 psi and the safety measures required in the event of failure, this retest will be both costly and difficult. As in the case of DOT 3AA cylinders, the test pressure must load the vessel close to the point of design plastic collapse. See Section 3 for more discussion on this.

6.3.7.5 An Alternative to the Periodic Pressure Test

Periodic visual inspection or other NDE must be performed to detect damage due to corrosion, abrasion, arc burns, etc. in the manner practiced for DOT gas cylinders. See Section 3 for more discussion on this.

6.3.7.6 Protection from Overpressure

The vessel must be protected from failure due to overpressure resulting from exposure to the action of fire. At a minimum, protection equivalent to that required for DOT-3AA and DOT-3AAX cylinders is necessary. The protection required in Section VIII Division 1 or 2 is probably more appropriate for a storage vessel.

6.3.7.7 Fatigue Design

Metal fatigue must not be a high priority concern, or it must be controlled with other additional design provisions. The frequency of pressure cycling in DOT gas cylinder service is low. The basic margin provides adequate control against fatigue failure in these conditions. If the pressure cycling rate is increased above one every few days, or if the fatigue strength of the vessel metal is adversely affected by exposure to hydrogen, fatigue margins may override the burst margin and require stresses to be reduced with added wall thickness.

When the wall thickness is determined by a burst margin in thick vessels, the fatigue stress at the inside surface will be higher due to the radial compressive stress and thick wall effects. It is anticipated that autofrettage and/or layering may be necessary to provide beneficial prestress in the sidewall to reduce the equivalent stress at the inside surface. This will require design calculations as provided in Section VIII Division 3. Since autofrettage is an intentional pressurization that causes plastic strain of the inner portions of the vessel wall, it satisfies the requirement for a discriminating pressure test.

If fatigue is a design concern, the vessel should exhibit a leak-before-break (LBB) failure mode at MNOP. ISO TR 12391 contains guidance in developing and validating tests to verify LBB of gas cylinders. LBB may not be feasible with the thickness required for 15,000-psi vessels. Reducing the stress by increasing the thickness may be required, but the added thickness will again adversely affect LBB. It may be necessary to provide layering on an inner liner to ensure LBB in 15,000-psi vessels.

If fatigue is a design concern, the vessel should be designed and verified by test to reliably fail by fatigue in the cylindrical portion of uniform parallel sidewall and the fatigue crack should be oriented normal to the principal tangential (hoop) stress. This is often difficult to assure if the end is convex to pressure, but is essential for both LBB and effective NDE to detect growing fatigue cracks.

When fatigue is a design concern, the vessel must be tested to establish the actual fatigue cycle life as related to the intended number of lifetime use cycles. Fatigue design margin is considered separately below.

If LBB cannot be assured, as may be the case with thick walled vessels, it will be necessary to practice a stringent periodic inspection for growing fatigue cracks as discussed in Section 3. With the very high severity of any rupture failure of a hydrogen vessel at high pressure, the vessel must be removed from service when there is still a substantial margin in remaining fatigue life before the next inspection interval. Considerations for verifying the reliability of the inspection practices are included in Section 3.

External hoop reinforcement can be used to ensure LBB even if it is not relied on to carry operating pressure loads. An early example is the use of wire winding to prevent fragmentation of compressed gas cylinders as a result of gunfire in combat [63].

6.3.7.8 Hydrogen Compatibility

The cylinder materials must be compatible with hydrogen. The metal of the vessel must not be susceptible to failure by hydrogen embrittlement. The combination of minimum elongation in the tensile test and the required flattening test impose an effective upper limit on the tensile strength of DOT-3AA cylinders at about 140,000 psi. Additionally, the manufacturers have an interest in limiting the hardness for machinability. The tensile strength is normally in the range of 105,000 to 130,000 psi with rare excursions above that range. IGC Document 100/03/E contains supplementary requirements for steel hydrogen cylinders in Europe. European cylinder specifications have generally required lower tensile elongation than DOT-3AA and there have been failures of higher strength steel cylinders in hydrogen service, resulting in the IGC standard. The maximum tensile strength for steel cylinders according to the IGC standard is 950 MPa (137,750 psi), virtually the same as the de facto limit for DOT-3AA cylinders. This limit may not be conservative at 15,000 psi and materials must be tested for compatibility at the intended hydrogen operating pressure.

Factors that should be considered in material compatibility include the operating pressure and temperature, the uniformity of the metallurgy and any effects of plastic strain resulting from autofrettage. Regarding uniformity, banding of adjacent regions of relatively alloy rich and alloy poor regions was identified as the local cause of the 3T trailer tube failure in sour gas service [72]. It was concluded that the vessel would probably have ultimately failed without the banding, but banding accelerated the failure at that specific location. Steels with enhanced resistance to hydrogen, to resist hydrogen induced cracking (HIC) as an example, are produced with additional stringent controls on microstructure and this variable should be accounted for in any material studies.

6.4 Design for 15,000 psi Composite Reinforced Vessels

6.4.1 Potential Advantages of Composite Vessels for 15,000 psi

Composite pressure vessels may be inherently advantageous for 15,000-psi service. Compared to ASME Section VIII Division 3, the only standard now inherently suited for 15,000-psi vessels; composites share many of the techniques that are included in Division 3 for high-pressure vessels.

6.4.1.1 Layering

Composite vessels are constructed of a large number of very thin layers of composite. Layering is an essential strategy in the design of many high-pressure vessels. As in Division 3, this allows for the theoretical reduction of tensile stress variation through the thick wall required for high-pressure vessels.

6.4.1.2 Autofrettage

Virtually all-metal-lined composite cylinders use autofrettage to manage peak fatigue stresses in the metal liner. It is also advantageous for very high-pressure vessels.

6.4.1.3 Required Metal Wall Thickness

Many of the concerns discussed in the previous section about all metal 15,000 psi designs dealt with the effects of increased thickness for the metal wall. This thickness can be reduced for liners to be reinforced with composites. The thickness reduction may range from 50% for Type 2 designs to 80 to 90% for Type 3 designs. The reduced thickness eliminates or alleviates many of the concerns about heat treatment and resulting toughness that are important for all metal designs.

6.4.1.4 Required Total Wall Thickness

The very high strength level of carbon fiber composites has the potential to reduce the total wall thickness of the vessel, reducing the negative impact of very thick walls on stress uniformity.

6.4.1.5 Increased Resistance to External Impact and Improved Detection

Relative to lower, more conventional pressures, the increased wall thickness of the 15,000-psi vessel should result in an increase in the inherent resistance to damage from impact. Composites, particularly carbon composites, are susceptible to damage by impact, which may be difficult to detect. The most damaging deformation is similar to "oil-canning" in metals when the surface is deflected inward and then released. Increasing the pressure to 15,000 psi should be a significant advantage in this failure mode since the resulting thick composite wall will be more resistant to "oil-canning" deformation. If resistance to impact is a major design driver in the margin study recommended for general carbon cylinders, the margin for 15,000-psi vessels could conceivably be lower than for conventional pressure vessels. Depending on the results of impact tests that simulate the magnitude of impacts that must be expected in service, an absolute minimum wall thickness in the design requirements may provide for the necessary impact resistance without adding a new design qualification test for each new vessel design. An absolute minimum wall thickness is a common design control against excessively fragile metal cylinders in DOT cylinder specifications.

The increased impact energy necessary to reduce the strength of the thicker composite sections is also more likely to leave visible evidence on the exterior of a gas cylinder where it can be detected in the prefill inspection. This may reduce the amount of undetected damage that must be provided for in the original design margin.

6.4.1.6 Material Compatibility with Stored Gas

The strength and composition of materials in contact with hydrogen must be limited to prevent failure due to hydrogen induced cracking (HIC). Much or all of the structural material in a composite vessel is isolated from the contained gas by the liner. If the liner is metal, only that portion of the vessel must be designed with limited strength to resist the contained gas. This assumes that the reinforcing fibers are not subject to hydrogen damage or the permeation rate through the liner is negligible.

6.4.2 Potential Disadvantages of Composites for 15,000 psi

6.4.2.1 Susceptibility to Sympathetic Failure

Although the number of composite pressure vessels operating at low margins is small, there have been instances of sympathetic failure when the rupture of one cylinder caused another to also rupture. Since vessels or gas cylinders are often in compact groupings, this presents the risk of very high-severity failures if a single vessel failure cascades into failures of neighboring vessels. The acceptability of this failure mode should be evaluated with comprehensive hazard analysis techniques. If the analysis results find this failure mode to be unacceptable and if the vessels are not known to be resistant to this failure, they should be isolated or located in an area that provides for safe failure of a complete assembly of vessels.

6.4.2.2 Accuracy of Design Stress Calculations

The preceding discussion on general margins for composite vessels regardless of pressure described the lack of any standardized design rules for composite cylinders. This lack is probably a more critical concern at 15,000 psi. The original design code referenced in DOT FRP-1 was a netting analysis and was predicated on thin wall assumptions. This design code has been superceded in use by proprietary design methods, "other suitable analysis techniques" as termed in FRP-1. As an example of another technique, the Type 2 design theory developed by Walters assumes that there is no stress gradient through the composite thickness. As in metal vessels, 15,000 psi results in significant deviation from the thin wall assumption in composite vessels. In a worst-case burst of a ductile vessel, plastic stress redistribution limits the ultimate result of these errors but there is no plastic capacity in composites. An accurate and peer reviewed analysis technique may be more important for 15,000-psi vessels but will probably be harder to achieve.

6.4.2.3 Nonmetallic Material Compatibility with High-Pressure Gas

Increasing the maximum pressure in cyclically pressurized nonmetallic components can lead to internal pressure fatigue or decompression failure within the polymer material structure. This is a common design concern for elastomeric seals at conventional gas cylinder pressures. Since 15,000 psi exceeds the strength of polymer liner materials, decompression failure due to pressure cycling should be identified as a potential design concern. Different gases produce different effects on different polymers and elastomers. Standards developed for lower pressure plastic lined cylinders contain some provision for resistance to cyclic gas pressure, but the criteria at the end of the test is leakage from a joint or seam, not permeation as might be expected if the liner were made porous by decompression failure. The resistance to gas cycling at 15,000 psi may require more stringent tests using hydrogen if that is the intended charging gas

6.4.2.4 Increased Sensitivity to Failure in Fire Exposure

Large composite cylinders generally require special pressure relief devices to prevent rupture in a fire. These are generally temperature activated and long vessels may require multiple devices for protection against local fire exposure. NGV2 contains requirements for design qualification fire tests but it is not known what modifications will be necessary for vessels as large as trailer tubes. These special devices are required not only for transportation vessels but also for stationary vessels. Since they are usually not activated by pressure, the devices will be in addition to any normally required Code devices for stationary vessels.

7 REVIEW OF SCOPE, LIMITATIONS AND MODIFICATION OF EXISTING STANDARDS FOR LARGE AND SMALL 15,000-PSI VESSELS

This section summarizes the scope of the reference standards in the context of 15,000-psi vessels. It also identifies the general limitations of the standards and identifies necessary modifications that are needed for 15,000-psi vessels. The composite vessel standards are treated in a general, not detailed way here because Section 8 contains a more detailed review of all reference composite cylinder standards and their applicability to 15,000-psi storage vessels or cylinders. The material characteristics of composites are reviewed with the objective of providing background for estimating composite margins in the context of metal vessel experience. Metal vessels are treated in some detail here because they are not included in the later Section 8.

7.1 Intended Scope of Modified Standards

The scope for new pressure vessel standards with operating pressures up to 15,000 psi includes two classes of compressed gas shipping container and one class of stationary pressure vessel for industrial or filling station use. The scope is not limited to hydrogen vessels, but specific concerns about hydrogen will be discussed. The first two classes of vessels correspond in general size to the DOT-3AA and DOT-3AAX specifications respectively with the division between cylinders and trailer tubes at 1,000 pounds water capacity. There is no lower limit on the size of DOT-3AA cylinders, but the usual concerns about small cylinders being thin and fragile do not apply at these higher pressures. DOT trailer tubes range up to about 24 inches in diameter and up to 40 feet in length. The third class of stationary vessels is similar in size to Appendix 22 seamless forged vessels. These typically range from about 100 lb water capacity.

One standard is now clearly applicable to 15,000-psi vessels, Section VIII Division 3. This division combines a desirable low margin with provision for techniques such as autofrettage that are beneficial for 15,000-psi vessels. The one major deficiency when considering stationary storage vessel applications is the lack of necessary fatigue and fracture toughness properties for materials exposed to hydrogen. This is a deficiency shared with every other standard studied here and should be addressed with a separate research program.

DOT and ISO metal gas cylinder standards contain no maximum pressure limit, but there is no significant experience base and Division 3 offers many advantages for 15,000-psi designs.

All of the composite standards are intended for operating pressures well below 15,000 psi. With the exception of Code Case 2390, these standards also limit the maximum size of vessels making them undesirable for large storage and transport applications. All composite cylinder standards except ISO 11119 also impose a maximum life not in excess of 20 years, a significant disadvantage in both portable and storage applications.

The vehicle fuel tank standards, particularly for composite designs, may rely on protection against external damage provided by the vehicle structure. The limited tolerance required of the individual cylinder for impact and casual abuse is not known to be adequate for the typical hazards to transportation cylinders. In addition, some designs have shown a susceptibility to sympathetic failure, one vessel failure triggering a second adjacent vessel to fail. Considering the close proximity of adjacent cylinders in both transportation and storage applications, this sympathetic failure mode is only acceptable based on a hazard analysis due to the potential for very high-severity occurrences.

7.2 NOP or Service Pressure of New Hydrogen Transport Cylinders

High-strength cylinders must be designed specifically for high-pressure hydrogen service due to the special material compatibility requirements. This generally means less efficient designs than those for other gases. If cylinders are dedicated to hydrogen service there is a rationale to help offset this negative effect while maintaining margins comparable to those of gas cylinders in ordinary gas service.

If the scope of the proposed specification is limited to high-pressure hydrogen cylinders and vessels, a special service pressure may be justified. Applying the margin at MNOP to the thermodynamic characteristics of hydrogen requires us to start with hydrogen at the MNOP conditions, 6,600 psig at 55°C as an example, and then calculate a filling pressure at the convenient 21°C reference temperature used for DOT filling specifications as 5,880 psig. This calculation uses values for Z, the compressibility factor, extrapolated from the *Compressibility Chart for Hydrogen, 33-32* [64]. This service pressure is 330 psi, 5.9%, greater than the service pressure for general gases because the pressure increase of hydrogen with elevated temperature is much less. This approach to margin equates the margin of any new specification for hydrogen cylinders to the well-proven margin of generic DOT-3AA cylinders in use for more than 60 years. This approach is also consistent with the gas-specific maximum developed pressure used in fatigue design of ISO 11119, the newest international gas cylinder standard.

It is likely that any new cylinder specification intended specifically for high-pressure hydrogen will be authorized by DOT exemption rather than by immediate incorporation into the CFR. The exemption makes it relatively easy to apply special narrow use requirements, facilitating the special service pressure (NOP) for hydrogen cylinders.

7.3 Scope, Limitation, and Modifications for Ductile Metal 15,000-psi Vessels

Metal vessels are treated in some detail here because there is not a separate section reviewing the metal standards later as is the case for composites in Section 8.

7.3.1 Inspection and Test Requirements

Section 3 contains an extensive discussion of this issue but a quick summary is that if LBB is feasible for these vessels, the proven hydrostatic, visual or other NDE techniques used for metal gas cylinders are necessary and sufficient. There is a significant probability that LBB cannot be ensured on efficient, simple, single layer metal vessels for 15,000-psi hydrogen. In this case, UT or other NDE must be practiced at intervals frequent enough to prevent fatigue cracks from growing to critical size. The simple geometries recommended in the individual specifications will facilitate these examinations.

The requirements for UT of gas cylinders do not normally go as far as addressing the probability of detection because fatigue failure is a remote likelihood in any case. This may not be true in hydrogen vessels and a performance based NDE as recommended in Section 3 may be necessary. LBB by design is a more reliable integrity control than in service NDE and should be provided wherever possible.

7.3.2 ASME Section VIII Division 3

Although pressures up to 15,000 psi are not excluded from ASME Section VIII Divisions 1 and 2, Division 3 is the only standard that is intended for pressures as high as 15,000 psi. However, there are still some recommended modifications.

Section VIII Division 3 vessel designs are subject to fatigue analysis dependent on failure mode, LBB or burst. The fatigue properties provided do not account for the expected degradation due to hydrogen exposure. The materials for hydrogen vessels must be characterized in both fracture toughness and fatigue for the gas service, pressure, operating pressure, and operating temperature.

It may be preferable to develop a new Code Case that uses some of the Section VIII Division 3 technical approach but is simplified for the specific case of 15,000-psi hydrogen vessels. Since the special material properties must be addressed as a special case, this approach could significantly simplify the design calculations by eliminating those features that are commonly excluded in DOT gas cylinders and Section VIII Division 1 Appendix 22 vessels. The opening designs can be limited as in IGC Document 100/03/E to eliminate the difficult issue of nozzle or thread failures in fatigue. The provision for autofrettage should be maintained. With the probable reduced number of material options that will be available for hydrogen vessels, the design requirements would be much simpler with no loss in utility of the vessel. This could be seen as a hybrid of the DOT-3AAX, ISO 11120, ASME Section VIII Division 1 Appendix 22, and ASME Section VIII Division 3 specifications. If the vessels are to be used in transportation, it will also be necessary to provide different rules for pressure relief along the lines of CGA S-1.1.

Consideration should be given to incorporating a hydrostatic expansion test or autofrettage with measurement of volumetric expansion. This test should be modeled on the DOT-3AA test except that it is now feasible to require greater accuracy in the measurement of pressure and expansion, similar to the requirements of Code Case 2390-1. This expansion test has proven to be very effective in assuring the operating stresses in the vessel are in the elastic range at pressures exceeding MNOP. This test is also discussed further below in the DOT section.

7.3.3 DOT-3AA/3AAX and ISO 9809/11120 Metal Gas Cylinder Standards

These standards are addressed together because they are very similar in intent. This discussion assumes that the tensile strength of the steel will be limited to ensure hydrogen compatibility. If this is not true and hydrogen is not the intended gas, the ISO 9809-1 and 9809-2 standards or the DOT-3F draft prepared by CGA should be used.

The equations required for wall thickness in both ISO and DOT specifications will probably not be accurate in providing the minimum margin at 15,000 psi. It will be necessary to adopt a plastic collapse equation as in ASME Section VIII Division 3 for purposes of burst margin. The formula should be verified empirically over the pressure range of interest before it is incorporated in new rules. In the event that adjustments are needed, the modified formula should be checked against the normal pressure DOT-3AA specification cylinder as a benchmark.

These standards assume that fatigue is a remote likelihood. Since this may not be true in hydrogen service, a fatigue analysis as required in ASME Section VIII Division 3 will probably be necessary. An alternative would be to develop a factor against either pressure or the number of cycles to account for the hydrogen effect on fatigue life as determined by vessel test. Either approach must be material specific, but the choice should probably depend on input from material experts.

LBB should be required or the approach recommended for non-LBB ASME-Section VIII Division 3 vessels should be used for requalification. The nozzle recommendations of IGC Document 100/03/E should be adopted in lieu of the 15:1 thread shear factor of DOT-3AA. The ISO limits on bottom shape and thickness should not be adopted unless they are first modified and verified to assure LBB. Since hydrogen may affect the material toughness, a simple LBB verification test is not an option. As in the fatigue case above, specific material expertise is needed to develop either the properties for analysis or factors to be applied to an empirical LBB test.

IGC Document 100/03/E Appendix F provides rejection criteria for visual inspection. This has apparently been developed from experience with existing cylinders and may not be optimum for a new specification, but similar criteria will be necessary for inspection. It may be advantageous to provide improved surface condition to obtain acceptable fatigue life with 15,000 psi hydrogen and the inspection criteria should be established accordingly.

The DOT, not the ISO, model should be followed with respect to pressure relief devices. Considering the history of NGV2-92 with respect to CGA S1.1 and PRD durability, it may be advisable to include some typical rupture disc materials in the testing for compatibility with high-pressure hydrogen. Plain rupture discs without fusible metal backing are commonly used in large DOT trailer tubes and fatigue of the disc may be an issue if hydrogen affects the alloy.

Autofrettage should be permitted by eliminating the requirement that pressures applied before the hydrostatic test must be less than the test pressure. It has been amply demonstrated that a small amount of yielding is not harmful to metal vessels. This is permitted in the DOT specification test, is incorporated in several million FRP-1 and FRP-2 cylinders and is provided as a "process treatment" in a number of DOT exemptions for small cylinders fabricated by welding.

Since autofrettage is likely to be used, one undesirable current effect of the hydrostatic expansion test should be eliminated. This is a simple test but subject to a number of variables and potential equipment failures. In an effort to simplify enforcement against fraudulent retesters, DOT has severely limited the options to repeat a test that gave an unacceptable result. From at least one manufacturer's perspective, this has led to the condemnation of numbers of cylinders that on subsequent examination show no defect. Since a small amount of yielding is not a safety concern and since the intent of the test is to assure that the tested cylinder is essentially elastic up to the test pressure, repeat of a test at a pressure increased by 100 psi should be permitted in all cases. If the cylinder then meets the permanent expansion requirement, it can be considered elastic at pressures up to test pressure. Considering the higher test pressure for 15,000-psi cylinders, the 100 psi increase may need to be increased.

The present DOT-3AA specification limits the usable minimum tensile strength to slightly less than 105,000 psi. If the ISO 11114/IGC Document 100/03/E maximum tensile strength can be used with hydrogen at 15,000 psi, it is feasible to increase minimum tensile strength to about 120,000 psi, as required in SA-372 E70. Applying a maximum tensile strength limit rather than a maximum stress at test pressure as is done now in DOT-3AA makes sense for hydrogen and may allow a significant increase in cylinder efficiency, depending on the hydrogen-limited tensile strength.

Providing a special fill or service pressure for hydrogen as described at the start of this section can also increase the cylinder efficiency without exceeding the MNOP.

DOT-3AA permits a variety of steel alloys and, by current steel making standards, allows high levels of sulfur and other impurities. Since the performance of the material in hydrogen is a critical concern, these impurities should be limited as required in IGC Document 100/03/E. Further reductions in impurities, special steel making processes, or modified alloy compositions may also improve the performance in hydrogen and should be addressed in the materials research.

Section 3 recommends UT or equivalent NDE at manufacture as required in IGC Document 100/03/E. This is a reasonable precaution for new hydrogen cylinders and vessels in which fatigue is expected to be a greater concern. The NDE also provides the initial flaw basis for any required fatigue analysis.

Charpy impact tests are not normally required for DOT-3AA cylinders but should be considered for the new specification. Any assurance of LBB will be dependent on the toughness of the material and the Charpy test is a good process verification test. In addition, the greater section thickness of 15,000-psi vessels increases the risk of nonuniform heat treatment. If impurities are closely limited, it is probably not necessary to require transverse specimens since the difference between longitudinal and transverse impact properties is largely dependent on sulfur content, as well as the amount of working in the different directions. The impact values required in ISO 9809-1 are not particularly stringent for steels in the 120-138 ksi tensile strength range. Since optimum heat treatment may be very desirable for hydrogen compatibility, the impact requirements should probably be determined as part of the hydrogen compatibility study. As an alternative, the impact requirements in NGV2-92 were developed specifically for modern "clean" 4130X alloy steel with a maximum tensile strength of 140 ksi.

The location from which tensile and Charpy specimens are taken should be considered. In lower pressure designs, DOT tensile and Charpy specimens are usually taken from nearly the whole sidewall thickness, but the increased thickness of 15,000-psi vessels makes it likely that specimen sizes will be much less than the wall thickness. ASME has addressed these issues for Section VIII vessels and the expertise should be applied here.

Consideration should be given to permitting composite reinforcement of the sidewall only as a means to ensure LBB. This reinforcement is not expected to carry significant loads in service but functions only as a rip-stop to prevent crack opening and the resultant running fracture on fatigue failure. This eliminates the acute concern for stress rupture that limits glass composite pressure vessels. Hoop wrapping as a means to improve fracture performance of military compressed gas cylinders has a long and successful history under MIL-DTL-7905H. This is similar in intent to the long established practice of wire winding DOT-3AA cylinders to make them nonshatterable as required in MIL-DTL-7905. This reinforcement may make UT at requalification both unnecessary and infeasible.

One requirement of DOT-3AA/3AAX should not be incorporated into any new standard. The DOT standards, including the later FRP and CFFC standards but excepting DOT-3T, require that batch tests be performed on samples taken at random from each lot. In comparison, NGV2 requires that the samples be representative of the lot and ISO 9809-1 requires only that the test material be from a finished, probably interpreted as heat-treated, cylinder. A strict definition of random requires every member of the batch to stand an equal likelihood of selection, requiring that the lot be complete before samples are selected and tested. This is not a convenient or common practice for many cylinder manufacturers, and actual practices are more closely modeled on the NGV2 definition with the independent inspector verifying that the test samples are representative and not selected for some favorable result. Random sampling is important for statistical use, but the sample size of one or two in a batch of 200 has very little statistical significance at best. Similar ASME materials property tests in steel plate are not random. ASME [65] requires that tensile specimens from plates be taken at specified locations, typically at the beginning, center and end of each coil or group of plates. This nonrandom but intentionally representative method is acceptable.

7.4 Scope, Limitation, and Modifications for Composite Vessels

None of the existing composite cylinder standards is intended for 15,000 psi service and only one, Code Case 2390 is intended for large vessels. The gaps in the existing individual standards for application to 15,000-psi vessels are noted and discussed in Section 8, but a summary will be presented here.

Since composites, particularly low-margin carbon designs are relatively new, the long-term experience base with low-margin high-pressure vessels is limited to metal designs. This experience may be valuable if applied to composites but it is necessary to bear in mind the basic differences between the two structural materials as well as the impact of layered construction.

7.4.1 Designs for Code Composite Reinforced Vessels

ASME Section X provides requirements for composite pressure vessels and requires a margin of 5 after completion of fatigue pressure cycling. This is approximately 50% greater in margin than the DOT FRP-1 [66] composite gas cylinders that have been manufactured in large volumes for more than 25 years. For this reason, ASME X was not considered in evaluating the margin for composite reinforced vessels.

7.4.2 Composite Material Characteristics and the Applicability of Metal Design Controls and Experience

Fiber reinforced plastic composites have markedly different characteristics from the ductile metals used in pressure vessels. These different characteristics may affect the reliability of design margins that are known to be adequate for older metal vessel designs if applied to composite designs. The following basic differences must be recognized.

7.4.2.1 Composite Anisotropy

Fiber reinforced plastics (FRP) materials are not homogeneous. Compared to the small differences in directional properties of pressure vessel metals, FRP properties are almost entirely directional. Strength and stiffness are high only in the direction parallel to the fibers and both fall rapidly as the direction of tensile load diverges from fiber direction. This characteristic requires a complex pattern of fibers to carry the triaxial stresses present in pressure vessels. Loads are transferred between fibers by shear stresses in the composite resin matrix, but some degree of matrix cracking is very common. There may be shear between layers where there is bending, such as could occur in the domes. Load is transferred radially into the composite layers and reacted in the hoop and axial directions. The result is that fiber stresses in all of the different layers and directions may be difficult to calculate, and there is no simple analog to the different design formulas used for metal vessel sidewalls.

7.4.2.2 Perfectly Elastic Behavior

The individual fibers that provide the strength of composites are not ductile. FRP materials are generally considered to be perfectly elastic. They demonstrate ideal elastic behavior with no plastic deformation prior to failure. The tensile load increases linearly with strain up to the ultimate limit and there is no plastic behavior before failure. This behavior in a metal would be characterized as brittle and avoided in pressure vessels, but it is the nature of FRP and is not completely analogous to brittle failure in metals. This analog should not be extended to composites as the generally good long-term safety record of large numbers of DOT FRP-1 composite gas cylinders demonstrates. The very large number of individual fibers connected with relatively weak shear stresses in the resin results in different crack propagation behavior in FRP than in brittle metal. The complex structure of composites with many individual fibers in many different directions appears to interfere with the linear crack propagation that characterizes brittle fracture in metals. Stress corrosion cracking of glass composites is a notable exception and must be addressed with separate controls.

The elastic nature of composites also makes invalid the design and test approach initiated in DOT-3A cylinders and continued in DOT-3AA designs. The early U.S. gas cylinder specifications, as represented by DOT-3A, imposed a maximum ratio of yield strength to tensile strength. The test pressure was then selected such that any significant loss in yield strength or thickness would result in plastic deformation during the test and failure of the test criteria. If the loss is significant, the cylinder will fail a retest at a slightly increased pressure because of the very large difference between the elastic and plastic moduli. In composites there is no perceptible plastic modulus. With no difference between the yield and ultimate strength of composites (Y:T = 1.0), it is not possible to test to a value on the verge of yielding, also the same as fracture, without high risk of rupture or permanent damage to the reinforcing fibers.

7.4.2.3 Response to Design or Manufacturing Stress Concentrations

Brittle metals are avoided because materials, designs, manufacturing and operating controls are never perfect. The loads are never uniformly applied across the section and there are always discontinuities, either inherent or service-induced, that result in localized regions of higher stress. With a ductile material, these small areas of high stress can yield, relieving the stress concentration by redistributing the load to the surrounding material, and the material that yielded retains all of its original load carrying capacity, or a little more due to strain hardening. This slight local yielding has no adverse safety impact as evidenced by the success of autofrettaged designs. The elastic nature of FRP prevents this plastic redistribution of a local overstress condition. If the local stress exceeds the capacity of the fiber, the fiber will break and the strength and stiffness of the structure is permanently reduced while the entire load from the failed fiber is transferred to surrounding fibers, increasing their loading. Composites should therefore be considered to be more sensitive to inaccuracies or imperfections in the design calculations.

7.4.2.4 Response to Service-Induced Stress Concentrations

In addition to adjusting to the geometric deviations in design and manufacturing, the plastic behavior of metals also allows for the plastic redistribution of high local stresses that may occur as a result of damage during the service lifetime of the vessel. Dents, pits, scratches, and similar discontinuities have little affect on the burst pressure of ductile metal vessels because the plastic deformation at a very low plastic modulus allows the local overload due to the discontinuity to be redistributed over a relatively large region in the surrounding metal. As a result of this capability to redistribute stresses to the surrounding area, CGA C-6 [67], permits significant corrosion pits, dents etc. to be accepted during inspection of steel cylinders. Plastic tensile elongation of ductile metals is required to be in the range of 12 to 20% in 2 inches for typical vessel alloy steels. This is in addition to the elastic elongation of about 0.3%. This contrasts with the total elongation of FRP materials that range from less than 1% for some carbon fiber composites to more than 2% for glass composites. This very low elongation to failure with no capacity for plastic deformation limits the size of the region over which the overload due to a service-induced discontinuity can be redistributed. The result is that the stress remains more concentrated, increasing the likelihood of progressive stress rupture and failure of the vessel. CGA C-6.2 [68] contains allowable defect sizes for DOT FRP cylinders. While the criteria vary significantly for different designs, they appear to be on the same order as the criteria for UT at manufacture required in ISO 9809-1 and significantly less that the acceptance criteria for metal cylinders as specified in CGA C-6. It is obvious that the composite designs can tolerate some degree of damage and remain safely in service. It is interesting to note that many DOT FRP-1 designs have significantly smaller acceptable defects in the dome region, about one half of the defect depth permitted in the straight section.

7.4.3 Composite Design

Efficiently designed composite laminates intersperse thin layers that are oriented to carry either hoop loads or longitudinal loads. This directional layering within the solid composite material and the transfer of loads through the resin matrix makes it difficult to empirically determine strains or stresses in the different layers and fiber directions. This compounds, or is perhaps the cause of, the lack of generally accepted and peer reviewed design formulas for composite cylinders. Many composite design tools for conventional gas cylinders treat the composite as a thin membrane, sometimes ignoring the matrix entirely.

7.4.4 Composite Durability

The strength of composites is derived from the fiber but much of the durability is dependent on the plastic matrix that makes little contribution to the measured composite strength. This results in significant independence between strength and durability for any composite design. For the case of carbon fibers, the fibers are very stiff and should not be subjected to bending or rubbing. This requires that each fiber be surrounded and isolated by a “soft” resin layer in much the same way that hard stone is isolated by mortar in a masonry wall. This isolation is dependent on the details of fiber sizing, resin matrix and impregnation process. For glass fibers, the matrix is relied upon to prevent accelerated aging, stress corrosion cracking, or stress rupture by protecting the fiber from moisture. This is not generally a concern for carbon, but can be critical for glass [69].

7.4.5 Developed Strength of Composites

The composite materials are combined and cured into a solid mass during the manufacture of the actual vessel, and the resulting properties are not a simple sum of the individual components and their volume fractions. The fibers must be aligned with the applied stress, making for complex designs in the triaxial loadings common in pressure vessels. It is normal for the resulting strength and stiffness to be less that the sum of the volume fractions and properties of fiber and resin in the composite. This is a marked difference to normal ASME Section II properties since the strength of the material is more dependent on the manufacturing process for the vessel, not just on the material supplier or heat treatment.

7.4.6 Performance Tests Relative to Composite Stress Ratios

NGV2 and derivative standards contain an accelerated stress rupture test of prototypes as an empirical verification that the design composite stresses, combined with the resin matrix system, provide a minimum level of protection against stress rupture. The test provides a measure of resin properties and residual stress from the manufacturing operation. The test requires that the cylinder be pressurized to the maximum fill pressure, 1.25 times service pressure, and held at 65°C, for 1,000 hours after which the burst pressure must exceed 75% of the minimum design burst pressure. This is less than the maximum material service temperature of 82°C. This is an example of a performance test of material resistance to stress rupture that has been applied across a range of designs with the result that significantly different composite properties are required to meet the test requirement. In the case of a full composite design with nonmetallic liner, all of the structural strength is derived from the composite and the 75% criterion allows a composite strength loss in the range of 25 to 35% as a result of the 1,000 hour exposure.

For a glass reinforced cylinder the minimum post exposure stress ratio is about 2.62, too low for continued safe service. For a carbon or aramid reinforced cylinder, the minimum postexposure stress ratio is 1.69. In either case the condition of the cylinder at the completion of 1,000 hours exposure should be considered unsafe for service. In the case of a cylinder hoop-wrapped with fiberglass, the composite may carry more than 60% of the hoop stress at the design minimum burst because of the von-Mises yield criteria affect on the load capacity of the liner. If the design is at the critical burst as defined by Walters, the wrap must lose about 68% of its strength to result in a 25% loss in cylinder burst pressure. The postexposure stress ratio is only accurate if no allowance is made for stress load redistribution due to creep and elastic expansion of the liner against the reduced constraint of the compromised composite. The burst ratio of the cylinder with respect to service pressure could be as low as 1.69 and the cylinder should again be considered unsafe for service after the environmental exposure.

7.4.7 Translation

There is also the composite design factor termed "translation" this accounts for the fact that the actual strength delivered by the composite in a vessel is less than the sum of all of the individual fiber filaments. With no capacity for plastic elongation, all fibers in a region of the vessel must reach their failure strain simultaneously to achieve a translation of 100%. This is not practically possible and translation is considered to account for the degree of imperfection in fiber loading for a certain combination of vessel design and manufacturing process. The actual scope of the translation factor is much wider and it is used to account for the difference between some theoretical design prediction of burst pressure and the actual burst pressure.

Translation is affected by geometry, material compatibility, and a large number of independent process variables. This factor covers a very significant empirical element in the design of any composite vessel, and designs are often not as simple as design by analysis and then verify by test. There often are empirical iterations. It is common to adjust vessel design calculations by changing the assumed strength of the composite via the translation factor until the calculation and empirical tests are in reasonable agreement. While this is convenient in empirical design, it leaves open the question of whether the need for a translation factor is due to process factors that degrade the fiber strength or due to errors in the design calculations themselves. This may be similar to using thin wall maximum principal stress theory for all pressure vessels and then developing translation factors to account for the difference between calculated and actual results. A weld efficiency factor in a metal vessel is another possible analog except that it is applied after the weld strength is determined by test.

7.4.8 Stress Rupture of Carbon Composites

Carbon fiber composites are believed to be much more resistant to stress rupture than glass or aramid. Robinson presents a graphite composite stress rupture design chart developed from admittedly sparse data [49]. He recommends that the chart be used "...for first-order life estimates of carbon composite pressure vessel stress rupture vessel life." Used in this way, the design stress for 1:1,000,000 failures in 25 years is about 45% of the ultimate composite strength. Inverting this value gives a margin of 2.22, very similar to the margin of DOT-3AA cylinders at service pressure. This is also essentially the same as the NGV2 stress ratio of 2.25 for carbon. This makes sense in comparison to metals unless carbon fiber is actually susceptible to strength reduction by stress rupture in this time span and steel is not susceptible to stress rupture. The charts present only time to failure at a constant stress. There is no way to infer what the reduction in strength would be if the sample is stressed at a level too low to actually cause failure in the time period and then failed in a short-tern tensile test. This would be more representative of how a margin is significant in a pressure vessel, providing a margin against unintended overload at any time during the usable life.

The objective in designing a vessel for a safe service life is to provide a minimum level of integrity at the end of the life, arbitrarily assumed at 25 years in this discussion. If stressing for a period of time reduces the strength of carbon composites, this time-dependent strength loss should be factored into the design margin when new. Unfortunately the Robinson estimates are based on sparse data and significant extrapolation. Additional data on long-term stress rupture resistance of carbon composite pressure vessels may now be available to either confirm the 2.25 stress ratio or support a different value with hard data. If we assume that all forms of in-service degradation except stress rupture are equal for carbon composites and steel, we can simply divide the minimum acceptable margin for steel vessels with the stress rupture factor for carbon to arrive at an equivalent design margin for carbon. This is an oversimplification because carbon composites are more sensitive to mechanical damage than are metals, and carbon fibers are less sensitive to environment degradation (e.g., corrosion) than metals.

7.4.9 Design Qualification by Similarity

All of the composite standards except Code Case 2390-1 allow nominally similar designs to undergo reduced design qualification testing. The rationale for these provisions depends on the accuracy of the design similarities, and the empirical design process with translation factor limits the accuracy of this assumption.

The margins that are developed on more definitive properties data for composite cylinders should also recognize the limitations of the design process for these cylinders, particularly if no standard design code for the sidewall is adopted.

Fiber reinforced composite materials must generally be treated as susceptible to stress rupture, creep or impact induced fracture and the margins known to be adequate in metals that are free of these effects may not be adequate for FRP cylinders. There are also many other significant differences in the way that FRP materials behave under load when compared to ductile metals.

7.4.10 Resistance to Fracture of Carbon Composite Vessels

Design stress margin may not be the primary design driver for carbon composite vessels and Robinson takes this position in his conclusions stating: "The carbon data seem to exhibit very little stress rupture degradation, and therefore offer very high homologous stresses in operation. Such high stress potential (and high performance) may not be a practically usable characteristic. The lower design stresses required for the glass and Kevlar also provide a certain amount of damage tolerance during the service life. In addition, both S-glass and Kevlar are inherently resistant to moderate impact and casual damage. Carbon composites, on the other hand, susceptible to physical damage and abuse. Such susceptibility, coupled with very high operating stresses, could lead to premature or catastrophic failures in cases of casual damage to a carbon composite vessel operating so close to its expected strength." And Robinson also states that "the carbon composite pressure vessels must be protected from environmental damage or designed to resist and tolerate the service environment" [49].

7.4.10.1 Fracture of Carbon Composite NGV2 Cylinders

Subsequent experience has demonstrated that Robinson's concern was well founded because there have been "…premature or catastrophic failures in cases of casual damage…" The best known is probably the failure of two carbon composite CNG cylinders on board a transit bus. According to a letter from the manufacturer, [70] a summary of the incident follows.

A carbon composite CNG container designed in accordance with NGV2-1992 ruptured while being filled. The rupture occurred at a pressure well below the MNOP and probably below the service pressure (NOP) as well. The cylinders burst during refueling and the cylinder was propelled toward the rear of the bus where it impacted a second identical cylinder, causing the second cylinder to rupture. The first cylinder was deflected up into the empty passenger compartment. All of the other EDO cylinders were inspected and tested before any bus was returned to service. There was no ignition of the natural gas and no subsequent fire.

A later report [71] identified the failure initiation as being on the bottom portion of the first cylinder but was not conclusive about whether the damage occurred in service or during installation or maintenance.

In postaccident inspections of other buses, a third cylinder with suspected damage was identified. This cylinder also ruptured when pressurized. Several possible damage scenarios have been proposed but it is not known whether there was any effort to duplicate the results and choose one most probable root cause. Three scenarios for potential root causes follow.

(a) The vessel may have been damaged by impact with a road obstacle. A common form of impact to a bus is "curbing" when the bus cuts a corner and the lower chassis impacts the street curb. This impact would be expected to occur at the transition area between the dome and the straight sidewall of the cylinder. This scenario would seem more likely if the damaged cylinder was mounted on the right side, but it was located behind the driver's seat. Since the bus would have been operating on natural gas, the cylinder would have been pressurized and less susceptible to external impact, but the failure location was on the bottom.

(b) The vessel may have been damaged by misplacement on a service hoist, supporting part of the vehicle weight on the cylinder instead of the intended jacking point. The location of the first

cylinder was consistent with this scenario. The cylinder would have been pressurized unless the storage system was being serviced.

(c) The third scenario is that the cylinder was damaged in handling during removal for service. This suspected scenario resulted in added performance tests in NGV2-1998 to ensure some minimum level of resistance to such handling damage, but not against the other two potential causes. The cylinder would probably have been vented before removal and therefore most sensitive to external impact, but it would be quite a coincidence that the impact area is at the bottom of the reinstalled cylinder.

This incident and the subsequent failure analysis may contain information relevant to any new Code rules for carbon fiber full-wrapped pressure vessels.

7.4.10.2 Sympathetic Failure

The failure incident above illustrates that certain NGV2-92 cylinders constructed of carbon fiber composite were susceptible to sympathetic failure, the failure of a cylinder adjacent to the initial failed cylinder and the second failure caused by the first. In the particular bus involved in the failure, the chassis was composed of a tubular space frame structure with many small bays separated from each other by struts. Cylinders were located in these separate bays. The bus structure may have prevented progressive sympathetic failure of more cylinders. This type of structural isolation is not typical of either gas cylinder, trailer tube or storage vessel use.

Metal cylinders of the type used for compressed gas transport and storage are not susceptible to sympathetic failure. One illustration of this was the rupture of a 22 inch x 34 ft DOT-3T trailer tube in 1977 [72]. The energy from this failure destroyed the trailer and impacted an adjacent tube with enough energy to impart a very visible bend. There was no evidence that any of the other tubes were close to failure as a result of the rupture of one of the bundle. The low elongation to failure of FRP also means that relatively little energy is required to initiate and propagate a fracture. The recommended hazard analysis should be completed before permitting installations where a cascade failure of a whole load of cylinders or pressure vessels can result from a single failure.

7.4.11 Inspection Capability for Carbon Composite Cylinders

The scope of this report also includes estimating the impact of in service inspection and testing on the necessary design margin. Section 3 contains a detailed discussion of issues relating to inspection and test, but the following sections recapitulate and restate the issues in terms more specific to the comparison of metal and composite designs with low margins. All of the referenced standards except ASME Section VIII are associated with clear requirements for such inspection and testing. As a result, the design margin service history of composite cylinders is valid only with inspection and testing as effective as that practiced in the historical sample. Detection of physical damage is an area of significant difference between composite and metal vessels.

8 REVIEW OF EXISTING COMPOSITE CYLINDER STANDARDS FOR APPLICABILITY TO HYDROGEN STORAGE AT 15,000 PSI

This section is devoted to the reference standards and their applicability to storage vessels or portable gas cylinders operating at pressures up to 15,000 psi. The significant scope and technical issues of each standard if used at 15,000 psi are identified. In most cases there is little discussion because related issues have been covered in detail in earlier sections of this report.

The scope for this work includes a review of the scope and applicability of these existing standards with regard to both storage (stationary) vessels and portable (shipping containers) vessels. It is easily seen that these two different applications have many issues in common as well as many issues unique to the specific application. The two different but somewhat similar applications are treated as completely independent in the following two sections. Common issues are listed first followed by issues unique to storage or portable vessels.

8.1 Scope of Review

The existing identified composite standards to be reviewed include:

DOT FRP-1	NGV2-2	ISO 15869 T2
DOT FRP-2	NGV2-3	ISO 15869 T3
DOT CFFC	NGV2-4	ISO 15869 T4
ISO 11119-1	ISO 11439-2	Code Case 2390
ISO 11119-2	ISO 11439-3	ASME VIII-3
ISO 11119-3	ISO 11439-4	

8.2 Requirements of Existing Composite Cylinder Standards and the Applicability to 15,000-psi Hydrogen Storage Vessels or Cylinders

8.2.1 General Requirements of Existing Composite Cylinders

The various standards are very similar in many details and have been developed sequentially, a new standard derived from the older standards over a period of about 30 years. The standards share many characteristics that are not appropriate for 15,000-psi storage vessels.

None of the standards contain rules for design analysis that are sufficient to determine the operating stresses and margins within the vessel. This is a pronounced contrast with ASME Section VIII and the newer ISO 9809 and ISO 11120 standards for metal vessels. This lack in the composite standards permits designers to use specialized proprietary methods and commercially available finite element analysis tools to develop a design necessary to meet the performance tests in the standard and then verify the design by those same tests.

The fatigue life of all designs must be determined and verified empirically by pressure cycle testing of prototypes and batch samples during production. In all cases, the fatigue cycling is performed using a fluid that will not in itself cause any degradation in the fatigue resistance of the vessels. This is not true of the actual working fluid, hydrogen. Many materials will demonstrate a reduction in fatigue life if tested in hydrogen, and the determination of fatigue life without accounting for this effect may be invalid and nonconservative for any vessel type. This shortcoming applies to all tests that incorporate fatigue cycling as an element of the test procedure. The issue of the working fluid and its impact on the fatigue life needs careful consideration in the design, inspection and operation of these vessels.

The standards do not require that designs fail by leakage as a result of fatigue. This is now a general characteristic of composite gas cylinders, but the use with 15,000 psi hydrogen may change this natural tendency and additional controls are required. Some standards require that designs must be demonstrated to fail LBB or achieve a minimum additional margin in fatigue cycle life. LBB occurs when the stress intensity at the crack is less than the material fracture toughness at a through-wall crack depth, or when there is additional structure that is not subject to failure by fatigue crack propagation of the crack and that structure provides enough support to prevent the fatigue crack from opening up into a typical rupture.

If required, the LBB test is performed with a benign fluid, not hydrogen. Hydrogen can cause a time-dependent, temperature-dependent and perhaps pressure-dependent loss of fracture toughness in many materials. This effect of hydrogen on the vessel material is not accounted for in the LBB test. Further investigation is necessary to evaluate whether designs demonstrating LBB when hydrogen is not present may actually fail by burst after a period of time in hydrogen service due to loss of material toughness. IGC Document 100/03/E and ASME Section VIII Division 3 both require attention to the design of threaded openings for hydrogen vessels and high-pressure vessels respectively. As discussed in KD-141 fatigue at the root of a thread is particularly difficult to manage from the standpoint of LBB and the standards should address this.

The severity of hydrogen gas damage depends on the equilibrium fraction on monatomic hydrogen in the gas [73]. This equilibrium fraction is temperature dependent and increases with temperature. Any test that must account for the effects of hydrogen on materials should be run at the representative maximum gas temperature, not at ambient temperature.

Permeation and leakage requirements in the existing standards are not intended to be used for hydrogen at 15,000 psi. Permeation and leakage must be tested with hydrogen to obtain valid results for small-molecule gases. Some of the standards are specific about how this is to be performed in an enclosure, but there is no requirement for verification of the sensitivity of the test equipment against a calibration standard hydrogen source.

Hydrogen cycling may also damage nonmetallic materials and the standard tests do not protect against this type of failure. When a gas cycling test is included for Type 4 cylinders as in ISO DIS 15869, NGV2, and ISO 111439, there is an assumption that the permeability of the liner and bonds will not be affected by cycling. This may not be true in the 15,000-psi hydrogen case due to the ready permeation of hydrogen into the plastic material and the fact that plastics have a tensile strength below the working pressure of the cylinder. It should be verified that the plastic will not experience progressive decompression failure as a result of hydrogen cycling and this requires measurement of permeation after the test.

8.2.2 Specific Present Composite Cylinder Standards

8.2.2.1 DOT Composite Gas Cylinder Standards

The DOT standards for composite gas cylinders will be discussed in detail first since the other standards are largely derived from them.

8.2.2.1.1 DOT FRP-1 and FRP-2

These are the current standards for aluminum lined full-wrapped and hoop-wrapped composite gas cylinders incorporating glass fiber reinforcement. These standards are very similar and are addressed together here. The standards are not directly applicable to hydrogen vessels due to the following gaps:

(a) The maximum water capacity is only 200 lbs, smaller than typically desired storage vessels or the largest gas cylinder.

(b) The maximum service pressure is 5,000 psi, implying a maximum normal operating pressure of 6,000 psi.

(c) The limitation to 6XXX, effectively 6061-T6, aluminum liners will limit the operating pressure due to thread and nozzle stresses.

(d) The standards have not been incorporated into the CFR and DOT continues to require an exemption with special technical review requirements for each new design or manufacturer.

(e) Critical issues such as operational life, requalification and limits on use are contained in DOT Exemptions that are issued on an individual basis for designs and manufacturers.

(f) The referenced NASA design code assumes thin wall conditions, inappropriate for very high-pressure vessels, especially if they incorporate relatively low-strength metal liners. It should be noted that the cylinders and spheres studied by NASA were intended for aerospace use, had a 1.5 safety factor, and used higher strength materials.

(g) The referenced NASA design code does not address metal liner failures in nozzles.

(h) The referenced NASA design code is obsolete and probably not usable as a third-party design verification tool.

(i) Lack of explicit design calculation requirements may lead to wide variation in accuracy of the critical design stress levels and stress ratios required for resistance to stress rupture failure of the composite.

(j) The standard requires an unrealistic thread design margin of 15 in shear. This will not be feasible at15, 000 psi.

(k) The design life limitations to 15 years are not compatible with storage vessel use.

(l) The limited design life that is not contained in the standards, but is incorporated into all DOE Exemptions for the use of FRP-1 and FRP-2 cylinders is not consistent with the service conditions of storage vessels.

(m) Regardless of pressure cycles, the service life limited to 15 years.

(n) The service life is limited to 15 years. This limitation by DOT recognizes susceptibility of glass composites to time-dependent stress rupture and the lack of established in-service requalification methods for composite cylinders that are verified to detect all of the expected forms of in-service degradation.

8.2.2.1.1.1 General Technical Issues

The following issues should be considered for DOT FRP-1 and FRP-2 regardless of the pressure and gas contained:

(a) The reinforcing wrap is limited to glass composite and glass fiber has been demonstrated to be susceptible to stress corrosion cracking (SCC) failure in gas cylinder service. The FRP standards contain no controls against this failure, and the failure mode in an FRP-1 design is burst.

(b) Composite materials are subject to failure due to a number of different other environmental factors. DOT FRP-1 and FRP-2 address only a few of these factors.

(c) The environmental test requirements in the FRP standards address only the effects of temperature extremes and humidity.

(d) There is no coverage in the standard for corrosion, UV, abrasion or other environmental degradation.

(e) There is no validation test coverage for stress rupture as a result of long-term exposure to heat and moisture while under operating loads.

(f) When the low margin in fatigue cycles and the low total fatigue life requirement is combined with the limited capability to detect degradation in service, it is necessary to protect against a high-severity failure mode in fatigue. Leak-Before-Break is (LBB) is the normal control is such cases.

(g) There is no requirement for a LBB failure mode. This could be a critical lack given the low design margin in fatigue cycles. It is generally believed that the FRP-1 design will be LBB because of the strength of the fiber wrap. The exception here could be a tensile thread failure due to longitudinal stress, a credible scenario at very high pressures (see KD-141).

(h) It is also generally believed that FRP-2 designs will be LBB, but with the bare metal ends, this is not always a valid assumption. It is well established that the details of the end design are critical to LBB in all-metal cylinders, and the same is true of FRP-2 designs.

(i) The in-service retest and inspection requires periodic hydrostatic expansion retest. The hydrostatic expansion test is inconvenient for a storage vessel because it requires removal of the vessel, contamination of the interior with a test fluid, cleaning, and reinstallation.

8.2.2.1.1.2 Design Margin and Fiber Stress Ratios

For FRP-1 cylinders, the design margin in burst is 3.0 but the design margin in fiber stress ratio is 3.33. When allowances are made for the load transfer due to autofrettage prestressing, the required minimum burst pressure of 3.0 does not give direct assurance that the operating stress in the fiber is at low enough level to result in high reliability for the 15-year design life. The typical burst pressure margin required to satisfy the stress ratio requirement is 3.5. If the composite were to fail due to high operating stress, the likely failure mode is burst.

8.2.2.1.1.3 Sample Selection for Batch Testing

As discussed previously for DOT-3AA cylinders, the DOT wording requiring random selection should not be used. This is not a required practice in ANSI-NGV2 or ISO standards and is not required for the similar laminate procedure qualification of Code Case 2390. The samples should be representative, not random. While random sampling is unnecessary, it is extremely inconvenient, especially for large vessels that are produced slowly in batches up to 200.

8.2.2.1.2 DOT CFFC

This is the current DOT standard for aluminum lined full-wrapped and hoop-wrapped composite gas cylinders incorporating carbon and glass fibers together. This standard shares all of the shortcomings of DOT FRP-1 and DOT FRP-2 except the susceptibility of glass fiber to stress corrosion cracking and stress rupture at relatively low design stress margins. Areas of concern unique to the CFFC standard are discussed below.

The standard requires only a “reliable” model to calculate the critical design stresses, and then only in the cylindrical portion. There is no guidance as to how reliability may be judged in the model, but the result must verify stress ratios in the glass and carbon fibers as well as the design stress and burst values. The minimum method is thin shell theory, probably not reliable for 15,000-psi vessels. There is no design requirement for the ends or nozzles, except for thread shear. It is assumed that stresses in the ends are lower than in the sidewall because the failure location in burst must be in the sidewall, but this does not imply any particular stress level at operating pressure or any particular failure location in fatigue.

With most DOT cylinders, the cause of most failures at requalification is failure of visual inspection criteria. It is well recognized that carbon composites are susceptible to impact damage that is very difficult to detect reliably by visual examination, but there is no established alternative.

As discussed previously for DOT-3AA cylinders, the DOT wording requiring random selection should not be used. This is not a required practice in ANSI-NGV2 or ISO standards and is not required for the similar laminate procedure qualification of Code Case 2390. The samples should be representative, not random. While random sampling is unnecessary, it is extremely inconvenient, especially for large vessels that are produced slowly in batches up to 200.

8.2.2.2 ISO Composite Gas Cylinder Standards

ISO 11119 is the current ISO standard for composite gas cylinders incorporating carbon, glass aramid fibers or metal wire, alone or in combination. This discussion does not cover the option of wire reinforcement and is limited to the fiber options. This standard is not directly applicable to hydrogen storage vessels due to the gaps discussed below, but the standard contains unique concepts that should be considered for a hydrogen vessel standard. The standard is divided into three parts for Types 2, 3, and 4 cylinders respectively, and comments common to all three parts will be addressed first.

(a) Issues with the scope of ISO 11119 if applied to 15,000-psi hydrogen storage vessels

The maximum working pressure is 6,283 psi, only 42% of that needed for a storage vessel.

The hydrogen compatibility requirements are not known to be valid at pressures as high as 15,000 psi. The standard covers hydrogen vessels and makes reference to ISO 11114-1 for compatibility of metallic materials. ISO 11114-1 contains a limit on tensile strength for alloy steel typical of SA 372 E70. Neither ISO 11114-1 nor IGC Document 100/3 is limited in scope to conventional pressures, but there is reason to believe that different material compatibility requirements may be necessary at 15,000 psi.

(b) General Technical Issues with ISO 11119

(1) As in the earlier DOT standards, the lack of explicit design calculation requirements may lead to wide variation in the accuracy of design stress levels and fiber stress ratios.

(2) All stress calculations are performed with nominal material thickness and properties, not minimums.

(3) Glass fiber composite has been demonstrated to be susceptible to SCC failure but there is no design control against this failure mode.

(4) Service life may be limited to 15 years before requalification and there is no guidance about what is required for such requalification.

(5) No requirements for resistance to corrosion.

(6) The standards permit the use of carbon fiber for reinforcement but the tests for impact resistance are limited to small high-velocity penetrations affecting only small areas on the most uniform part of the vessel and resistance to blunt impact is required only against a plane surface. The blunt impact test is intended to provide assurance that the vessel is resistant to damage that may occur in handling the vessel on installation, but the drop heights and requirement for plane surfaces only are not be representative of actual handling mishaps.

(7) LBB performance in fatigue is not ensured. This has been discussed in the previous DOT-FRP-1 and 2 Section 8.2.2.1.1.

(8) In-service retest and inspection requires periodic hydrostatic retest of doubtful effectiveness at a low percentage of the vessel's ultimate strength.

(c) ISO 11119-1 Hoop-Wrapped

(1) ISO 11119-1 is for metal-lined hoop-wrapped composite gas cylinders incorporating carbon, glass or aramid fibers, alone or in combination.

(2) The low glass stress ratio indicates a potential susceptibility to failure within the design life; especially since unlimited life cylinders may be produced to the standard. This issue has been discussed in regard to the 15-year life DOT FRP-2 designs.

(3) There may be no actual use history at minimum allowable stress ratio. There is a discussion at the end of this section regarding the accuracy of traditional design calculation methods for hoop-wrapped cylinders and the implications for the safe service precedents.

(4) The definition of stress ratio prohibits the use of extra composite to reduce liner stresses and also prohibits low stress ratios for carbon in hybrids containing glass. This is a major shortcoming since composite is the structural material most vulnerable to degradation in service.

(d) ISO 11119-3 Plastic Lined Full-Wrapped

(1) ISO 11119-3 is for plastic lined full-wrapped composite gas cylinders incorporating carbon, glass, or aramid fibers, alone or in combination. This standard also allows non-load-sharing metal liners but it is believed that these will be very limited in fatigue life.

(2) The required mass decay method of permeation measurement may not be sensitive enough for hydrogen.

(3) The standard lacks a requirement for resistance to hydrogen fast-fill temperatures.

8.2.2.3 NGV2 Fuel Containers

(a) NGV2 fuel containers are intended for use as vehicle fuel tanks containing compressed natural gas (CNG). NGV2 includes Type 1 (all metal) 2, 3, and 4 containers reinforced with glass, aramid, carbon, or combinations of fibers. The standard was developed to be performance based with the minimum reliance on design limitations.

(b) NGV2 is the only composite standard other than Code Case 2390 that is intended to be comprehensive enough for self-certification. This is significant given the lack of any regulatory agency with design approval authority over storage vessels.

(c) NGV2 requires that an independent inspection agency approve all design qualification tests. This provides a level of third party review consistent with the agencies available in the United States.

8.2.2.3.1 Scope Issues with NGV2

(a) The maximum service pressure is 3,600 psi.

(b) NGV2 containers are not intended for hydrogen. The material requirements do not address compatibility with hydrogen. However, it should be noted that this is expected to be addressed in the current revision.

8.2.2.3.2 General Technical Issues with NGV2

(a) There are no explicit design calculation methods and no criteria for the selection, validation, and use of the critical calculation methods is provided.

(b) Design stress calculations are necessary to determine compliance with the composite stress ratios but NGV2 requires only "…suitable techniques that have been demonstrated to adequately

predict the stresses and strains…" This allows more latitude than is desirable and gives no objective measure of "adequate."

(c) The accelerated stress rupture test is performed at a temperature less than the maximum material temperature, eliminating any acceleration. This test probably does not add any safety above that provided by the design stress ratios. The test provides a measure of resin properties and residual stress from the manufacturing operation.

(d) Compliance with the limiting fiber stress ratios is necessary to reliability, but is dependent on the undefined calculation methods.

8.2.2.3.3 NGV2-2 Hoop-Wrapped

This section of the standard provides coverage for Type 2 containers, metal-lined hoop-wrapped containers.

(a) NGV2 defines Type 2 in terms of minimum liner burst strength at least equal to the MNOP, 1.25 times service pressure. This eliminates any possible conflicts due to the addition of longitudinal fiber reinforcement to prevent matrix cracking.

(b) As do other standards for hoop-wrapped cylinders, NGV2-2 allows a lower fiber stress ratio for glass because the inherent liner strength is expected to prevent rupture of the container in the event of stress rupture of the glass fiber as a result of the higher fiber operating stresses.

(c) The glass fiber stress ratio is low enough that stress rupture failures of the fiber should be expected in a large population of containers. This type of failure has not incurred in the very similar DOT FRP-2 cylinders that have been in volume production for over 25 years, but this may not be a precedent for the fiber stress ratio as discussed at the end of this section.

(d) NGV2 lacks explicit consensus-based design calculation requirements.

(e) NGV2 is unique among the standards in making allowance to permit a conservative design in the composite by adding composite above the amount required to meet the minimum burst pressure. This allows the composite stress ratio to be reduced for enhanced performance in stress rupture and fatigue without forcing a similar overdesign of the metal liner that is not subject to stress rupture and stress corrosion cracking.

8.2.2.3.4 NGV2-4 Plastic Lined Full Wrapped

NGV2-4 lacks requirements for durability of permeation resistance to verify that the liner is not affected by pressure cycling to 15,000 psi.

8.2.2.4 ISO 11439 Vehicle Fuel Cylinders

Gas cylinders are intended for use as vehicle fuel tanks containing compressed natural gas. In addition to all-metal cylinders, ISO 11439 includes both hoop-wrapped and full-wrapped cylinders with load sharing metal liners and full-wrapped cylinders with plastic liners.

8.2.2.4.1 Scope Issues with ISO 11439

(a) The standard does not limit the design pressure, but the intent was clearly not to include pressures as high as 15,000 psi. All of the precedents used in developing the standard were limited to pressures up to 5,000 psi as stated in FRP-1 and FRP-2.

(b) The scope does not include hydrogen.

(c) There are no material compatibility requirements for hydrogen.

8.2.2.4.2 General Technical Issues with ISO 11439

(a) There are no explicit consensus-based design calculation methods and no criteria for the selection and use of calculation methods is provided.

(b) The stress ratio requirements in ISO 11439 are based on the design calculations and design minimum burst pressure. This is an area where the standard is not performance based.

(c) Compliance with the limiting fiber stress ratios is necessary to reliability, but is totally dependent on the undefined calculation methods.

(d) ISO 11439 does enumerate seven requirements for the stress calculation method, but is not explicit about how a method is to be evaluated as determined to be accurate.

(e) The empirical method of determining stress ratios given in Annex G is applicable only to Type 2 cylinders, the one design where a common design calculation method is possible. For Types 3 and 4, the method is not applicable to verification of the stress ratio in the helical fibers and there is no requirement that the stresses be highest in the hoop fibers. The stress analysis of Types 3 and 4 cylinders are required in both the tangential (hoop) and longitudinal direction, but Annex G requires that the strain gages be aligned parallel to the fibers, never in the longitudinal direction as required in the stress analysis being verified. Empirical strain gage verification of stress levels are not required but permitted.

(f) Empirical strain gage method applicable only to circumferential strains, not longitudinal.

(g) Empirical strain gage method does not verify liner stresses that are important to fatigue performance.

(h) Hybrid composite designs are common when carbon fiber is used, but the standard gives inadequate guidance to determining the stress ratios of composites comprised of differing fibers.

(i) Design calculations are not required for ports and heads.

(j) ISO 11439 contains ambiguous requirements for actual fire protection by PRDs. The designs must be qualified by test with effective PRDs, but the actual installation may be exempted from the design PRDs based on the requirements of the authority having jurisdiction.

(k) Permeation test chamber is not required to be essentially impermeable, potentially invalidating test results.

8.2.2.5 ISO DIS 15869 Draft for Hydrogen Vehicle Fuel Cylinders

This Draft International Standard is largely derivative of ISO 11439 but with a few different requirements in recognition of the intended use with hydrogen gas. The key differences relevant to 15,000 psi hydrogen service between ISO 11439 and ISO DIS 15869 are as follows.

(a) The standard is intended for vehicle fuel tanks, not stationary pressure vessels or gas cylinders.

(b) The standard imposes no specific requirement for design fatigue cycle life, leaving this as a variable to be established between the designer and the user. This is similar to the common ASME approach to fatigue, but is a radical departure for composite cylinder standards.

(c) Although the scope is hydrogen cylinders, there is no requirement that the key pressure cycling and LBB tests represent performance when filled with hydrogen. The test fluids are not hydrogen and there is no design mechanism to account for the difference in performance that should be expected in a hydrogen application. This is the key difference required in a performance standard and ISO 15869 is not an acceptable model without it.

8.2.2.6 ASME Code Case 2390

This Case is the most comprehensive of the standards for metal-lined composite reinforced vessels. It is the only standard with explicit requirements for design, but still leaves much to the judgment and experience of the designer. The Case requires less destructive sample testing during manufacture, a particular advantage with large vessels.

8.2.2.6.1 Scope Issues with Code Case 2390 Hoop-Wrapped Vessels

(a) The Case is limited to a maximum design pressure of 3,625 psi, too low for hydrogen storage vessels.

(b) The Case includes none of the material-specific requirements for hydrogen compatibility.

8.2.2.6.2 General Technical Issues with Code Case 2390

(a) The Case requires that the laminate strength be determined by test in accordance with ASTM D2290. Standards for composite vessels with low design margins normally require that the actual laminate strength be determined in a vessel burst test. Laminate strength is required as part of the procedure qualification test.

(b) The Case is not explicit with regard to design calculations but does require a fracture mechanics fatigue calculation. The use of von Mises yield criteria is permitted but not required, allowing a significant source of error for 15,000 psi designs. Von Mises is permitted only as an alternative to the more conservative Tresca approach that is otherwise required.

(c) The composite design stress is defined in terms of membrane stress and may not be accurate for the composite thicknesses of glass reinforced 15,000-psi vessels.

8.3 Review of Existing Standards for Composite Cylinders for Specific Applicability to 15,000 psi Hydrogen Storage Vessels

This section addresses only issues that are related to storage vessels but not to cylinders. All of the issues identified in the previous section apply to both storage vessels and cylinders.

8.3.1 Scope of New Vessels

(a) Storage vessels are defined as stationary vessels analogous to the cylindrical or spherical ASME vessels used for storage of compressed natural gas at vehicle refueling stations. These are usually larger than compressed gas cylinders and have water capacities of several thousand pounds.

(b) The design pressure of storage vessels is normally 110% of the normal operating pressure to allow for pressure fluctuations due to temperature and the required pressure relief valve set at design pressure. The design pressure of storage vessels for 15,000-psi operation is therefore estimated as 16,500 psi.

(c) State or local authorities often regulate storage vessels by requiring ASME Code vessels.

8.3.2 Scope of Present Composite Standards

With the exception of Code Case 2390, the current composite standards are not intended for storage vessels but for vehicle fuel tanks or portable gas cylinders. The standards lack requirements for resistance to external loads as may occur with very large storage vessels. The requirements for pressure relief devices for protection against rupture in a fire have been developed for the scenarios expected in transportation accidents. Some standards require partial exposure fire tests, but localized exposure to fire can still cause vessel failure in a fire. Large composite gas cylinders are not normally fitted with pressure-activated PRDs because the insulating effect of the composite can slow the heating of the gas and resultant pressure increase until the vessel strength is lost and a rupture occurs. Fire is therefore a greater concern with composites than metals due to this change in sensitivity. The PRD requirements should be designed specifically for the storage vessel environment.

With the exceptions of NGV2 and ASME Code Case 2390, the standards are not intended to be comprehensive enough for self-certification. In the US, there is generally no third party certification authority for storage vessels.

With the exception of Code Case 2390, none of the standards are intended for large stationary storage vessels. All of these standards are performance standards and share common strengths and weaknesses when applied to the specific application of 15,000-psi hydrogen storage vessels. All of the standards are derived in large part from the original DOT FRP-1 and FRP-2 standards for metal-lined composite reinforced gas cylinders. In the interests of a compact and clear presentation, these common characteristics will be discussed first. The later sections dealing with individual standards will only discuss the differences with this common base of characteristics.

8.3.3 Specific Present Composite Cylinder Standards

8.3.3.1 DOT Composite Gas Cylinder Standards

The DOT standards for composite gas cylinders will be discussed in detail first since the other standards are largely derived from them.

8.3.3.2 DOT FRP-1 and FRP-2

These are the current standards for aluminum lined full-wrapped and hoop-wrapped composite gas cylinders incorporating glass fiber reinforcement. These standards are very similar and are addressed together here. The standards are not directly applicable to hydrogen vessels due to the following gaps.

(a) These standards are intended for gas cylinders used in transportation, not storage vessels. This is reflected in both the technical and regulatory scope of the standards.

(b) The standard scope is also too narrow to cover the size and design pressure of storage tanks.

(c) The maximum water capacity is only 200 lb, far smaller than typically desired storage vessels.

(d) There is no coverage for external loads that may be imposed on large vessels

(e) The maximum service pressure is 5,000 psi, implying a maximum normal operating pressure of 6,000 psi.

(f) The scope of the standard is not complete enough to be a stand-alone document.

(g) The standards have not been incorporated into the CFR and DOT continues to require an exemption with special technical review requirements for each new design or manufacturer.

(h) Critical issues such as operational life, requalification, and limits on use are contained in DOT Exemptions that are issued on an individual basis for designs and manufacturers.

(i) Hydrogen storage tanks are outside the regulatory scope of DOT and any exemption granted will contain a disclaimer of any endorsement for a storage application.

(j) The standard is not intended for self-certification as is common for existing Code storage vessels and requires a design approval review by DOT as a part of the exemption grant process.

(k) There is no requirement for a third party vessel certification agency to perform design approval on storage vessels.

(l) The number of lifetime pressure cycles is too low for typical fuel storage vessel service.

(m) The standard requires only very low cycle fatigue.

(n) The design test is only 10,000 cycles to service pressure.

(o) Exemptions authorizing the use of FRP-1 and FRP-2 cylinders refer to the retest requirements as applied to DOT-3HT cylinders, incorporating a maximum lifetime cycle count of 4,380. Since storage vessels may be cycled many times in a single day, this would limit the useful life to a few months to a few years.

8.3.3.3 Issues with The Scope Of ISO 11119 If Applied to 15,000-Psi Hydrogen Storage Vessels

(a) This standard is intended for gas cylinders used in transportation, not storage vessels.

(b) This standard is not intended to be comprehensive enough for self-certification. It assumes the requirement of a Notified Body to verify the design for Type Approval. There is no U.S. national authority that approves a Notified Body in the United States to provide Type approval for a storage vessel.

(c) The maximum water capacity is 990 lb, smaller than is desirable in a storage vessel, but possibly feasible.

(d) There is no coverage for external loads imposed on large vessels.

8.3.3.4 NGV2 Fuel Containers

(a) NGV2 is the only composite standard other than Code Case 2390 that is intended to be comprehensive enough for self-certification. This is significant given the lack of any regulatory agency with design approval authority over storage vessels.

(b) NGV2 requires that an independent inspection agency approve all design qualification tests. This provides a level of third party review consistent with the agencies available in the United States.

8.3.3.5 Scope Issues with NGV2

The maximum water capacity is 2,200 lb, somewhat smaller than typical ASME storage vessels.

8.3.3.6 ISO 11439 Vehicle Fuel Cylinders

ISO 11439 is not intended to be comprehensive enough for self-certification. It requires the use of a third-party approval agency appointed by the national authority. This is always problematic in the United States where no such statutory authority exists.

8.3.3.7 Scope Issues with ISO 11439

The maximum water capacity is 2,200 lb, somewhat smaller than typical ASME storage vessels. NGV2 containers are not intended for hydrogen.

8.3.3.8 ISO DIS 15869 Draft for Hydrogen Vehicle Fuel Cylinders

This Draft International Standard is largely derivative of ISO 11439 but with a few different requirements in recognition of the intended use with hydrogen gas. The key differences relevant to 15,000 psi hydrogen service between ISO 11439 and ISO DIS 15869 are as follows.

The standard imposes no specific requirement for design fatigue cycle life, leaving this as a variable to be established between the designer and the user. This is similar to the common ASME approach to fatigue, but is a radical departure for composite cylinder standards.

8.4 Review of Existing Standards for Composite Cylinders for Applicability to 15,000 psi Portable Hydrogen Cylinders

8.4.1 Scope of New Cylinders

Portable cylinders are defined as transport containers for compressed hydrogen and are analogous to compressed gas cylinders as regulated in 49CFR178. The size of portable cylinders is limited to 1,000 lb maximum water capacity.

MNOP for transportation cylinders and trailer tubes must be greater than the service pressure to allow for the pressure increase that may result in heating to as much as 55°C in transportation. This pressure is estimated as 16,800 psi based on extrapolation of compressibility factors from.

All transport containers must be authorized by specifications included or incorporated by reference in 49CFR178 or must be authorized by the exemption process.

8.4.2 Scope of Present Standards

All of the reference standards allow cylinders in the size range common for DOT compressed gas cylinders, but not necessarily up to 1,000 lb water capacity.

8.4.3 Scope Issues with DOT FRP-1 and FRP-2 Cylinders

(a) The 15 year limited design life that is not contained in the standards, but is incorporated into all DOE Exemptions for the use of FRP-1 and FRP-2 cylinders is not consistent with general gas cylinder usage.

(b) Regardless of pressure cycles, the service life IS limited to 15 years. This limitation by DOT recognizes susceptibility of glass composites to time-dependent stress rupture and the lack of established in-service requalification methods for composite cylinders that are verified to detect all of the expected forms of in-service degradation.

(c) The number of lifetime pressure cycles is too low for typical gas cylinder service.

(d) The standard requires only very low cycle fatigue.

(e) The design test is only 10,000 cycles to service pressure.

(f) Exemptions authorizing the use of FRP-1 and FRP-2 cylinders refer to the retest requirements as applied to DOT-3HT cylinders, incorporating a maximum lifetime cycle count of 4,380.

(g) The maximum water capacity is only 200 lb, far smaller than the maximum compressed gas cylinder.

(h) The standards have not been incorporated into the CFR and DOT continues to require an exemption with special technical review requirements for each new design or manufacturer.

(i) Critical issues such as operational life, requalification and limits on use are contained in DOT Exemptions that are issued on an individual basis for designs and manufacturers.

8.4.4 DOT CFFC

The requirements for resistance to impact are designed for small cylinders and are not appropriate for large cylinders or trailer tubes.

It is not clear that the impact requirements are adequate to assure against sympathetic failures, particularly with larger cylinders.

8.4.5 ISO Composite Gas Cylinder Standards

ISO 11119 is the current ISO standard for composite gas cylinders incorporating carbon, glass aramid fibers or metal wire, alone or in combination. This discussion does not cover the option of wire reinforcement and is limited to the fiber options. This standard is not directly applicable to hydrogen vessels due to the gaps discussed below, but there are unique concepts that should be considered for a hydrogen vessel standard. The standard is divided into three parts for Types 2, 3, and 4 cylinders respectively, and comments common to all three parts will be addressed first.

8.4.5.1 General Technical Issues with ISO 11119

The standards permit the use of carbon fiber for reinforcement but the tests for impact resistance are limited to small high-velocity penetrations affecting only small areas on the most uniform part of the vessel and resistance to blunt impact is required only against a plane surface. The blunt impact test is intended to provide assurance that the vessel is resistant to damage that may occur in handling the vessel on installation, but the drop heights and requirement for plane surfaces only may are not representative of actual handling mishaps.

The impact requirements are inadequate to assure against sympathetic failures, particularly with larger cylinders.

In service retest and inspection requires periodic hydrostatic retest of doubtful effectiveness at a low percentage of the vessel's ultimate strength.

8.4.5.2 ISO 11119-3

ISO 11119-3 is for plastic lined full-wrapped composite gas cylinders incorporating carbon, glass, or aramid fibers, alone or in combination.

8.4.6 NGV2

NGV2 containers are not intended for the transportation of compressed gas. There are no requirements for resistance to the types of impact and abrasion damage that occur to portable gas cylinders. NGV2 requires that the vehicle structure protect the containers from such damage. Additionally, NGV2-3 and NGV2-4 lack requirements for resistance to casual damage in transport and resistance to sympathetic failure.

8.4.7 ISO 11439 CNG Fuel Cylinders

These cylinders are intended for use as vehicle fuel tanks containing compressed natural gas. In addition to all-metal cylinders, ISO 11439 includes both hoop-wrapped and full-wrapped cylinders with load sharing metal liners and full-wrapped cylinders with plastic liners

ISO 11439 containers are not intended for the transportation of compressed gas. There are no requirements for resistance to the types of impact and abrasion damage that occur to portable gas cylinders. ISO 11439 requires that the vehicle structure protect the containers from such damage.

8.4.8 ISO DIS 15869 Draft Standard for Hydrogen Vehicle Fuel Cylinders

This Draft International Standard is intended only for vehicle fuel tanks and lacks requirements for resistance to casual handling damage such as is common for gas cylinders as well as resistance to sympathetic failure.

8.4.9 ASME Code Case 2390

This Case is the most comprehensive of the standards for metal-lined composite reinforced vessels. It is the only standard with explicit requirements for design, but still leaves much to the judgment and experience of the designer.

(a) The Case requires less destructive sample testing during manufacture, a particular advantage with large vessels.

(b) There are no requirements for resistance to the types of impact and abrasion damage that occur to portable gas cylinders.

(c) The Case appears to be directed towards very large vessels as opposed to smaller gas cylinders.

(d) Code Case 2390 does not specifically address hydrogen.

9 NECESSARY VESSEL INSTALLATION CODES

This section is recognition of the limitations on protection against all failure modes through vessel design and the necessity to provide installation requirements that may be specific to certain vessel types. It is probably most effective to include these requirements in the new standard where they are continually available for reference by those developing system and application codes.

Leak-before-break, LBB, is an acceptable and relatively benign failure mode only if the severity of such a failure is low. This requires that a small leak not produce a large hazard and that the leak be detected so that failed vessel can be removed from service. The new vessels should be used with installation codes that provide for ample ventilation and automatic leak detection. These provisions are consistent with the intent of ASME Section VIII Division 3 that LBB be considered only if a leak is tolerable and they will allow the fatigue design to take advantage of LBB considerations.

Adequate leak detection and ventilation is also needed to protect against the occurrence of a leak in a nonmetallic liner of a composite vessel. There have been six reported instances of single or multiple CNG cylinders leaking in North America due to issues with the plastic liners [74].

Vessels should be installed with sufficient clearance to permit any required visual or other external NDE without disassembly. Since composites, particularly carbon fibers, are sensitive to handling damage, every effort should be made to minimize disassembly after installation. This is also important from the viewpoint of breaking and re making piping connections that must seal hydrogen at 15,000 psi.

Compressors discharging into pressure vessels as receivers or cascade vessels should be equipped with aftercoolers. This was not a consistent practice with CNG compressors for many years and was only made a uniform practice in order to allow coalescing filters to effectively remove compressor oil and moisture. Since hydrogen will probably be much purer in this regard than natural gas, there may be a temptation to just let the gas cool in the vessel. Composite materials have lower thermal conductivity than metals and the temperature of the liner may be significantly higher than the ambient temperature if hot gas is charged into the vessel. Since both hydrogen damage to metals and permeation through nonmetals are increased at higher temperatures, the installation code should require aftercoolers to prevent elevated vessel temperatures. In the event that high gas temperatures are needed for the process, the vessel design may have to be adapted and different material properties limits developed and applied.

Vessels that are sensitive to impact damage, especially when not pressurized, should be proof tested after installation or assembly into brackets or modules. This is a prudent control against unreported but damaging impact during handling and shipment.

The vessel assembly should not be leak or pressure tested using air or any other gas that can react with hydrogen. The severity of the failure mode in the event that a cylinder is pressurized with an explosive mixture of hydrogen is extreme. The only known fatal accident involving an NGV2 cylinder resulted from deflagration of a flammable mixture of air and natural gas resulting in three fatalities [54]. The potential severity of such a failure with hydrogen gas would be much greater due to the probable detonation, not deflagration reaction.

If a vessel of impact-sensitive composites is not known to be resistant to sympathetic failure, and a hazard analysis shows that multiple failures are not acceptable, the installation design should provide adequate isolation and/or containment to prevent a failure cascade.

Vessels, and particularly composites, should be protected from direct sunlight. The resin matrix materials are generally sensitive to UV damage and even if inhibitors are added, an unlimited life is a very long time for any polymer to resist UV. The solar load from direct sunlight can also result in significant pressure surges in vessels of any material. Given the reduction in storage efficiency that can result from solar heat gain, this is a sensible practice for all vessels.

REFERENCES - PART I

[1] "Sensitivity of Steels to Degradation in Gaseous Hydrogen" Hydrogen Embrittlement: Prevention and Control, ASTM STP 962, L. Raymond, Editor, American Society for Testing and Materials, Philadelphia, pp. 134 - 152 (1988).

[2] Section VIII Division 1 "Rules for Construction of Pressure Vessels," American Society of Mechanical Engineers (2003).

[3] 49CFR Part 173.301a(c) "General Requirements for Shipment of Compressed Gases in Cylinders and Spherical Pressure Vessels," U.S. Code of Federal Regulations Title 49 (2003).

[4] 49CFR Part 173.301(a)(8) "General Requirements for Shipment of Compressed Gases in Cylinders and Spherical Pressure Vessels," U.S. Code of Federal Regulations Title 49 (2003).

[5] 49CFR Part 173.302a(b) "Special Filling Limits for DOT 3A, 3AX, 3AA, 3AAX and 3T Cylinders," U.S. Code of Federal Regulations Title 49 (2003).

[6] IGC Document 100/03/E "Hydrogen Cylinders and Transport Vessels," Revision TN 26/81, European Industrial Gases Association (2003).

[7] "Recommendations on the Transport of Dangerous Goods Model Regulations," 12th Edition, United Nations (2001).

[8] ISO 11119-1, 2, and 3 "Gas Cylinders of Composite Construction - Specifications and Test Methods," International Organization for Standardization (2000).

[9] ISO 11439 "Gas Cylinders - High Pressure Cylinders for the On-board Storage of Natural Gas as a Fuel for Automotive Vehicles," International Organization for Standardization (2002).

[10] Section VIII Division 2 "Alternative Rules, Rules for Construction of Pressure Vessels," American Society of Mechanical Engineers (2003).

[11] Section VIII Division 3 "Alternative Rules for Construction of High Pressure Vessels, Rules for Construction of Pressure Vessels," American Society of Mechanical Engineers (2003).

[12] 49CFR Part 173.301(f) "Pressure Relief Device systems," U.S. Code of Federal Regulations Title 49 (2003).

[13] CGA S-1.1 "Pressure Relief Device Standards Part 1 - Cylinders for Compressed Gases," 9th Edition, Compressed Gas Association, Inc. (2001).

[14] Case 2390-1 "Composite Reinforced Pressure Vessels Section VIII Division 3," American Society of Mechanical Engineers (2003).

[15] CGA C-5 "Requalification of High Pressure Cylinders: Special Fill Limits and Extended Requalification Period," 6th Edition, Compressed Gas Association, Inc. (1997).

[16] Equation 6.370 "Engineering Design," Joseph Henry Faupel and Franklin E. Fisher, John Wiley & Sons (1981).

[17] Section II Part A "Ferrous Materials Specifications," American Society of Mechanical Engineers (2003).

[18] Section II Part D "Materials Properties," American Society of Mechanical Engineers (2003).

[19] 49CFR Part 178.36 "Specification 3AA and 3AAX Seamless Steel Cylinders," U.S. Code of Federal Regulations Title 49 (2003).

[20] ISO 9809-1 “Gas Cylinders - Refillable Seamless Steel Gas Cylinders - Design, Construction and Testing,” International Organization for Standardization (1999).

[21] ISO 11120 “Gas Cylinders - Refillable Seamless Steel Tubes of Water Capacity between 150 l and 3000 l - Design, Construction and Testing,” International Organization for Standardization (1999).

[22] ISO 11114-1 “Transportable Gas Cylinders - Compatibility of Cylinder and Valve Materials with Gas Contents, Metallic Materials,” International Organization for Standardization (1999).

[23] “DOT Exemption E 6530, 12th Revision,” U.S. Department of Transportation Research and Special Programs Administration (2000).

[24] 49CFR Part 173 Subpart G “Gases; Preparation and Packaging,” U.S. Code of Federal Regulations Title 49 (2003).

[25] CGA Pamphlet C-1 “Methods for Hydrostatic Testing of Compressed Gas Cylinders,” 7th Edition, Compressed Gas Association, Inc., Arlington, Virginia (1996).

[26] CGA Pamphlet C-6 “Standards for Visual Inspection of Steel Compressed Gas Cylinders,” 7th Edition, Compressed Gas Association, Inc., Arlington, Virginia (1993).

[27] U.S. Code of Federal Regulations, Title 49 - Transportation, Part 178 Specifications for Packaging Subpart C - Specifications for Cylinders, Office of the Federal Register, National Archives and Records Administration, Washington, D.C. (2001).

[28] 49 CFR Part 107, “Hazardous Materials: Requirements for DOT Specification Cylinders; Proposed Rule,” *Federal Register*, Vol. 63, No 210 (October 30, 1998).

[29] “Managing Stress Corrosion Cracking,” R. Scrivner (Transco) and D. Katz (Northwest Pipeline). Presentation to Gas Integrity Management Program. U.S. Department of Transportation, Research and Special Programs Administration (December 2003).

[30] U.S. Department of Transportation, Research and Special Projects Administration. Exemption E 10922, October 27, 1993.

[31] AMKO Inc. “Exemption 8944 for Retesting DOT 3AAX and 3T Tube Trailers,” (www.praxair.com) (1984).

[32] “Basic Requirements for Compressed Natural Gas Vehicle (NGV) Fuel Containers,” ANSI/CSA, NGV2-2000, CSA International.

[33] CGA Pamphlet C-6.4 “Methods for External Visual Inspection of Natural Gas Vehicle (NGV) Fuel Containers and their Installations,” Compressed Gas Association, Inc., Arlington, Virginia (1998).

[34] Webster, C.T.H. et al., “Compressed Natural Gas Storage Optimization for Natural Gas Vehicles” Final Report to the Gas Research Institute. GRI-96/0394 (December 1996).

[35] Connolly M. P. et al. “Field Study of Composite NGV Fuel Containers” SWRI Final Report No. 06-6468 for The Gas Research Institute (September 1994).

[36] “Hydrogen Cylinders and Transport Vessels” IGC Document 100/03/E, European Industrial Gases Association (2003).

[37] “Examination of Nondestructive Evaluation of Composite Gas Cylinders” Final Report . NTIAC (September 2002).

[38] CGA Pamphlet C-6.2 “Standards for Visual Inspection and Requalification of Fiber Reinforced High Pressure Cylinders,” Compressed Gas Association, Inc., Arlington, Virginia (1998).

[39] "Development and Validation of a Prototype Acoustic Emission System for Inspection of Metal NGV Fuel Cylinders," GRI-94/0041, Gas Research Institute (May 1995).

[40] D. Carter et al. "An Examination of a Failed FRP Hoop-Wrapped 6061-T6 Alloy CNG Cylinder," PowerTech Report to CNG Cylinder Company, November 1993.

[41] Aerospace Corporation. "Nondestructive Evaluation (NDE) Techniques Assessment for Graphite/Epoxy (Gr/Ep) Composite Overwrapped Pressure Vessels," Report Number TR-98 (8504)-3, Prepared for Space and Missiles Center, Air Force Material Command (1998).

[42] ASME Boiler and Pressure Vessel Codes, Section X, Article 11 "Acoustic Emission Examination of Fiber-Reinforced Plastic Vessels," ASME (2003).

[43] G. K. Knight. "Residual Strength of Carbon/Epoxy Pressure Vessels Subjected to Low Velocity Impacts," ANTEC, pp. 1486-1488 (1989).

[44] M. P. Connolly. "A Review of Factors Influencing Defect Detectability in Infrared Thermography: Applications to Coated Materials," *Journal of Nondestructive Evaluation*, Vol. 10, No. 3 (1991).

[45] M. P. Connolly. "Reliability Based Assessment of Inspection Requirements," *Materials Evaluation* (October 1995).

[46] H. D. Beeson "Composite Overwrapped Pressure Vessels," NASA White Sands Test Facility: Report Number NASA/TP-2002-210769 (2002).

[47] "Basic Considerations of Cylinder Design" 1.2.4.4 Periodic Requalification, Compressed Gas Association, Inc. (1974).

[48] DOT FRP-2 Standard "Basic Requirements for Fiber Reinforced Plastic (FRP) Type 3HW Composite Cylinders," Revision 1, U.S. Department of Transportation Research and Special Programs Administration (1987).

[49] E. Y. Robinson. "Design Prediction for Long-Term Stress Rupture Service of Composite Pressure Vessels," The Aerospace Development Corporation (1991).

[50] 49CFR Part 173.301(a)(2) "General Requirements for Shipment of Compressed Gases in Cylinders and Spherical Pressure Vessels," U.S. Code of Federal Regulations Title 49 (2003).

[51] J. A. Walters. "Hoop-Wrapped, Composite, Internally Pressurized Cylinders, Development and Application of a Theory," ASME Press (2003).

[52] ANSI/CSA NGV2-2000 "American National Standard for Basic Requirements for Compressed Natural Gas Vehicle (NGV) Fuel Containers," CSA International (2000).

[53] DOT CFFC Standard "Basic Requirements for Fully Wrapped Carbon-Fiber Reinforced Aluminum Lined Cylinders (DOT-CFFC)," Revision 4, U.S. Department of Transportation Research and Special Programs Administration (2000).

[54] "Incident Report Number 1511623, Incident File Number PIMC0068396," Commission de le santé et de la securité du travail du Québec (2001).

[55] 49CFR Part 571.303 "Standard No. 303; Fuel System Integrity of Compressed Natural Gas Vehicles," U.S. Code of Federal Regulations Title 49 (2003).

[56] NFPA 52 "Compressed Natural Gas (CNG) Vehicular Fuel Systems Code," National Fire Protection Association (2002).

[57] C. T. Webster. "Ground Storage NGV Cylinder Safety," Canadian Gas Association (1991).

[58] "Summation of NTSB Public Meeting, 9-17-02, Tube Trailer Incident, 5-01, Oklahoma, 2000.

[59] J. B. Dimmick. "Test Data to Support the Request for Exemption (E 9791) of High Strength Seamless Compressed Gas Steel Cylinders," Pressed Steel Tank Co., Inc. (1987).

[60] J. A. Walters. "The Fundamental Nature of the K Factor as Used for Evaluating Elastic Expansion in the Hydrostatic Testing of Gas Cylinders" (2000).

[61] ISO TR 13763 "Safety and Performance Criteria for Seamless Gas Cylinders," ISO (1994).

[62] Federal Specification RR-C-901D "Cylinders, Compressed Gas, Seamless, Shatterproof, High Pressure, DOT 3AA Steel, and 3AL Aluminum," U.S. Department of Defense (DOD) (2003).

[63] MIL-DTL-7905H "Cylinders, Steel, Compressed Gas, Non-Shatterable, 1800 psi and 2100 psi," U.S. DOD (2003).

[64] "Compressed Air and Gas Data," 3rd Edition, A. W. Loomis, Editor, Ingersoll-Rand (1980).

[65] Section II Part A "Ferrous Material Specifications," Specification SA-20, American Society of Mechanical Engineers (2003).

[66] DOT FRP-1 Standard "Basic Requirements for Fiber Reinforced Plastic (FRP) Type 3FW Composite Cylinders", Revision 2, U.S. Department of Transportation Research and Special Programs Administration (1987).

[67] " CGA C-6 Standards for Visual Inspection of Steel Compressed Gas Cylinders," Compressed Gas Association, Inc. (2001).

[68] "CGA C-6.2 Guidelines for Visual Inspection & Requalification of Fiber Reinforced High Pressure Cylinders," Compressed Gas Association, Inc. (1996).

[69] M. Connolly et al. "Assessment of Design and Durability Issues for Composite NGV Fuel Cylinders, Topical Report," Southwest Research Institute (1993).

[70] "Update of August 21, 1996 CNG Cylinder Rupture at Los Angeles County Metropolitan Transportation Authority (LACMTA)," J. Douglas Moore, Pres. and CEO, EDO Canada Ltd. (1996).

[71] "Study Finds Cylinder Damage Prior to Rupture, not Installation," *NGV News* (August 1997).

[72] "Analysis of the Pneumatic Bursts of a Large Seamless Steel Pressure Vessel in Natural Gas Service" Bruce W. Christ, U.S. DOT Report No. DOT/MTB/OHMR-78-4 (1978).

[73] Private communication with Dr. John Lee, McGill University (2000).

[74] Known In-service Failures of NGV Cylinders (Since 1976), Powertech, a Subsidiary of BC Hydro (January 2004).

PART II - A Study of Existing Data, Standards, and Materials Related to Hydrogen Service (Storage and Transport Vessels)

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1 INTRODUCTION

1.1 Background

The ASME B&PV Code Committee has formed a hydrogen project team to develop code rules for storage vessels, transport tanks, and portable tanks for up to 15,000 psi hydrogen gas service. In order to support this effort, the ASME Standards Technology, LLC (formerly the Codes and Standards Technology Institute) is developing H_2 standardization interim technical reports to address priority topics related to infrastructure applications.

1.2 Scope of Report

The scope of Part II of this report is to:

(a) identify problems and recommend possible solutions in using existing standards for 15,000-psi vessels.

(b) identify existing commonly used materials, evaluate their resistance to hydrogen cracking at 15,000 psi, and determine the implication on design and in-service inspection.

(c) communicate successful service data for H_2 storage and transport tanks.

1.3 Service Conditions

Only gaseous dry hydrogen at ambient temperature and pressure up to 15,000 psi is within the scope of this report.

The pressure is limited to internal pressure, and the design basis is limited to the pressure design. Loadings due to external conditions (impact, live and dead loads, seismic, wind, thermal and thermal gradient, vibration and support) are not considered in this report.

Mixtures of hydrogen with other gases are outside the scope of this report. The presence of the other gases has various effects (both positive and negative) on the hydrogen compatibility of materials.

1.4 Executive Summary

Vessel standards for 15,000 psi hydrogen service will need to account for the challenges of both high pressure and hydrogen compatibility.

Metal vessels and liners will need to be constructed of materials that are resistant to hydrogen embrittlement. There is limited data on commonly used carbon steel (CS) alloys, but the existing data support limitations on tensile strength. New research is needed to cover higher pressures and potentially new alloys. Linings made of more compatible materials such as aluminum or 316 stainless steel show promise.

Ultrasonic or other NDE evaluation for inclusions and inner surface cracks is critical. The limited data available indicate that hydrogen can accelerate crack growth 50 to 150 times faster than an inert gas. Critical stress intensity (K_H) values and crack growth data must be established for higher pressures. By expanding research, fracture mechanics can be used to set limits on initial crack size, estimate rate of crack growth, and determine safe intervals for in-service inspections. Without the data, cycle testing of each design would need to be conducted using hydrogen.

Fully metallic vessels become less practical at 15,000 psi. They are significantly heavier than equivalent composite vessels. Formability, heat treatment and single-sided quenching become difficult above a 1.5 inch wall. Thin-wall design calculations lose their validity, suggesting Section

VIII Division 3 methods should be used to account for collapse, thick-wall effect, and high radial compressive stress.

Wall thicknesses can be reduced by lowering design margins. Margins for seamless vessels designed using Division 1 and 2 methods can be safely reduced to 2.25 with appropriate material selection, initial screening for critical cracks, and in-service inspections for crack growth. A design margin of 2.25 matches the margin for DOT 3AAX “plus” rated vessels, which have seen successful service for over 60 years.

All fully metallic vessel standards will need increased guidance on head forms, discontinuities, and outlet openings. Current reliance on straight thread o-ring seals or tapered threads may need to shift to welded, cone-and-thread, or new designs, and tolerancing will become critical to ensure leak-free service.

Composite vessel construction may be ideal for future 15,000 psi hydrogen service. Many composite vessels are already constructed with highly compatible aluminum liners. Of the existing composite standards, ISO/DIS 15869 addresses the most hydrogen-specific aspects of design and testing.

Challenges for composite vessels include proper curing of a thick laminate layer and effecting a good seal between the end boss and liner. Since composite vessels are constructed to performance standards instead of design standards, verification tests become critical. Tests such as cycle or leak-before-break (LBB) cannot be run using inert gases or liquids and then extrapolated for hydrogen. Tests must be conducted using hydrogen.

Certainly, existing standards have been used successfully and safely at pressures as high as 10,000 psi. Increasing the pressure to 15,000 psi will require expanded hydrogen compatibility research, diligence in inspection and screening of materials, design methods that account for thicker walls, a decrease in design margin (when coupled with in-service inspection), greater use of composite vessels, and more representative performance testing using hydrogen as the pressurizing medium.

2 ISSUES RELATED TO USING EXISTING STANDARDS FOR HIGH-PRESSURE VESSELS

Existing vessels used for hydrogen service can be classified as:

(a) Storage vessels

(b) Transport vessels

(c) Portable cylinders

(d) Fuel tanks

Most existing hydrogen vessels operate at pressures less than 5,000 psi, but a relatively small number are designed for pressures as high as10,000 psi. The existing standards under which these vessels are designed, manufactured and tested do not cover the scope and technical challenges posed by 15,000 psi hydrogen service.

In a general sense, the design of the future high-pressure hydrogen tanks will depend on their service.

(a) Large stationary storage vessels may continue to be the fully metallic type when weight is not a consideration.

(b) For large transportation service (tube trailers), fully metallic vessels conforming to DOT standards (49 CFR 178 [1]) are the primary vessels authorized for hydrogen transportation in the United States. A limited number of exemptions have been granted for composite vessels. Higher pressures combined with weight restrictions may require more composite vessel designs.

(c) Thousands of portable DOT 3AA metallic cylinders are currently in hydrogen service, and DOT CFFC [2] fully wrapped carbon fiber vessels are also approved. Higher pressures may demand more composite cylinders in order to keep the packages lightweight and portable.

(d) Onboard hydrogen fuel tanks are almost exclusively composite-type and, in order to keep them lightweight, that trend will continue for higher pressures.

In order to clearly address the issues related to the existing standards, this evaluation is divided into the two categories of vessel construction: fully metallic and composite.

2.1 Metallic Vessels

Standards being evaluated for fully metallic-type vessel construction are:

(a) CFR Title 49, Subpart 178.37 Specification 3AA and 3AAX Seamless Steel Cylinders (for DOT transportation vessels)

(b) ASME Section VIII, Div 1, Appendix 22 [3] (for stationary storage vessels)

(c) ANSI/CSA NGV2-1 [4] (vehicle fuel tank, natural gas)

(d) ISO/DIS 15869 [5] (draft status, based on natural gas vehicle fuel tank standard ISO 11439)

Note that although NGV2 and ISO/DIS 15869 standards offer a fully metallic option (Type 1), the great majority of fuel tanks manufactured to these two standards are the lightweight composite (Type 2, 3, 4) vessels. However, this section will only discuss the full metallic (Type 1) vessel.

2.1.1 Design Issues

2.1.1.1 Material Compatibility

Of the listed standards, only ISO/DIS 15869 was written specifically for hydrogen. Hydrogen with its unique property of material embrittlement may affect the mechanical properties of materials it comes in contact with during processing, storage or transportation. Suitable material selection for hydrogen, based on service conditions, is a mandatory part of design. Standards will either need to give guidelines or provide pointers to other standards for material selection for hydrogen service. IGC Document 100/3 [6] is an example of a guideline for allowable composition of various alloy steels for hydrogen service.

49 CFR 178.37 allows five different materials for the construction of 3AA and 3AAX tubes, but alloy 4130X is the most widely used. ASME Section VIII Division 1, Appendix 22 allows only SA 372 [7] (various grades). For high-pressure hydrogen service, other suitable materials may be desirable and will need to be included.

2.1.1.2 Effect of High Pressure and Wall Thickness

Only NGV2 limits the maximum service pressure[1], but the scope sections of the remaining standard imply they are intended for pressures much lower than 15,000 psi. Design rules (when provided) apply to relatively thin-walled vessels and are not intended for design against collapse with high pressures. As design pressures increase, vessel wall thicknesses will also increase if similar strength materials are used. High wall thickness has a nonuniform through thickness stress distribution (thick wall effect) and higher radial compressive stress at the inner surface of the vessel. ASME Section VIII Division 3 [8] rules may be the right guideline to explicitly cover the design of pressure vessels for pressures to 15,000 psi. Division 3 addresses many design aspects related to high pressure, such as design margin against collapse, thick wall effect, and high equivalent stress at the ID of the vessel.

2.1.1.3 Tensile Strength and Other Material Property Limitations

Hydrogen embrittlement is directly related to tensile strength of alloy steels [9], so it is necessary to limit tensile strength of certain materials for high-pressure hydrogen service. The standards that are not specifically written for hydrogen have no limits beyond those in the ASME/ASTM material specifications. For example, SA372 Grade F Class 70 material has a maximum tensile strength of 145 ksi. NGV2 allows a maximum tensile strength to 175,000 psi.[2] Future hydrogen standards must limit the tensile strength of alloy materials to a tested and approved figure provided by a competent standard development organization. As an example, IGC Document 100/03 limits the tensile strength of materials to 138 ksi in hydrogen service. This figure may not be conservative for 15,000 psi hydrogen service.

It is also recommended that limits or ranges be specified for other critical material properties such as elongation, ratio of yield stress to ultimate stress, hardness, and impact toughness.

2.1.1.4 Microstructure and Heat Treatment

Investigations of failed cylinders and current knowledge indicate that microstructure of the material influences hydrogen-induced degradation [9]. Microstructure is dependent on the chemical composition, but is also greatly affected by the heat treatment of the alloy. To obtain successful resistance to hydrogen embrittlement and at the same time realize the optimum properties of the

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[1] Currently 3,600 psig, although a draft standard is increasing the pressure to 10,000 psig.

[2] Special testing is required for tensile strengths in excess of 138,000 psi.

alloys, heat treatment guidelines to attain specific microstructure need to be specified in future standards.

2.1.1.5 Surface Defects and Inclusions

Harmful inclusions and surface defects play a major role in hydrogen-accelerated fatigue cracks [10]. Such cracks are initiated at critical inclusions and surface defects. The growth of fatigue cracks is accelerated by the presence of high-pressure, high-purity hydrogen. Hence, for 15,000 psi hydrogen service, one means of avoiding hydrogen-accelerated failures is to exclude harmful inclusions within the metal and avoid critical surface defects. The reference standards have only general rules on testing for external quench cracks by magnetic particle or liquid penetrant and visual tests. Future 15,000-psi vessels should include surface condition and surface finish rules defined to quantitative values so that they can be verified by tests. Rules on inclusions within the metal also need to be addressed in a similar fashion.

2.1.1.6 Fatigue Life

3AAX and Appendix 22 do not require that fatigue life be determined by analysis or through verification tests. There is no explicit design guideline for either the number of cycles or the pressure fluctuations allowed for the cycles. Storage tanks at vehicle filling stations will be subject to frequent pressure fluctuations, and the amplitude of those fluctuations will be dependent on the control strategy at the station. Some vessels may fluctuate from “full” to near “empty,” while others are refilled after dropping only 10% in pressure. The cycle frequency, the maximum stress, and the amplitude of the pressure swing are all critical to determining the fatigue life of a vessel in hydrogen service. Hence fatigue life of vessels must be determined and potentially verified by cycling pressure tests at worst-case operating conditions.

NGV2 and ISO/DIS 15869 do require cycle testing, but not with hydrogen gas.

The difficulty with determining fatigue life by analysis (using fracture mechanics methods) is due to (1) limited information on threshold fracture stress intensity factor (Kh) below which a crack would arrest under sustained loading, and (2) lack of data at high pressures on the cyclic range of fracture stress intensity factor (dKh) above which hydrogen will significantly accelerate fatigue crack growth rates.

2.1.1.7 Leak-Before-Break (LBB)

The recent trends in composite high-pressure cylinder designs have considered LBB as the preferred and sometimes required failure mode. LBB criteria require a fracture mechanics analysis to ensure that a vessel failure mode will be ductile rather than brittle fracture. This analysis can only be completed by expanding the limited fracture mechanics data for materials in high-pressure hydrogen service.

2.1.1.8 Design Life

ASME VIII Appendix 22 does not specify a maximum design life for the vessels, nor does it have guidelines on extending service life by in-service inspection or qualification tests. Although corrosion is not a concern in dry hydrogen service, degradation is possible due to hydrogen embrittlement and fatigue-related crack growth.

49 CFR requires that DOT 3AAX vessels be requalified at 5- to 10-year intervals, depending on service. There is no limit to how many times a vessel may be requalified; however, the standard hydrostatic expansion test is not adequate to detect critical cracks. By exemption only, an acoustic emissions test (with a UT follow-up) may be substituted for a hydrostatic test. This AE/UT test is

capable of detecting cracks as small as 3 to 5% of the vessel wall and should be the preferred re-qualification method for high-pressure hydrogen service.

NGV2 and ISO/DIS 15869 have defined design lives (20 years) and regular requalification intervals (36 months for NGV2 and at the manufacturer's specified interval for ISO/DIS 15869). NGV2 re-qualification is achieved by following the manufacturer's recommendations (including any NDE tests approved by the manufacturer) and by inspecting according to procedures provided in CGA C-6.4 [11]. ISO/DIS 15869 requalification is also performed based on recommendations from the manufacturer. This type of "discretionary" requalification will not ensure that critical cracks are detected.

Hydrogen embrittlement and accelerated crack growth make it imperative that future high-pressure hydrogen vessel standards consider design life and mandate initial and in-service inspection methods that are capable of detecting critical cracks.

2.1.1.9 Design Margin

The lowest design margin for metallic cylinders in compressed gas service is that of DOT 3AA and 3AAX. Vessels of this design have safely operated for over 60 years at 110% of service pressure (with short-term excursions above this during fill). The "design margin" for these vessels (defined as burst pressure using ASME Section VIII Division 3 plastic collapse formula divided by 110% service pressure) is 2.25.

For seamless high-pressure hydrogen vessels designed using a Division 1 or 2 approach, the use of a 2.25 design factor is warranted when it is combined with careful material selection (considering hydrogen embrittlement and tensile strength) and inspection of the interior for cracks. The 2.25 design factor should only be used with design life limits or periodic in-service inspections capable of detecting the growth of critical surface flaws (such as AE testing with follow-up UT for active sites).

For vessels designed per Division 3 methods, the existing 1.732 design margin should be retained.

Because welded all-metal designs present a considerable challenge for high-pressure hydrogen service, welded vessels should default to the current Division 1 design margin of 3.5.

2.1.1.10 Autofrettage

The autofrettage technique is generally applied to metallic liners in composite vessels to manage fatigue stresses in the metallic liner. ASME Section VIII Division 3 rules on prestressing when applied to full metallic cylinders will reduce the local high equivalent inner wall stresses on thick-walled cylinders. Provisions for prestressed designs using autofrettage or other means will offset some of the adverse effects of a thick-wall condition. Future high-pressure hydrogen vessel standards may consider autofrettage as a recommended design practice.

2.1.1.11 Vessel Shape, Transition Region, Head, and Opening Design

A critical condition for safe operation of a lower design margin vessel for 15,000 psi will be limiting discontinuities in its design. The vessel should be fabricated without abrupt changes in shape, free of any type of stress raisers or discontinuities, and preferably without welding. The heads on each end should be integral with the cylindrical shell. The transition region from cylindrical shell to head represents an area of stress concentration and is prone to uneven formation of metal (folds) during the fabrication process. Heads may need to be thickened to compensate for the stress concentration of the opening. Openings should be allowed only on the head and only concentric with the longitudinal axis of the vessel in order to minimize localized stresses. ASME Section VIII Division 1 Appendix 22 provides some guidelines on the typical shape and profile of the vessel. 49 CFR 178, NGV2 and ISO/DIS 15869 do not provide much information on this aspect of the design. Future 15,000 psi hydrogen standards should provide details on the design of transition regions, heads, and openings and potentially verify these designs by appropriate methods such as finite element analysis.

2.1.1.12 End Connection

Threaded end connections (either tapered or straight) are the current primary method of attaching vessels to external piping or valves. For 15,000 psi hydrogen service, threaded connections would be difficult to seal because hydrogen is a relatively small-molecule gas. Seal welds can be used between the end plug and vessel neck to improve leak tightness (this is authorized by ASME Section VIII Division 1 Appendix 22); however, seal welds should not be used on the threads themselves, as the weld is prone to cracking.

Although end plugs are not integral with metallic vessels and are not part of the "coded" vessel, their design is critical to achieving a leak-tight system. Straight thread end plug designs with o-ring seals have their own set of challenges. O-ring materials will need to be evaluated for property degradation in hydrogen service and susceptibility to explosive decompression. Surface finishes, end plug torque, and dimensioning/tolerancing/perpendicularity of the O-ring groove and mating surface become critical at high pressures.

Small opening sizes will be encouraged to improve leak tightness; however, provision will still need to be made for visual inspection of the inner surface of the vessel for folds at the neck region. Boroscopes, miniature cameras, and other forms of inspection equipment will facilitate such inspection during production.

As much as possible, threads that are in contact with hydrogen should be avoided since they can act as stress raisers. Future standards on 15,000 psi hydrogen may need to include unique new details on the vessel opening and connection type.

2.1.1.13 Fatigue Analysis of Threads

For high-pressure applications, threads are sources of concern for fatigue crack growth and also from the standpoint of achieving LBB. Section KD 616 of ASME Section VIII Division 3 and IGC Document 100/03/E address the design of threaded openings in the case of high-pressure vessels. Future hydrogen standards should include this analysis.

2.1.1.14 Design Issues Specific to DOT 3AA and 3AAX Vessels

DOT vessels are infrequently used for stationary storage service in the United States because the pressure vessel laws of most states require the use of ASME vessels.

DOT design rules can be modified by "exemptions" that can be applied for and granted after special technical review and approval. This provision allows for variation in design and test parameters.

The DOT standard calls for a straight thread shear strength of 10 times the test pressure. This margin may not be feasible for a 15,000 psi service pressure.

The standard does not mandate the requirement of integral heads and allows welded heads. Flat ends are permitted and can be welded to the cylindrical shell. These designs will cause abrupt changes in shape and will act as stress raisers. Welding on any part of the pressure boundary is not acceptable in 15,000 psi hydrogen service. No detail guidance is provided in the standard on the shape of heads, size, location, and number of openings allowed on the head.

2.1.1.15 Design Issues Specific to ASME Section VIII Division 1, Appendix 22 Vessels

Appendix 22 vessels are commonly used in hydrogen service for stationary storage applications because they are ASME Code stamped and comply with the boiler and pressure vessel laws of most states. They are not authorized by DOT for use as transport tanks.

Appendix 22 limits the maximum allowable stress to 1/3 of minimum tensile stress, a design margin of 3.0. The recommended design margin is reduced to 2.25 for future high-pressure hydrogen service with careful initial material screening and periodic in-service inspections that can detect critical cracks.

The standard allows for multiple openings on the head at locations other than those concentric with the axis of the vessel. For high-pressure vessels with lower design factors, this practice will not be acceptable. Openings should be located only on the head, concentric with the axis of the vessel.

Threaded and flanged end openings are shown in typical sections of the standard; no details of these are provided. For 15,000 psi pressure vessels, more design details of the end openings will have to be provided (refer to Article KD-6 of ASME Section VIII Division 3).

ASME storage vessels shall be provided with protection against overpressure; however, relief devices need not be directly connected to the tank where the only source of overpressure is external to the tank and can be isolated. Overpressure protection shall be in compliance with ASME Section VIII Division 1, section M-5(b).

2.1.1.16 Design Issues Specific to NGV2-1 Vessels

NGV2 standards are performance based. Different manufacturers use in-house developed programs and finite element analysis to determine the strength of vessels. Performance based specifications have proven to produce cost-effective pressure vessels with an assurance of minimum safety levels. However, for fully metallic vessels, some basic thickness calculations should be provided.

NGV2-1 containers have a design margin of 2.25. This is consistent with the DOT 3AAX margin.

NGV2-1 allows welded vessels with a design margin of 3.5. For 15,000 psi hydrogen vessels, welded tanks are not recommended, even with a higher design margin.

NGV2-1 allows a fill pressure of 1.25 times the service pressure. This temporary increase above service pressure is acceptable.

The recommended maximum container temperature is 185° F (85° C) based on the draft ISO 15869 standard for hydrogen fuel cylinders. For consistency, the limit in NGV2 should be increased from its current limit of 180° F (82° C).

NGV2 vessel volume is limited to 1,000 liters (2,200 lb water capacity). For current hydrogen vehicle fuel tank sizes, this capacity is sufficient to attain acceptable vehicle range. For larger storage and transport vessels, this capacity could be a limitation.

2.1.1.17 Design Issues Specific to ISO/DIS 15869-2 Metallic Vessels

This standard is currently in draft status, being developed specifically for hydrogen vehicle fuel tanks based on the ISO CNG fuel tank specification ISO 11439 [12]. Hence, many issues related to hydrogen service conditions are addressed in this standard.

The standard (ISO 15869-2) provides two options for vessel design and material selection criteria. The standard by itself does not provide the basic design guidelines on stress calculations, but alternatively refers to the use of ISO 9809 [13] or ISO 7866 [14] as one of the options. ISO 9809 and ISO 7866 are gas cylinder standards for steel and aluminum, respectively, and contain rules for design analysis sufficient to determine the operating stresses and margins within the vessel. The second option is to follow the performance based guideline given in the standard. Hence, this standard allows an option to follow a design standard or a performance standard.

ISO 15869-2 refers to gas cylinder standards for material selection for steel and aluminum containers. However, gas cylinder standards ISO 9809 and ISO 7866 are general standards intended for much lower pressure, and the suitability of such material for high-pressure hydrogen application has not been evaluated. However, both options require the use of hydrogen-compatible material supported by hydrogen compatibility tests.

Seamless steel cylinder standard ISO 9809-1 has a design margin of 2.4, and option 2 of the reference standard has a design margin of 2.25. Hence, depending on which of the two design options is followed, ISO 15869-2 will have one of two design margins. The recommended design margin for 15,000 psi hydrogen fuel tanks is 2.25.

The standard also allows a fill pressure of 1.25 times the service pressure. This temporary increase above service pressure is acceptable.

2.1.2 Manufacturing Issues

Increasing to 15,000 psi pressure design will invariably increase the vessel wall thickness, even if design factors are reduced. Most manufacturing problems related to an increase to 15,000 psi pressure are related to the higher wall thickness encountered.

2.1.2.1 Heat Treatment

Vessels are typically constructed of materials that are quenched and tempered to obtain specific hardness and tensile strength. Increased thickness will affect the uniform and proper heat treatment critical to achieving the optimum properties. This is more critical in hydrogen service, since material susceptibility to embrittlement is basically a function of tensile strength and microstructure, which in turn is a function of the steel composition and heat treatment. Wall thicknesses of 1.3 to 1.5 inches represent a practical limit for achieving uniform through-wall properties in heat treatment based on one-side quenching. Thicker walled vessels will have difficulty passing qualifying material tests. This is a major limitation when using the existing materials in the reference standards for increasing to 15,000 psi pressure.

2.1.2.2 Forming of Heads

Integral heads are normally hot formed, shaped, and thickened to provide details of design and construction of openings. High thickness values will limit the hot forming and shaping of heads. Also, the vessel size may be limited by the available capacity to form integral heads.

2.1.2.3 Availability of Pipe Stock

Vessels are normally made from raw pipe material. The current commercial availability of large-diameter raw pipe stock is limited to a wall thickness of about 1.5 to 1.75 inches. Extending all-metal vessel pressures to 15,000 psi will require piping material manufacturers to increase wall thicknesses beyond their current practices.

2.1.2.4 Quench Cracks

The quenching process in heat treatment can cause cracks in the vessel. Chances of these cracks increase with thicker shells because of the through thickness temperature gradient caused by one-sided quenching. As per the standards, magnetic particle or liquid penetrant tests are required after the final heat treatment process.

2.1.3 Testing Issues

2.1.3.1 Hydrogen Compatibility Test

The material selected should be inherently compatible with hydrogen and not be susceptible to failure by hydrogen embrittlement. Hence, hydrogen compatibility of metallic materials in contact with hydrogen should be established experimentally (reference ISO 11114-4 [15]). Materials that are previously tested and approved for hydrogen application may be exempted from this test. Of the metallic specifications being evaluated, only the draft ISO-15869 standard mandates this test.

2.1.3.2 Surface Defect/Finish and Internal Inspection

Both internal and external surface conditions and defects are critical factors in hydrogen service. Because of the nature of hydrogen, it is essential that the internal surface of the vessels be examined during production. Of current NDE methods, angle beam ultrasonic testing has proved to be the most reliable method to detect material defects. Also, internal surfaces should have no harmful defects like fissures, pits, cracks, folds, and laps. Future high-pressure hydrogen standards should provide identification and test methods to evaluate surface finish and defects. They should identify stages of inspection, provide tests for both internal and external surfaces in the manufacturing process, provide a description and evaluation of defects, and supply the criteria for rejection. Section KE 233 of ASME Section VIII Division 3 discusses methods of examining cracks on the outside and inside surfaces of the shell and heads.

2.1.3.3 Dimension and Geometry Inspection

Each vessel must be verified for all dimensions; the most important of these is the thickness in different locations. Critical areas like head, neck, and opening should be inspected to ensure that the geometry complies with the approved cylinder drawing. Each vessel should be examined before and after end-forming operations for thickness.

2.1.3.4 Inclusions, Internal Defects and Fracture Performance Test

Inclusions and internal defects in the material should be identified prior to the forming process so as to eliminate undesirable stock material. Before any manufacturing process, all raw stocks should be examined for subsurface imperfections using approved NDE methods. The extent of examination should be 100%. Material with defects above the maximum allowable size should be rejected. Acceptance should be as per maximum allowable defect size and acceptance criteria developed for 15,000 psi hydrogen application.

In order for the design to ensure leak-before-break (LBB) and prevent the failure of the vessel by rupture, the maximum defect size for non-destructive examination should be determined. The maximum defect size is to be established by tests suitable to design. Introducing an internal flaw of predetermined size, detectable by NDE methods, and pressure cycling the cylinder to failure is a method to establish the maximum defect size. However, for large vessels manufactured in limited quantity, this will not be a cost-effective option, as multiple destructive tests may be needed to establish this factor; hence these tests may be possible only on smaller, serially produced vessels. For larger vessels, computerized simulation methodology may be the solution. Present reference standards do not address this fracture performance requirement.

2.1.3.5 Hydrogen Gas Cycling Test

Design fatigue life can be determined and verified empirically by pressure cycle test. This test is mandatory in NGV 2 and ISO/DIS 15869, but the fatigue cycling is performed using a benign fluid that may not represent the effect of hydrogen on the material during the test process. Many materials will demonstrate reduction in fatigue life if tested in hydrogen. Using a fluid other than hydrogen to determine the fatigue life may be invalid and non-conservative. Hence all tests incorporating fatigue cycling should be performed with hydrogen as the test medium. Any test that evaluates the effects of hydrogen on materials should also be performed at the representative maximum operating conditions (temperature, pressure, purity) of the gas.

2.1.3.6 Leak-Before-Break (LBB) Test

NGV 2 and ISO/DIS 15869 mandate an LBB test, but do not require hydrogen as the test fluid. An LBB test is intended to show that a vessel design will not fail by rupture. Vessels are pressure cycled, and they should either fail by leakage or exceed multiple times the number of filling cycles per design without failure. Hydrogen should be used as the test medium. An LBB test is anticipated as a test requirement for new high-pressure hydrogen tanks where analytical methods are not available.

2.1.3.7 Hardness Test

A hardness test should be carried out after the final heat treatment to verify the tensile properties, and the hardness values determined should be in the range specified in the design. In production tests, measurement of the correct hardness and its correlation to an established representation of tensile strength should be the methodology followed.

2.1.3.8 Impact Test

Future high-pressure hydrogen standards will have to address the relationship between Charpy impact test results and hydrogen compatibility (if any).

2.1.3.9 Hydrostatic Test

The hydrostatic test pressure recommended for 15,000 psi service is 1.3 times the design pressure (not to exceed yield). This recommendation is in line with the Section VIII Division 1 guideline and ensures that the test pressure exceeds the maximum fill pressure (1.25 times service pressure). Some of the current standards mandate higher hydrostatic test pressures:

(a) DOT 3AA/3AAX is 1.67 times service pressure.

(b) NGV2 and ISO 15869 both use 1.5 times service pressure.

2.1.3.10 End Fitting Leak Test

The joint between the vessel and its end fitting should be leak tested using hydrogen or helium.

Table 8 summarizes the design and testing issues for metallic vessel standards.

Table 8 - Comparison of Fully Metallic Standards

Standard	49 CFR 178 (3AA/3AAX Tubes)	ASME VIII-1 App 22	ASME VIII-3	NGV 2-1 (Fully Metallic Only)	ISO/DIS 15869 (Fully Metallic Only)
Design or service pressure limit	None	None	None	3,600 psi (soon to be increased to 10,000 psi)	None
Maximum temperature limit	None	200°F (93° C)	None (material temp limits exist)	180°F (82°C)	185°F (85°C)
Capacity size limit	3AA under 1,000 lb water capacity / 3AAX no limit	No limit (diameter limited to 24 in.)	No limit	1,000 liters (2,200 lb water capacity)	No limit
Normal operating pressure	110% service pressure (SP) at 70°F for "plus" rated cylinders - increased to 125% SP at 130°F during fill.	90% of MAWP (for operational reasons so that safety valves don't weep)	90% of design pressure (for operational reasons so that safety valves don't weep)	Service pressure (SP) - increased to 125% SP during fill	Service pressure (SP) - increased to 125% SP during fill
Design life stated?	No	No	No	20 years maximum	20 years maximum
Standard specifically addresses hydrogen applications	No	No	No	No (natural gas)	Yes
Design calculations provided for wall thickness	Yes	Yes	Yes	No (performance specifications only)	Yes (but also has performance option)
Design details provided for heads, openings, connections, and threads	No, but shear strength of straight threads must resist 10 x test pressure	Some (shape and profile of vessel)	No (some information on threads provided)	No	No
Allowable materials required to pass "hydrogen compatibly" test (refer to ISO 11114-4)	No	No	No	No	Yes
Design rules address collapse and thick-wall effect	No	No	Yes	Performance spec	No

Standard	49 CFR 178 (3AA/3AAX Tubes)	ASME VIII-1 App 22	ASME VIII-3	NGV 2-1 (Fully Metallic Only)	ISO/DIS 15869 (Fully Metallic Only)
Tensile strength limited to account for hydrogen embrittlement	No	No	No	No	Yes
Yield to tensile strength ratio limited	No	No	No	No	Yes
Acceptance/rejection criteria for inclusions and internal surface cracks included	No	No	No (fracture mechanics evaluation mandatory)	No	Yes
Fatigue life considered	No	No	Yes (by mandatory fatigue analysis)	Pressure cycle test required (but not with hydrogen)	Pressure cycle test required (but use of hydrogen optional)
Leak before burst (LBB) failure mode required	No	No	No (fracture mechanics evaluation mandatory)	Yes	Yes
In-service Inspections mandated	Yes (hydrostatic or AE/UT every 5 or 10 years)	No	No	Yes (every 36 months)	Yes
Design margin	2.25 when 10% overfill considered	3.0	1.732	2.25 or 3.5 for welded construction (both performance based)	2.4 (2.25 for performance option)
Autofrettage considered	No	No	Yes	No	No
Welding allowed on pressure boundary	Yes, but rarely used except for small portable cylinders.	No, except seal welding end fitting	Yes	Yes, but increases design margin	No. (no attachment welding is allowed)
Openings allowed at locations other than on the head concentric with the vessel axis	Not stated	Yes	Yes	No	Yes
Integral heads mandated	No (but integral heads most common)	Yes	No	No	Yes

Standard	**49 CFR 178 (3AA/3AAX Tubes)**	**ASME VIII-1 App 22**	**ASME VIII-3**	**NGV 2-1 (Fully Metallic Only)**	**ISO/DIS 15869 (Fully Metallic Only)**
Hardness testing mandated	No	Yes	Yes (KF-642)	No	Yes
Impact testing mandated	No	No (generally no, and yes under certain conditions; UG 20)	Yes (KM-230, KM-251, KT-2)	Yes	Yes
Geometry/thickness check mandated	No	Yes (refer UG 96)	Yes (KG-4)	Yes	Yes
Testing for external quench cracks mandated	Yes	Yes	Yes (KF-641, KE-201)	No	No?
Hydrostatic test pressure	1.67x service pressure	1.3x MAWP	1.25x design pressure	1.5x service pressure	1.5x service pressure
Opening fitting leak test mandated using hydrogen or helium	No	No	No	No	No
Pressure cycling test mandated	No	No	No	Yes (but use of hydrogen not required)	Yes (but use of hydrogen optional)
LBB test mandated	No	No	No	Yes (but use of hydrogen not required)	Yes (but use of hydrogen optional)

2.2 Composite Vessels

2.2.1 Design Issues

Design issues related to using existing composite vessel standards for 15,000 psi hydrogen vessels have been covered by a separate report, and hence will not be addressed here.

2.2.2 Manufacturing Issues

A review of the existing composite cylinder standards revealed that very few manufacturing and fabrication rules are available in these standards. All the existing reference standards provide only general guidelines on the manufacturing procedures for the fabrication of composite vessels. This is the case because the reference composite vessels standards are predominantly performance based, and hence the properties of the vessels are interdependent on material selection and processing, design and manufacturing. These factors are proprietary to each manufacturer. A performance standard allows the designer to use internally developed and proprietary design tools, manufacturing methods, and materials.

Composite vessels rated for 10,000 psi exist in gaseous hydrogen service today and are certified to various existing reference standards like NGV2, ISO/EIHP.[3] The manufacturers of these high-pressure hydrogen composite vessels do not foresee any critical issues in raising the pressure to 15,000 psi.

Even though the details of manufacturing are proprietary, the general manufacturing processes are common for all composite vessels. Larger and higher pressure vessels will require much thicker composite laminate layers wound over the liner material. In order to attain uniform and proper composite properties, curing is a critical part of the manufacturing process. For thicker composite shells, a uniform and even curing process for the multiple laminate layers may be difficult to achieve.

For 15,000-psi vessels, the leak-proof joining of the end boss to the liner may become an issue. This problem will be more prominent in nonmetallic liners where there is no integral end connection.

2.2.3 Testing Issues

Most current composite standards are performance standards with only broad limits on design. Future high-pressure composite vessels will continue to be designed to performance rather than design standards, since the design, material processing and manufacturing are proprietary to each manufacturer. A common requirement of all performance standards for composite vessels will be the qualification of a design by rigorous tests. In addition to these qualification tests are the routine production tests on every vessel.

Common and specific issues related to using the following existing standards for 15,000 psi hydrogen vessels are addressed the sections below. Composite standards evaluated include: DOT FRP-1 [16], DOT FRP-2 [17], DOT CFFC, ANSI/CSA NGV2, Code Case 2390 [18], ISO 11119 [19], and ISO 15869.

2.2.3.1 Common Testing Issues

The common assumption of all existing reference standards is that the performance tests conducted with fluid such as water, air or oil as the pressurizing media will be representative of the actual service gas. For hydrogen, whose presence has been proved to have varying effects on the material properties, this assumption may be invalid and nonconservative. No factors are incorporated into the

[3] European Integrated Hydrogen Project

design of the vessels to account for this difference in performance, nor are there any extrapolations of benign fluid test data for hydrogen environment. This characterization will assume greater significance with high-pressure hydrogen under cyclic loading conditions.

(a) Hydrogen Compatibility Test

Many materials in hydrogen service will show deterioration in their mechanical properties. The severity of hydrogen damage depends on hydrogen partial pressure, temperature, material properties and loading. Any hydrogen compatibility testing must be conducted with hydrogen at representative service conditions.

For 15,000 psi pressure hydrogen service, material compatibility has to be established through testing; present standards lack this requirement.

(b) Fatigue Tests

Fatigue life tests of each design must be verified by pressure cycle testing of prototypes and batch samples during production. In all existing standards, the fatigue cycling is performed using a fluid other than hydrogen. Hydrogen can accelerate the rate of fatigue degradation and crack growth. Many materials will show a reduction in fatigue life if tested in hydrogen. Determination of the fatigue life without accounting for this effect may be invalid and nonconservative.

(c) LBB Tests

As noted in the metallic vessel section, when LBB tests are mandated, they should be performed with hydrogen as the test fluid. Current standards allow for the use of inert gases or benign liquids, which will not account for the unique effect of hydrogen.

(d) Permeation and Leakage Test

Because of the ignition potential and small molecular size of hydrogen, permeation and leakage are recognized as major issues. Existing test standards are not intended for hydrogen at 15,000 psi, and rate limits are based on NGV fuel tanks. To obtain valid results for small-molecule gases like hydrogen, tests must be conducted with hydrogen or helium gas. Some of the current standards provide specific test procedures, but offer no guidance in test equipment sensitivity verification and calibration methodology. Since hydrogen loss by permeation can be a trace amount that is quickly dispersed, it can be challenging to obtain consistent and repeatable measurements. Different methods, including gas chromatography, pressure decay, and mass spectrometry, are employed for permeation and leak tests. Use of vacuum chambers and mass spectrometry may provide the most accurate measurements for permeation and leak tests, and this methodology should be considered for future high-pressure hydrogen standards.

For nonmetallic liners (Type 4 cylinders), permeability may be affected by pressure cycling, high service temperature, and softening of the polymer. High pressures may cause ready permeation of hydrogen into the plastic material, and then decompression failure upon release of pressure. This result requires permeation testing after extreme temperature and pressure cycling. The existing standard tests do not provide test results under these conditions.

(e) Inner Vessel Inspections

Most composite vessels in service use an aluminum or polymer material as a liner. Before the liners are wound with composite filament, the followings tests/inspections are recommended.

(1) *Aluminum*: material qualification tests, NDE tests, surface finish/defect inspection and hardness

(2) *Polymer*: material qualification tests, surface finish/defect inspection

2.2.3.2 Testing Issues Specific to Individual Standards

(a) DOT FRP-1 and FRP-2

FRP-1 and FRP-2 vessels are not currently allowed in hydrogen service.

(b) NGV2

The environment fluid exposure test and accelerated stress rupture test are performed at a temperature less than the maximum material temperature. Degradation under these conditions is expected to be accelerated under highest material temperatures, and hence these tests should be conducted at the maximum temperature.

Liner material qualification tests at service conditions are required for high-pressure hydrogen service.

(c) ASME CODE CASE 2390

This code case appears to be directed to larger vessels, and thus requires less destructive sample testing in qualification and manufacturing. This is of particular advantage with cost implications of larger vessels and the lower quantity of production associated with larger vessels.

This Division 3 code case design has a metallic cylindrical layer wrapped circumferentially with a layer of glass fiber laminate, leaving the metallic heads unwrapped. A major testing issue is that the standard does not require qualification tests for the metallic layer or heads. For high-pressure hydrogen service, material compatibility and inspections for hardness, tensile strength, surface finish/defect, defect/flaw size, fatigue life, and burst strength are recommended.

(d) ISO 11119

This standard is not specific to hydrogen service, but it refers to ISO11114-1 [20], which covers hydrogen service. ISO 11114-1 recommends quenched and tempered steel with a limit on tensile strength for hydrogen service, but it does not limit its coverage to a specific upper limit on hydrogen partial pressure. As concluded in topics discussed earlier for metallic vessels, for 15,000 psi hydrogen service, new sets of metallic liner material compatibility tests are required to supplement data from the 1960s and 1970s. Also, for the nonmetallic liner and composite, the standard does not specify compatibility requirements. This should be required for high-pressure hydrogen service.

ISO 11119 calls for a minimum of 30 cylinders to be made available for prototype testing. For larger vessels, manufactured in smaller quantities, this minimum quantity for prototype testing may become a serious issue affecting the cost of developing a new design.

(e) ISO/DIS 15869

Currently in a draft international standard status, ISO/DIS 15869 is being developed for vehicle fuel tanks for compressed hydrogen gas and hydrogen blends. This standard is largely derivative of the compressed natural gas fuel tank standard ISO 11439. It is divided into five parts:

(1) Part 1: General requirements

(2) Part 2: Metal tanks (Type 1)

(3) Part 3: Hoop-wrapped composite tanks with metal liner (Type 2)

(4) Part 4: Fully wrapped composite tanks with metal liner (Type 3)

(5) Part 5: Fully wrapped composite tanks with nonmetallic liner (Type 4)

ISO/DIS 15869 is the only standard that specifies the requirement of hydrogen compatibility tests for metallic materials in contact with hydrogen. The standard refers to ISO/FDIS 11114-4 (soon to be published) for hydrogen compatibility test requirements. However, the standard does not require the hydrogen compatibility test requirement for nonmetallic materials. For high-pressure hydrogen service, even nonmetallic materials should be tested for material compatibility for hydrogen service.

For metallic vessels and composite vessels with metallic liners, the standard mandates the requirement to establish the maximum defect size for nondestructive examination in production tests. However, the standard does not specify the testing methods to establish this criterion.

The standard mandates leak test only for type 4 (nonmetallic liner) vessels. For 15,000 psi hydrogen service, leakage from end fittings and their joint to the vessel assumes significance because of the nature of hydrogen gas and the high pressure. High-pressure hydrogen vessels should validate these factors by tests.

Table 9 provides a side-by-side summary of composite cylinder standards.

Table 9 - Comparison of Composite Standards

	FRP-1	FRP-2	CFFC	NGV2	ASME CC 2390	ISO 11119	ISO 15869
Construction	Aluminum Liner/Glass, Full Wrap	Aluminum Liner/ Glass, Hoop Wrap	Aluminum Liner/ Carbon and Glass, Full Wrap	Metal or Polymer Liner, Carbon/Glass/ Aramid, Hoop or Full Wrap	Metal Liner, Glass Hoop Wrap on Cylinder Only	Metal or Plastic Liner, Glass/Carbon /Aramid, Hoop or Full Wrap	Metal or Polymer Liner, Carbon/Glass/ Aramid, Hoop or Full Wrap
Standard specifically addresses hydrogen applications	No	No	No	No	No	No	Yes
Capacity (lb water or liters)	>200 lb	>200 lb	>200 lb	1,000 liters	No limit	450 liters	No limit
Pressure (psi)	5,000 maximum	5,000 maximum	5,000 maximum	3,600 maximum	3,625 maximum	6,283 maximum	No limit
Design margin	3	2.5	3.4	2.25 to 3.5	2.0	3.0	2.35 to 3.65
Filament stress at service pressure (SP)	30% burst	40% burst	30% burst		36% UTS	29 to 41%	
Liner service pressure		50% SP	60% yield				
Service life (years)	15 (per exemption)	15 (per exemption)	15 (extendable to 30 years with approval/ exemption)	20	20	15 (without requalification, unlimited with requalification after 15 years)	20
Material Qualification Tests							
Allowable materials required to pass "hydrogen compatibly" test (refer to ISO 11114-4)	No, but aluminum liner is resistant to embrittlement	No, but aluminum liner is resistant to embrittlement	No, but aluminum liner is resistant to embrittlement	No	No	Yes, by reference to ISO 11114-1	Yes (metals only)

	FRP-1	FRP-2	CFFC	NGV2	ASME CC 2390	ISO 11119	ISO 15869
Abrasion test	No	No	No	No	No	No	No
Composite and fiber test for susceptibility to SCC	No	No	No	No	No	No	No
Chemical and corrosive environment test	No	No	No	Yes (but not at maximum temperature)	No	No	Yes
Humidity exposure test	Yes	Yes	Yes	No	No	Yes	No
Long-term exposure to heat	No	No	No	No	No	Yes	Yes
Long-term exposure to UV	No	No	No	No	No	No	No
Long-term exposure moisture	No	No	No	No	No	No	No
Long-term exposure to corrosive atmosphere	No	No	No	Yes	No	No	No
Design Qualification Tests							
Accelerated stress test (for stress rupture)	No	No	No	Yes	No	Yes	Yes
Ambient temperature pressure cycle test (for fatigue cycle)	Yes, 10,000 cycles (not using hydrogen)	Yes, 10,000 cycles (not using hydrogen)	Yes, 10,000 cycles (not using hydrogen)	Yes	Yes	Yes	Yes
Boss torque test	No	No	No	No	No	Yes	Yes, type 4
Flaw tolerance test	No	No	No	Yes	No	Yes	Yes
Drop test (for rupture)	No	No	Yes	Yes	No	Yes	Yes
Extreme temperature pressure cycle test	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Hydraulic/ volumetric expansion test	Yes	Yes	Yes	No	Yes	Yes	No

	FRP-1	FRP-2	CFFC	NGV2	ASME CC 2390	ISO 11119	ISO 15869
Hydrogen gas cycle test	No	No	No	No	No	No	Yes (Type 4)
Hydrostatic burst test	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Leak before break test	No	No	No	Yes (type 2 & 3)	No	No	Yes, but does not mandate use of hydrogen
Leak test	No	No	No	No	No	Yes (Type 4)	No
Penetration tests	Yes	Yes	Yes	Yes	No	Yes	Yes
Permeation test	No	No	No	Yes (Type 4)	No	Yes (type 4)	Yes (type 4)
Resin shear strength test	Yes	Yes	Yes	Yes	Yes	No	Yes
Softening temperature of plastic test	No	No	No	Yes (Type 4 liner)	No	No	Yes (Type 4 liner)
Tensile properties of plastic test	No	No	No	Yes (Type 4 liner)	No	No	No
Thermal cycling test	Yes	Yes	Yes	No	No	No	No
Environment cycle test	Yes	Yes	Yes	Yes	No	Yes	No
Laminate cathodic disbondment test (for epoxy bonding)	No	No	No	No	Yes	No	No
Batch Tests							
Hydrostatic burst test	Yes	Yes >200	Yes >200	Yes	No	Yes	Yes
Tensile test	Yes (liner)	Yes (liner)	No	Yes (metal liner)	No	Yes (metal liner)	Yes
Impact test	No	No	No	Yes (steel liner)	No	No	Yes (steel liner)
Coating test	No	No	No	Yes	No	No	Yes
Pressure cycle test	Yes >200	Yes >200	Yes >200	Yes	No	Yes	Yes

	FRP-1	FRP-2	CFFC	NGV2	ASME CC 2390	ISO 11119	ISO 15869
Production Tests							
NDE (UT, magnetic particle) Acceptance/rejection criteria for inclusions and internal surface cracks included	No	No	No	Yes (Type 2, 3)	No	No	Yes (metal liner)
Visual and dimensional	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Surface finish				Yes	Yes	Yes	Yes
Strength (hardness)				Yes (Type 2, 3)	Yes		Yes (metal liner)
Hydrostatic	1.67 SP	1.67 SP	1.67 SP	1.5 SP	1.25 DP	1.5 DP	1.5 SP
Hydraulic/volumetric expansion	Yes	Yes	Yes		Yes	Yes	Yes
Leak test of boss joint	No	No	No	Yes, but only for nonmetallic liners	No	Yes, but only for nonmetallic liners	Yes, but only for nonmetallic liners
Acoustic emission examination	No	No	No	No	Yes	No	No
Third party inspection	Yes	Yes	Yes	Yes	No	Yes	No

3 SUCCESSFUL SERVICE DATA OF EXISTING VESSELS

3.1 Storage Vessels

The most common form of large ground hydrogen storage is fully metallic, ASME-coded vessels. These vessels are designed, manufactured, and tested to meet ASME VIII, Division 1, and, since 1962, have met the reduced (3:1) design margins of Code Case 1205 [21] and Appendix 22.

Appendix A provides successful service data for a sample of metallic storage vessels in hydrogen service. Table 13 summarizes data for three types of seamless forged ASME vessels operated by Air Products. Figure 6, Figure 7, and Figure 8 show the average age of the sample storage vessels in service.

3.2 Transport Tanks

For hydrogen transportation, the most common vessels used are all-metallic DOT 3AAX vessels.

Appendix A provides successful service data for a sample of metallic transport vessels in hydrogen service. Table 13 summarizes data for 3AAX vessels operated by Air Products. Figure 9 shows the average age of the sample transport vessels in service.

3.3 Portable Cylinders

Although thousands of metallic cylinders (DOT 3AA) are used in hydrogen service, a growing number are composite tanks conforming to one of the many standards (DOT, ISO, NGV2, ASME Code Case 2390).

Appendix B, Table 14 provides successful service data for composite portable storage vessels manufactured and operated by a variety of companies.

3.4 Vehicle Fuel Tanks

Hydrogen vehicle fuel tanks are composite tanks designed, manufactured and tested to various performance standards such as NGV2 and ISO 11439.

Appendix B, Table 14 provides successful service data for composite fuel tanks manufactured and operated by a variety of companies.

4 EFFECT OF HIGH-PRESSURE HYDROGEN ON EXISTING COMMONLY USED MATERIALS

4.1 Existing Commonly Used Vessel Materials

Metallic materials have been used with great success to transport and store hydrogen gas at pressures below 3,000 psig for over 60 years. A list of commonly used metallic materials for seamless vessels is located in Appendix A.

4.2 High-Pressure Hydrogen Exposure Degradation

4.2.1 Types of Hydrogen Embrittlement

Hydrogen gas embrittlement is a generic term that includes all of the different effects that engineering alloys might experience in hydrogen-gas or hydrogen-forming environments. There are three main categories of hydrogen embrittlement:

(a) Hydrogen reaction embrittlement

(b) Internal reversible hydrogen embrittlement

(c) Hydrogen environment embrittlement

4.2.1.1 Hydrogen Reaction Embrittlement

Hydrogen reaction embrittlement deals with the absorption of atomic or molecular hydrogen into the material, which then reacts to form a new phase. Such reactions may form CH_4 within low-alloy steels or hydrides in zirconium, titanium, and tantalum.

Hydrogen attack and decarburization are two other types of hydrogen reaction embrittlement. Hydrogen attack occurs in carbon steel or low-alloy steels at elevated temperatures higher than the scope of this document. Carbon within the alloy reacts with atomic hydrogen to form methane, which results in crack formation. The "Nelson chart," which can be found in API 941 [22], shows the operating limits for carbon and low-alloy steels. Decarburization is very similar to hydrogen attack, except that the reaction occurs at the surface of the material. It can occur in high-temperature hydrogen environments, as well as oxidizing environments.

4.2.1.2 Internal Reversible Hydrogen Embrittlement

Internal reversible hydrogen embrittlement is also referred to as slow strain rate embrittlement. This type of embrittlement occurs when atomic hydrogen is trapped within voids around nonmetallic inclusions. High gas pressure, from the combination of hydrogen atoms trapped around the inclusion, can generate highly localized stresses that may initiate a crack parallel to the rolling direction. As the cracks link up, stepwise cracks will form. To be reversible, the embrittlement must occur without the hydrogen reacting within the lattice. This type of embrittlement can occur with the electroplating of high-strength steel with cadmium, with processing treatments such as melting and pickling, during welding of high-carbon steels with wet electrodes or in a moist environment, and with corrosion-produced hydrogen. Hydrogen embrittlement due to corrosion-produced hydrogen is also referred to as hydrogen-induced cracking (HIC) or hydrogen stress cracking (HSC).

4.2.1.3 Hydrogen-Environment Embrittlement

Hydrogen-environment embrittlement deals primarily with embrittlement of a material exposed to room temperature hydrogen. Surface adsorption has been shown to be the overall rate-controlling step during hydrogen-environment embrittlement. The embrittlement in a hydrogen environment is immediate once a stress level greater than the yield strength is reached. In other words, the tensile strength/ductility is reduced. This type of embrittlement is often called hydrogen-assisted cracking.

Degradation in fatigue limits has been observed in susceptible materials during testing in dry hydrogen gas environments. Carbon steels, low-alloy steels, and stainless steels show such degradation, even at low pressures in hydrogen. The fatigue crack growth is more pronounced at ambient temperatures than when the materials are exposed to elevated temperatures. The degradation in fatigue properties in dry hydrogen gas service is due to the reduction in ductility of the material at the crack tip.

4.2.2 Metallurgical and Process Factors Affecting Hydrogen Embrittlement

4.2.2.1 Metallurgical Factors

Material variables that affect susceptibility to hydrogen embrittlement include composition, microstructure, and strength level. Large amounts of carbon and manganese have been found to increase the susceptibility of steels to hydrogen embrittlement [23]. Several alloying elements have either a neutral or beneficial affect on hydrogen embrittlement. Silicon and titanium offer some benefit, but they are not used in large quantities due to their effect on weldability. Nickel is believed to increase the austenitic stainless steels' resistance to hydrogen embrittlement, since nickel increases the stability of austenitic stainless steels [24].

Grain orientation of the material can also influence its susceptibility to hydrogen embrittlement. A random grain orientation improves resistance. The presence of brittle second phases such as martensite and delta ferrite can increase a material's susceptibility to hydrogen embrittlement. Forming or thermo-mechanical processing can result in a microstructure change that can also increase susceptibility to hydrogen embrittlement. For example, grinding of 304 stainless steel will result in the formation of a martensite phase on the surface, in which a crack may form when the surface is stressed in a dry hydrogen environment.

The strength level of a material is very important for resisting hydrogen embrittlement. Iron-based alloys with a ferritic or martensite structure have been restricted to a hardness of less than 22 HRC when exposed to atomic hydrogen. Steels having a similar strength often have different resistances to hydrogen embrittlement, since the heat-treatment process might have been different, resulting in different microstructures.

4.2.2.2 Process Factors

Hydrogen embrittlement resistance tends to decrease with increasing hydrogen pressure (for materials susceptible to hydrogen embrittlement). The rate of increasing severity with pressure is dependent on the alloy. For medium-strength steels, hydrogen effects are rarely encountered below 1,000 psi [25]. Above 1,000 psi and with other alloys, each case must be addressed separately.

A material's ability to resist hydrogen embrittlement decreases as the purity of the hydrogen gas increases. Several impurities will help inhibit hydrogen embrittlement; CO, CS_2, N_2O, and SO_2 are examples of inhibitors, but they are pollutants. Oxygen is another inhibitor, but it is undesirable due to safety implications. The effectiveness of these inhibitors decreases as the pressure of the system increases [26].

4.3 Hydrogen Embrittlement Literature Review

It has been shown that high-pressure hydrogen can seriously degrade the mechanical properties of many commonly used engineering alloys. During the late 1960s and early 1970s, extensive research was conducted to determine suitable materials for high-pressure hydrogen service.

Walter and Chandler [27] exposed various alloys to hydrogen gas to determine the alloys' susceptibility to hydrogen embrittlement. They exposed notched and unnotched cylindrical tensile specimens to 10,000 psi helium and 10,000 psi hydrogen. Triplicate tests were conducted in the hydrogen gas, while duplicate tests were conducted in helium gas. By comparing the ultimate strength and elongation obtained in the helium with the values obtained in hydrogen, they ranked the alloys as having extreme, severe, slight, or negligible embrittlement. A definition of each category and the materials in the categories are listed below:

(a) Extreme embrittlement (large reduction in notched and unnotched strength and ductility): high-strength steels and high-strength nickel base alloys

(b) Severe embrittlement (considerable reduction in notched strength and unnotched ductility): lower strength steels, Armco iron, pure nickel, and the titanium-base alloys

(c) Slight embrittlement (small reduction in notched strength): non-stable 300 series stainless steel, beryllium-copper, pure titanium

(d) Negligible embrittlement: aluminum alloys, stable austenitic stainless steels, copper

Table 10 provides complete results of the tests conducted in helium and hydrogen.

Fidelle et al. [9] performed experiments with disks shaped like rupture disks to determine a material's susceptibility to hydrogen embrittlement. They exposed disks to helium and hydrogen at a rate of 942 psi/min. The results of the helium tests were divided by the results of the hydrogen tests to determine susceptibility to hydrogen embrittlement. They grouped the materials into several categories similar to the categories described by Walter and Chandler. The categories and the materials follow:

(a) High or very high sensitivity ($pHe/pH_2 > 2$):

- Haynes 25
- 60Cr-40Fe
- Medium- and high-strength steels
- Badly processed, high-temperature, tempered steels
- Rolled or machined 304 stainless steel
- Electroformed nickel
- Annealed Ti-13V-11Cr-3Al alloy
- Ti-6Al-6V-2Sn ($\alpha + \beta$) alloy treated 1 hour at 750°C

(b) Moderate sensitivity (pHe/pH_2 from 1.25 to 1.83):

- Pure rolled cobalt
- 0.18C ferro-pearlitic steel
- Rolled nickel
- Ti-6Al-4V ($\alpha + \beta$) alloy treated 1 or 2 hours at 800°C.

(c) Little or no sensitivity (low pHe/pH_2):

- 7075-T6 Al
- Haynes 188
- Beryllium copper

- Austenitic stainless steels 304[4], 316, 310
- A286 age-hardened austenitic steels
- 430 ferritic steel
- Ti-5Al-2.5Sn, Ti-6AL-6V-2Sn ($\alpha + \beta$) treated 2 hours at 860°C, quench and tempered 4 hours at 595°C.

Loginow and Phelps [28] ran tests using wide-opening-loading (WOL) specimens to obtain a critical stress intensity level at which crack propagation spontaneously arrests (K_H). They conducted tests from 3,000 to 14,000 psi. For each combination of steel and hydrogen pressure, at least two and often five samples were exposed. The load on the sample was provided by a bolt, and the load exerted was recorded at least once a day. At the end of the exposure period, the test specimens were removed, broken open, and the initial and final crack lengths on the fracture surface were measured. K values (initial K_o and final K_t) were calculated according to the following relationship:

$$K = \frac{EBVC_3}{C_6\sqrt{BB_N a}}$$

where E = modulus of elasticity, B = total specimen thickness, B_N = net specimen thickness (in the notch), V = crack opening displacement, a = crack length, and C_3 and C_6 are functions of relative crack length.

The critical stress intensity in hydrogen (K_H) for a given steel was defined as the lowest K_t value obtained at the test pressure. Values of K_H for several material and hydrogen pressure combinations are shown in Table 11.

Through fracture mechanics, the critical stress intensity was used to calculate a critical size for a given shape of flaw under specific loading conditions. The crack shape and loading used was a semi-elliptical crack in bending. Table 11 shows the calculated critical flaws based on a maximum fiber stress equal to 40% of the measured tensile strength. For the various materials tested, the critical flaw depths ranged from 0.02 to 0.5 inches.

Loginow and Phelps concluded that the susceptibility of steels tested increased with yield strength. For steels with intermediate yield strengths (85 to 113 ksi), K_H tended to decrease as pressure was increased.

ISO 11114-1 states that for 34 CrMo 4 quenched and tempered steel, the maximum ultimate tensile strength should be 138 ksi (950 MPa) when exposed to gases that can cause hydrogen embrittlement. The equivalent ASTM material for 34 CrMo 4 is ASTM A372 Grade F Class 70.

Alloys can also suffer accelerated fatigue crack growth rates in H_2 gas compared to air or inert gas. In order to determine if a material is acceptable for use in cyclic service, fracture mechanics must be used. Hydrogen accelerates the rate of fatigue crack growth, which varies with the magnitude of applied fracture stress intensity factor range, dK. At low values of dK, the affect is usually small or negligible. Higher values of dK can accelerate growth by 50 to 150 times the rate in an inert environment. Detailed crack growth data of fracture stress intensity factors for subject steels is not available.

In 1966, U.S. Steel Applied Research laboratory examined a hydrogen cylinder that was exposed to hydrogen gas at 10,000 psi [29]. The cylinder was used in hydrogen gas for 16 years. The vessel had

[4] Rolled and machined 304 stainless steel had a ratio of pHe/pH2 = 4.62 due to the formation of martensitic stainless steel. Sensitization of stainless steel caused intergranular hydrogen cracking.

an outside diameter of 8.6 inches, a 1.2 inch wall thickness, and was 20 ft long. The material of construction was A-372 Class IV (or Grade D). A 1-foot section was removed from the vessel for analysis. The measured yield and tensile strengths before exposure were 83 and 117 ksi, respectively. The yield strength and tensile strengths after exposure to 10,000 psi hydrogen for 16 years were 82 and 112 ksi, respectively. The removed section was visually examined with a low-power (20x) microscope, and a magnetic particle inspection was also completed. No cracks or indications were found. The conclusion from the examination was that the performance of the vessel over a 16-year period in hydrogen at 10,000 psi had been completely satisfactory.

A literature search did not discover information pertaining to the compatibility testing of plastics at high hydrogen gas pressures. The Plastics Design Library Handbook Series - Chemical Resistance [30] indicates that resistance is very high for the common plastics [e.g., high-density polyethylene, nylon, polyvinyl chloride (PVC)], but the data do not indicate at which pressures the compatibility tests were performed.

Table 10 - Results of Tests in 10,000 psi Helium and in 10,000 psi Hydrogen

(From Walter and Chandler [27])

Material	Notched or Unnotched	Strength in 10,000 psi He: Yield, KSI	Strength in 10,000 psi He: Ultimate KSI	Ultimate Strength in 10,000 psi H_2: KSI	Ultimate Strength in 10,000 psi H_2: % Change from Helium	Ductility, % Elongation: 10,000 psi He	Ductility, % Elongation: 10,000 psi H_2	Ductility, % Reduction of Area: 10,000 psi He	Ductility, % Reduction of Area: 10,000 psi H_2	Properties in 10,000 psi He Containing 44 ppm H_2: Ultimate Strength KSI	Properties in 10,000 psi He Containing 44 ppm H_2: Percent Elongation	Properties in 10,000 psi He Containing 44 ppm H_2: Percent Reduction of Area	Vacuum Purged
Armco Iron	UN	54	56	57	+1.7	18	15	83	50				Yes
	N		121	105	-14			6.4	1.7				No
1042 Normalized	UN	58	90	89		29	22	59	27				No
	N		153	115	-25			8.5	2.8				No
4140	UN	179	186	178	-4	14	2.6	48	8.8				Yes
	N		313	125	-60			2.8	0.9				Yes
HY 100	UN	97	113	115		20	18	76	63				Yes
	N		224*	164	-27			7.3	3.8				Yes
ASTM 372-Class IV	UN	82	118	116	-1.7	20	9.6	53	18				Yes
	N		200	148	-26			2.0	2.8				Yes
Fe-9Ni-4Co-0.20C	UN	187	199	175	-12	15	0.5	67	15				Yes
	N		367	89	-76			6.3	0.2				Yes
18i (250) MAR	UN	248	250	171	-32	8.2	0.2	55	2.5				Yes
	N		423	50	-88			2.5	0.0				Yes
304 ELC Stainless	UN	24*	77	76		86	79	78	71				No
	N		102	89	-13			21	11				No
305 Stainless Steel	UN	51	90*	87	-3	63	65	78	75				Yes
	N		165*	147	-11			19	17	165		19	Yes
316 Stainless Steel	UN	64	94	99		59	56	72	75				No
	N		161	161				18	19				No

Material	Notched or Unnotched	Strength in 10,000 psi He: Yield, KSI	Strength in 10,000 psi He: Ultimate KSI	Ultimate Strength in 10,000 psi H_2: KSI	Ultimate Strength in 10,000 psi H_2: % Change from Helium	Ductility: % Elongation: 10,000 psi He	Ductility: % Elongation: 10,000 psi H_2	Ductility: % Reduction of Area: 10,000 psi He	Ductility: % Reduction of Area: 10,000 psi H_2	Properties in 10,000 psi He Containing 44 ppm H_2: Ultimate Strength KSI	Properties in 10,000 psi He Containing 44 ppm H_2: Percent Elongation	Properties in 10,000 psi He Containing 44 ppm H_2: Percent Reduction of Area	Vacuum Purged
430F Stainless Steel	UN	72	80	78	-2.5	22	14	64	37				No
	N		152	104	-32			1.9	0.6				No
410 Stainless Steel	UN	192	211*	166	-21	15**	1.3	60**	12				Yes
	N		386*	82	-78			2.2**	0.6	335		2.2	Yes
440 C Stainless Steel	UN	236	293	119	-60			3.2	0.0				Yes
	N		149	74	-50			0.2	0.0				No
17-7 PH	UN	150	164*	151	-8	17**	1.7	45**	2.5				Yes
	N		302*	70	-77			0.6**	0.4	277		0	Yes
A-286	UN	123	158	162		26	29	44	43				No
	N		233	227	-3			5.6	6.2				No
1100-0 Al	UN		16	16***		42	39	93	93				Yes
	N		18	25***				20	21				Yes
6061 T-6 Al Alloy	UN	33	39	40		19	19	61	66				No
	N		72	78				9.5	11				Yes
7075 T-73	UN	54	66	65		15	12	37	35				No
	N		116	114	-2			3.8	2.3				No
Titanium	UN	53	63			32	31	61	61				Yes
	N		126	120	-5			10	7.3				Yes
Ti-5Al-2.5 Sn	UN	106	113	114		20	18	45	39				Yes
	N		201	162	-19			3.1	1.8				Yes
OFHC Copper	UN	39	42	41		20	20	94	94				Yes
	N		87	86				20	24				Yes

Material	Notched or Unnotched	Strength in 10,000 psi He		Ultimate Strength in 10,000 psi H_2		Ductility				Properties in 10,000 psi He Containing 44 ppm H_2			Vacuum Purged
						% Elongation		% Reduction of Area					
		Yield, KSI	Ultimate KSI	KSI	% Change from Helium	10,000 psi He	10,000 psi H_2	10,000 psi He	10,000 psi H_2	Ultimate Strength KSI	Percent Elongation	Percent Reduction of Area	
Be-Cu Alloy 25	UN	79	94	93		22	22	72	71				Yes
	N		195	181	-7			12	13	186		13	Yes
Nickel 270	UN		48*	50		56**	52	89**	67	47	49	88	Yes
	N		77	54	-30			23	6.9	74		22	Yes
Inconel 718	UN	182	207	193	-7	17	1.5	26	0.8				Yes
	N		274	126	-54			1.7	0.2				Yes
Rene 41	UN	163	196*	165	-16	21**	4.3	29**	11				Yes
	N		280*	77	-73			3.4**	0.2	270		2.0	Yes

* Strength in air minus 10,000 psi to compensate for effect of 10,000 pressure.
** Ductility in Air
*** 5,000 psi H_2 or He

Table 11 - Values of K_H and Critical Flaw Depth

Under Pure Bending Conditions for Steels Exposed to Hydrogen at Various Pressures
(from Loginow and Phelps [28])

		K_H, ksi-in$^{1/2}$ (Critical Flaw Depth, in.)				
Steel	**Yield Strength, KSI (Tensile Strength, KSI)**	**3,000 psi (21 MN/m^2)**	**6,000 psi (41 MN/m^2)**	**9,000 psi (62 MN/m^2)**	**10,000 psi (69 MN/m^2)**	**14,000 psi (97 MN/m^2)**
Resistant Steels						
Type 304 SS	34 (82)				NCP-62 (> 0.48)	
A516 Gr 70	42 (83)				NCP-75 (> 0.50)	
A106 Gr. C	50 (81)					NCP-50 (> 0.39)
HY-80	85 (100)				NCP-106 (> 0.50)	NCP-81 (> 0.50)
Steels with Moderate Susceptibility						
A372, N&T	85 (118)	76 (0.41)	63 (0.33)	67 (0.36)	59 (0.31)	63 (0.33)
A372 Cl IV, Q&T-1100	87 (117)	64 (0.34)	50 (0.25)	64 (0.34)		40 (0.18)
4130, Q&T-1175	92 (119)	80 (0.43)	62 (0.32)	41 (0.17)	29 (0.09)	47 (0.22)
4145, Q&T-1100	97 (130)	66 (0.31)	61 (0.28)	50 (0.21)	55 (0.24)	28 (0.06)
A372 Cl IV, Q&T-900	101 (128)				50 (0.21)	
4147, Q&T-1235	105 (131)	88 (0.43)	85 (0.41)	60 (0.27)		42 (0.15)
A517, Gr. F	110 (121)	78 (0.41)	61 (0.31)	70 (0.37)	64 (0.33)	74 (0.39)
4147, Q&T-1200	113 (139)	112 (0.50)	37 (0.12)	41 (0.12)		27 (0.05)

		K_H, ksi-in$^{1/2}$ (Critical Flaw Depth, in.)				
Steel	**Yield Strength, KSI (Tensile Strength, KSI)**	**3,000 psi (21 MN/m^2)**	**6,000 psi (41 MN/m^2)**	**9,000 psi (62 MN/m^2)**	**10,000 psi (69 MN/m^2)**	**14,000 psi (97 MN/m^2)**
Steels with Appreciable Susceptibility						
4147, Q&T-1170	126 (146)	35 (0.08)	27 (0.05)	22 (0.03)		21 (0.03)
HY-130	136 (143)	33 (0.08)	29 (0.06)		22 (0.03)	
4145, Q&T-1050	153 (164)	20 (0.02)	17 (0.02)			

Legend:

NCP = No Crack Propagation

N&T = Normalized and Tempered

Q&T = Quenched and Tempered

The calculations of the critical flaw depth are based on a maximum fiber stress in a 1- in.- thick member equal to 40% of the measured tensile strength.

4.4 Recommended Metallic Materials For High-Pressure Hydrogen Service

4.4.1 Basis of Recommendations for Aluminum, Copper, Titanium, Nickel, and Stainless Steel Alloys

Table 12 shows the suitability of various alloys for use in H_2 gas. The maximum pressure for the alloys, except for the carbon and alloy steels, was derived from testing data [27][31] collected under a NASA contract in the 1960s and 1970s. Some results are shown in Table 10. The data compared the tensile strength (TS) in hydrogen to the TS in helium gas at various pressures. In Table 12, if the TS in hydrogen was greater than 10% less than the TS in helium, then the material was considered susceptible to hydrogen embrittlement and deemed not acceptable for hydrogen service at that pressure. A blank cell indicates that no information exists for that material and pressure combination. There is limited hydrogen embrittlement data for pressures greater than 10,000 psi.

4.4.1.1 Aluminum and Copper Alloys

Aluminum and copper alloys have been known to resist hydrogen embrittlement at high hydrogen pressures. Tests performed by Walter and Chandler [27] indicated that aluminum and copper do not experience hydrogen embrittlement.

4.4.1.2 Titanium Alloys

Only pure titanium is considered acceptable for hydrogen service. During welding of the titanium, care should be taken so that titanium hydrides do not form, since the hydrides are very susceptible to hydrogen embrittlement. The alloys of titanium have been found to be susceptible to hydrogen embrittlement at high pressures and should not be used in a stressed situation.

4.4.1.3 Nickel Alloys

Nickel alloys such as Inconel 625 or Hastelloy C-276 are not acceptable for hydrogen service.

4.4.1.4 Stainless Steel Alloys

The stable austenitic stainless steels (e.g.. 316, A-286) are immune to hydrogen embrittlement when exposed to high-pressure hydrogen [25]. The metastable austenitic stainless steels (e.g., 304 and 310) become embrittled when the alloy is cold worked, thus forming a martensite layer that is prone to hydrogen embrittlement. The martensistic and ferritic stainless steels (e.g., 410, 420, 430) are prone to hydrogen embrittlement at high hydrogen pressures and should not be used at high pressures.

4.4.2 Basis of Recommendations for Carbon and Alloy Steels

The maximum hydrogen pressure for carbon and alloy steels was derived from data in the 1975 paper "Steels for Seamless Hydrogen Pressure Vessels" by A. W. Loginow and E. H. Phelps [28]. This paper is the most complete source of hydrogen embrittlement data for steels available in the literature. The results are provided in Table 11. Note that in general, K_H decreases as the TS increases and, at the same TS, K_H decreases as hydrogen pressure increases. That is, steels become more susceptible to hydrogen embrittlement with increasing TS and H_2 gas pressure. Also, hardness is proportional to TS, so increases in hardness would also increase susceptibility to hydrogen embrittlement. By grouping the data with similar tensile strengths, a relationship between tensile strength and pressure can be developed for different K_H.

The carbon and alloy steel cells in Table 12 that are designated as "yes" indicate that the materials are recommended for use in hydrogen gas at the pressure indicated without additional requirements. These materials are recommended because the K_H values for these tensile strength and pressure combinations are greater than 60 ksi-in$^{1/2}$. A K_H greater than 60 would correspond with a very large critical flaw that would probably be easily detected using the initial pressure test. A 9,000 psi shelf was also chosen for the carbon steel materials, since there is limited experience above this pressure, and approximately 50% of the K_H data was below 60 ksi-in$^{1/2}$.

The materials listed as "maybe" are recommended only if the vessel is inspected with suitable technology to detect the corresponding critical flaw for that material and pressure combination. Materials with a K_H between 30 and 60 ksi-in$^{1/2}$ "may" be used in hydrogen service if the vessel is inspected. The "no" designation was derived by assuming that a K_H less than 30 ksi-in$^{1/2}$ was not suitable for a hydrogen gas environment, since the corresponding critical crack might not be detected by current inspection technology.

Table 12 - Material Recommendations for High-Pressure Hydrogen Gas

Material	< 3,000 psi	< 5,000 psi	< 8,000 psi	< 10,000 psi	< 15,000 psi
Stainless Steel					
316 Stainless steel	Yes	Yes	Yes	Yes	Yes
310 Stainless steel	Yes	Yes	Yes	Yes	
321 Stainless steel	Yes	No	No	No	No
305 Stainless steel	Yes			No	No
304 Stainless steel	Yes	Yes	Yes(1)	No	No
347 Stainless steel	Yes	Yes			
410 Stainless steel	Yes			No	
430 Stainless steel				No	No
440 Stainless steel				No	No
17-4 PH			No	No	No
17-7 PH			No	No	No
A-286	Yes	Yes	Yes	Yes	
Nitronic 60	Yes	Yes			
Aluminum					
6061	Yes	Yes	Yes	Yes	Yes
7075-T6	Yes	Yes	Yes	Yes	Yes
1100-0 Al	Yes	Yes	Yes	Yes	Yes
Copper					
OFHC copper	Yes	Yes	Yes	Yes	Yes
Beryllium copper	Yes	Yes	Yes	Yes	
Titanium					
Pure titanium (Gr 1,2)	Yes	Yes	Yes	Yes	
Ti-6Al-4V		No	No	No	No
Ti-3Al-2.5V (Gr. 9)			No	No	No
Ti-5Al-2.5Sn	Yes	No	No	No	No

Material	< 3,000 psi	< 5,000 psi	< 8,000 psi	< 10,000 psi	< 15,000 psi
Nickel Alloys					
Nickel 270		No	No	No	No
Inconel 625		No	No	No	No
Inconel 718		No	No	No	No
Hastelloy C-276	No	No	No	No	No
Hastelloy X		No	No	No	No
Carbon and Alloy Steels					
< 127 ksi tensile	Yes	Yes	Yes	Maybe	Maybe
127-132 ksi tensile	Yes	Yes	Maybe	Maybe	Maybe
132-138 ksi tensile	Yes	Maybe	Maybe	Maybe	Maybe
138-143 ksi tensile	Maybe	Maybe	No	No	No
>143 ksi tensile	No	No	No	No	No

Notes:

(1) Non-work-hardened.

Key:

Yes = material expected to show little or no hydrogen embrittlement at the specified pressure.

No = material will likely suffer embrittlement at the specified pressure and should not be used.

Maybe = material might be acceptable with baseline testing

Blank = no data.

OFHC = Oxygen-Free High Conductivity

5 SUMMARY AND RECOMMENDATIONS

The standards reviewed for this report for storage and transport vessels, portable cylinders, and fuel tanks are not intended 15,000 psi hydrogen service. Future versions will need to account for two challenges: high-pressure and hydrogen compatibility.

Standards for full metallic vessels and for metal liners will need to provide material recommendations similar to those found in Table 12. Many commonly used alloys suffer embrittlement (loss of strength and ductility) in hydrogen gas, especially at high pressures. Existing hydrogen embrittlement data are limited and primarily based on testing conducted in the 1960s and 1970s. Industry or government funded research programs will need to expand data to include higher pressures and potentially new alloys. Research can be used to select the most compatible materials, support limits on tensile strength and hardness, and determine if limits on properties such as yield to tensile ratio or impact energy are critical to hydrogen safety.

Standards must also provide definitive methods for analyzing metallic materials for cyclic service. Limited crack growth data exist, yet indications are that hydrogen can accelerate growth 50 to 150 times faster than an inert gas. It is imperative that critical stress intensity (K_H) values and crack growth data be established for higher pressures. Only with additional research can fracture mechanics be used to set limits on initial crack size, estimate rate of crack growth, and determine safe intervals for in-service inspections. Without the data, empirical performance testing of each design would be required. Cycle testing would need to be conducted using hydrogen and the results could then be the basis of future fracture mechanics analyses.

Once critical flaw sizes are determined, methods of detecting initial and in-service flaws must be proven. Ultrasonic or equivalent evaluation methods of detecting inclusions and inner surface cracks will be the minimum inspection required. Hydrostatic tests are useful only for finding gross flaws. Even acoustic emissions and follow-up angle beam UT tests are limited to finding cracks between 3 and 5% of wall thickness. Commonly used materials may have such small critical cracks at 15,000 psi that they are undetectable using current technology. This may force the use of more compatible materials for the entire vessel wall or suggest lining high-pressure carbon and alloy steel vessels with more compatible materials such as aluminum or 316 stainless steel.

Fully metallic vessels become less practical at pressures approaching 15,000 psi. In addition to weight issues, raw pipe in excess of 1.75 inch wall is not commercially available. Formability, heat treatment and single-sided quenching become difficult above 1.5 inch wall. Quench cracks become more prevalent. Thin-wall design calculations no longer apply. There is some evidence of successful hydrogen service at 10,000 psi using thin-wall design methods, but at some pressure, Section VIII Division 3 methods will be required in order to account for collapse, thick-wall effect, and high radial compressive stress. Autofrettage should be considered.

In an effort to reduce wall thicknesses, consideration should be made for reducing design margins for vessels designed using Section VIII Division 1 methods. Current Appendix 22 margins of 3:1 (minimum tensile: allowable hoop stress) can be further reduced to 2.25 with in-service inspections for crack growth. This would match the margin for DOT 3AAX "plus" rated vessels that have seen successful service for over 60 years. This reduced design margin would only apply to seamless vessels with no welding allowed (except for seal welding the end plug).

Reduced wall thicknesses would also be possible with higher strength alloys, but once again, research would be required to find alloys that are not susceptible to hydrogen embrittlement and accelerated crack growth.

All fully metallic vessel standards will need increased guidance on head forms, discontinuities, and outlet openings in order to minimize stress concentrations. Current reliance on straight thread o-ring seals or tapered threads may need to shift to welded, cone-and-thread, or new designs to achieve leak-free service, and tolerancing will become critical.

Composite vessel construction holds the most promise for future 15,000 psi hydrogen service. Although winding and manufacturing methods are proprietary to each supplier, some design guidance can be given especially for metallic liner thickness and material. Many composite vessels are already constructed with highly compatible aluminum liners, but initial inspections for surface finish and crack depth should still be included. Of the existing composite standards, ISO/DIS 15869 addresses the most hydrogen-specific aspects of design and testing. However, even this standard fails to require testing in a hydrogen environment, which will be critical for 15,000 psi service. Cycle tests and LBB tests using inert gases or liquids cannot be extrapolated for hydrogen. Other challenges for composite vessels include strength and attachment of the end boss, and ensuring the composite laminate will not degrade with environmental exposure.

None of the existing standards for fully metallic or composite vessels were intended for 15,000 psi hydrogen service. There are insufficient material test data for the metallic standards and the thin-wall design basis becomes invalid at high pressures. For proprietary composite designs, performance tests become critical and must be completed using hydrogen gas at design conditions. These are critical gaps in current standards and they must be addressed in future standards for 15,000 psi hydrogen service.

REFERENCES - PART II

[1] 49CFR Part 178.37 "Specifications for 3AA and 3AAX Seamless Steel Cylinders," U.S. Code of Federal Regulations. Title 49 (2003).

[2] DOT CFFC Standard "Basic Requirements for Fully Wrapped Carbon Fiber Reinforced Aluminum Lined Cylinder (DOT-CFFC)," Revision 4, U.S. Department of Transportation Research and Special Programs Administration (2000).

[3] Section VIII Division 1 "Rules for Construction of Pressure Vessels," American Society of Mechanical Engineers (2003).

[4] ANSI/CSA NGV2 "Basic Requirements for Compressed Natural Gas Vehicle (NGV) Fuel Containers," (2000).

[5] ISO/DIS 15869 "Gaseous Hydrogen and Hydrogen Blends - Land Vehicle Fuel Tanks," (2004).

[6] European Industrial Gas Association "Hydrogen Cylinders and Transport Vessels," IGC Document 100/03/E.

[7] Section II Part D "Material Properties," American Society of Mechanical Engineers (2003).

[8] Section VIII Division 3 "Alternate Rules for Construction of High Pressure Vessels, Rules for Construction of Pressure Vessels," American Society of Mechanical Engineers (2003).

[9] J. P. Fidelle, R. Bernardi, R. Broudeur, C. Roux, and M. Rapin. "Disk Pressure Testing of Hydrogen Environment Embrittlement," *Hydrogen Embrittlement Testing*, ASTM STP 543, American Society for Testing and Materials (1974).

[10] K. F. Windgassen. "Experiences Concerning the Transport and Storage of Pressurized Hydrogen in Europe," Annual Meeting of IOMA (1979).

[11] CGA Pamphlet C-6.4 "Methods for External Visual Inspection of Natural Gas Vehicle (NGV) Fuel Containers and Their Installation," Compressed Gas Association (2003).

[12] ISO 11439 "Gas Cylinders - High Pressure Cylinders for the On Board Storage of Natural Gas as Fuel for Automotive Vehicles," International Organization for Standardization (2002).

[13] ISO 9809-1, 2 "Gas Cylinders - Refillable Seamless Steel Gas Cylinders - Design, Construction and Testing," International Organization for Standardization (1999).

[14] ISO 7866 "Gas Cylinders - Refillable Seamless Aluminum Alloy Gas Cylinders - Design, Construction and Testing," International Organization for Standardization (1999).

[15] ISO/FDIS 11114-4 "Transportable Gas Cylinders - Compatibility of Cylinder and Valve Materials with Gas Contents - Part 4: Test Methods for Selecting Metallic Materials Resistant to Hydrogen Embrittlement," International Organization for Standardization.

[16] DOT FRP-1 Standard "Basic Requirements for Fiber Reinforced Plastic (FRP) Type 3FW Composite Cylinder," Revision 2. U.S. Department of Transportation Research and Special Programs Administration (1987).

[17] DOT FRP-2 Standard "Basic Requirements for Fiber Reinforced Plastic (FRP) Type 3HW Composite Cylinder," Revision 1. U.S. Department of Transportation Research and Special Programs Administration (1987).

[18] Case 2390-1 "Composite Reinforced Pressure Vessels Section VIII Division 3," American Society of Mechanical Engineers (2003).

[19] ISO 11119-1, 2, 3 “Gas Cylinders of Composite Construction - Specification and Test Methods,” International Organization for Standardization (1999).

[20] ISO 11114-1 “Transportable Gas Cylinders - Compatibility of Cylinder and Valve Materials with Gas Contents - Part 1: Metallic Materials,” International Organization for Standardization (1999).

[21] Case 1205-4 (Special Ruling), Integrally Forged Vessels, SA-372, American Society of Mechanical Engineers (August 14, 1962).

[22] API RP 941 “Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants,” American Petroleum Institute, Washington, D.C. (2004).

[23] A. W. Thompson and I. M. Bernstein. In *Advances in Corrosion Science and Technology,* Vol. 6, M. G. Fontana and R.W. Staehle, Editors, Plenum Press, New York (1976).

[24] H. Barthelemy. “Hydrogen Gas Embrittlement of Some Austenitic Stainless Steels,” Hydrogen and Materials Conference, Beijing (May 1988).

[25] J. A. Brooks and A. J. West. “Development of Materials for Hydrogen Storage and Transport,” SAND-75-0426 p. 8, Sandia Laboratories, Albuquerque, New Mexico (February 1976).

[26] A. J. Jacobs and W. T. Chandler. *Scripta Metallurgica,* Vol. 9 (1975).

[27] R. J. Walter and W. T. Chandler. “Effects of High Pressure Hydrogen on Metals,” Technical Information Presentation, Rocketdyne Research Materials (1968).

[28] A. W. Loginow and E. H. Phelps. “Steels for Seamless Hydrogen Pressure Vessels,” *Journal of Engineering for Industry* (February 1975).

[29] A. W. Loginow. Internal Memorandum at USS Applied Research Laboratory, “Examination of Alloy Steel Tank After Long-Term High Pressure Hydrogen Service,” Ref. No. 40.001-021 (1966).

[30] *PDL Handbook Series-Chemical Resistance*, Vol. 1 - *Thermoplastics*, 2nd Edition, ISBN 1-884207-12-X (1996).

[31] J. A. Harris, Jr. and M. C. Van Wanderham. “Properties of Materials in High Pressure Hydrogen at Cryogenic, Room, and Elevated Temperatures,” NASA Contract NAS8-26191 (1971).

[32] Federal Motor Vehicle Safety Standard No. 304 - Compressed Natural Gas Fuel Container Integrity, National Highway Traffic Safety Administration (1995).

[33] DOT Exemption E 10945, 14th revision, U.S. Department of Transportation Research and Special Programs Administration (2004).

APPENDIX A - METALLIC VESSEL SERVICE DATA

Table 13 - Full Metallic Vessel Hydrogen Service Data

(Storage and Transportation)

Type of Service	Number of Vessels in Sample	Age of vessels (years)	Years of Operation	Design Const Code	Water Volume	Size (OD or ID)	Minimum Wall Thickness	Length	Material	MAWP	Operating Pressure	Design Temp
					(ft^3)	(in.)	(in.)	(ft)		(psi)	(psi)	(° F)
Storage	333	1-3	1-3	ASME VIII-1; Appendix 22	1.4	8 ID	0.784	4.5	SA 372 Gr F Cl 70	7,000	6,300	-50 to 200
Storage	338	32-62	1-16	ASME VIII-1, forged vessel	20-27	11.75 OD	0.414-0.571	35-45	API-5A-J-55; API-5A-N-80; SA-53; and SA372 Cl 4	2,000-2,500	1,800-2,250	-40-200
Storage	1,065	3-44	1-16	ASME VIII-1, Appendix 22	60	24 OD	0.871	23.5	SA 372 Gr D or J Cl 65	2,450	2,200	-40 to 200
Transport	2,060	1-57	1-57	49 CFR 178.37 3AAX-2400	81.6	22 OD	0.536	36	4130X	2,400 (plus rated for 2,640)	2,640	Not stated

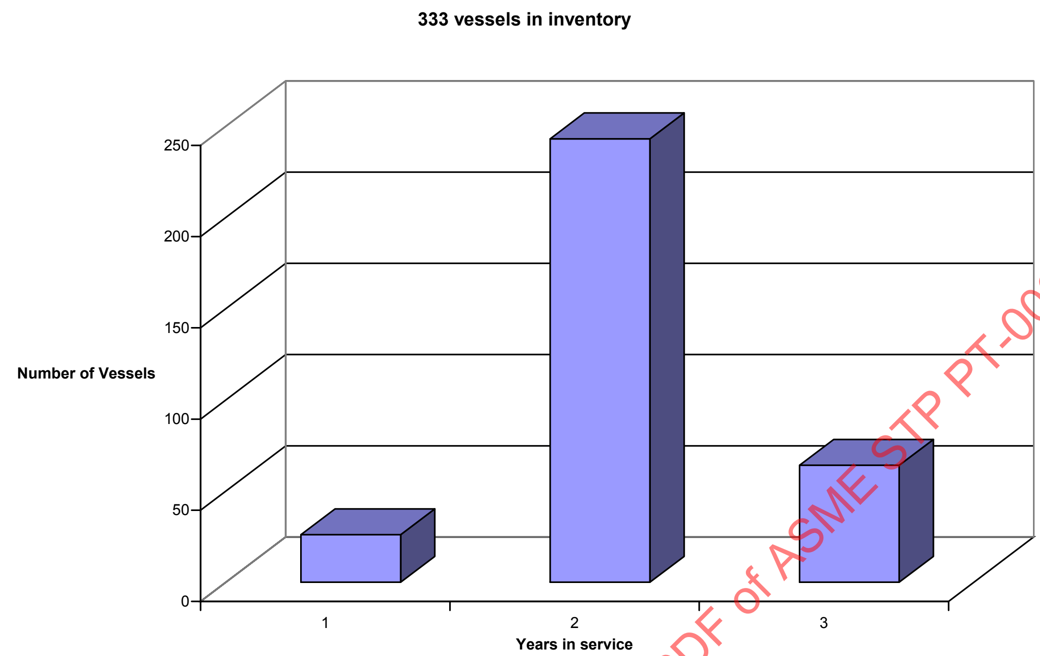

Figure 6 - Appendix 22 Storage Vessels (7,000 psig MAWP-10 in. OD)

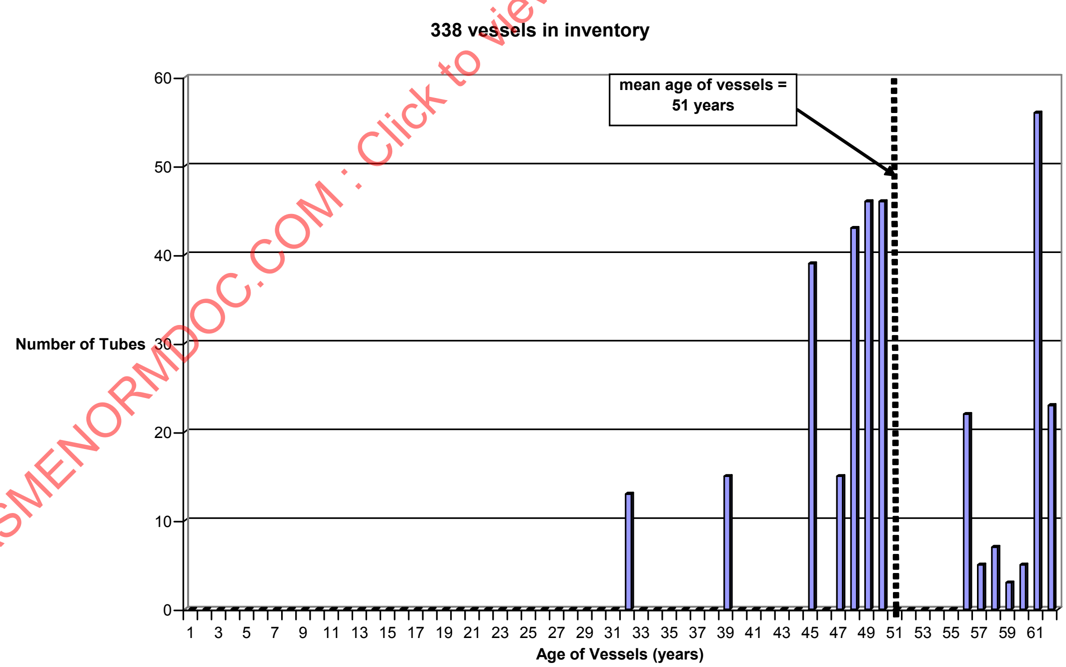

Figure 7 - Division 1 Storage Vessels (2,000-2,500 psig MAWP - 11.75 in. OD)

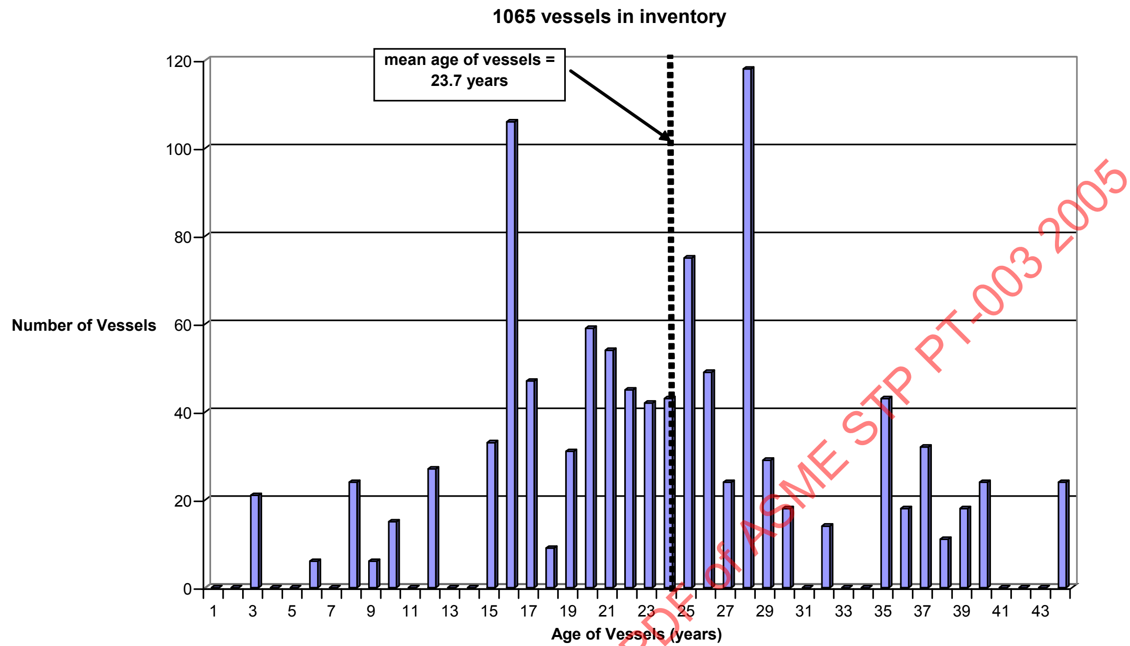

Figure 8 - Code Case 1205 and Appendix 22 Storage Vessels (2450 psig MAWP - 24 in. OD)

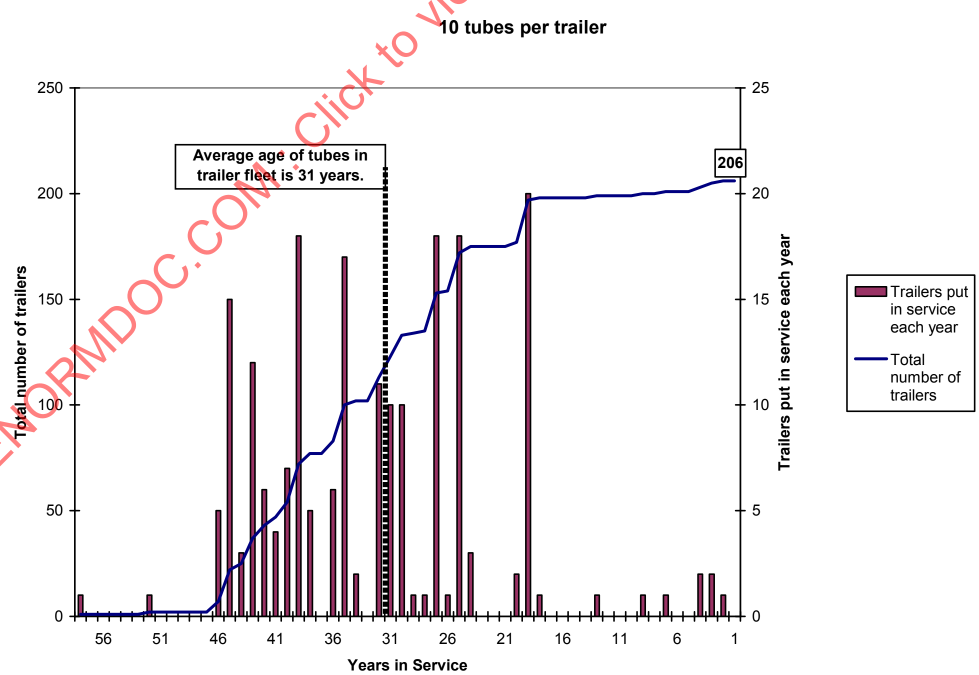

Figure 9 - 3AAX Trailer Tubes (2400 Service Pressure, plus Rated, 110% Overfill - 22 in. OD)

APPENDIX B - COMPOSITE VESSEL SERVICE DATA

Table 14 - Composite Vessel Hydrogen Service Data

(Fuel Tank, Transport/Portable, Storage)

Type of Service	Year put in Service	Design Const Code	Capacity	OD	Length	Material		Operating Press	Operating Temperature
			(liters)	(in.)	(in.)	Liner	Composite	(psi)	(°F)
Fuel tank	1999	NGV2, EIHP, Betten 9	160	17	65	Polymer	Carbon fiber/epoxy	5,000	-40 to 185
Fuel tank	1999	DOT FMVSS 304 [32]	240	22	60	Polymer	Carbon fiber/epoxy	5,000	-40 to 185
Fuel tank	1999	NGV2, EIHP, Betten 9	34	12	33	Polymer	Carbon fiber/epoxy	5,000	-40 to 185
Fuel tank	2001	NGV2, EIHP, Betten 9	60	14	38	Polymer	Carbon fiber/epoxy	10,150	-40 to 185
Fuel tank	2001	NGV2, EIHP, Betten 9	26.5	10	32	Polymer	Carbon fiber/epoxy	10,150	-40 to 185
Fuel tank	2003	NGV2	313	16.5	120	Aluminum 6061-T6	Carbon fiber/epoxy	5,000	-40 to 180
Fuel tank	2003	NGV2	270	16.5	105	Aluminum 6061-T6	Carbon fiber/epoxy	5,000	-40 to 180
Fuel tank	2001	KHK (Japan)(1)	73	17	32	Aluminum 6061-T6	Carbon fiber/epoxy	5,000	
Fuel tank	2001	KHK (Japan)	101	17	44	Aluminum 6061-T6	Carbon fiber/epoxy	5,000	
Fuel tank	2001	NGV2, EIHP, KHK	150	16.3	60.4	Aluminum	Carbon fiber/epoxy	5,000	-40 to 180
Fuel tank		NGV2/ISO		14	82	HDPE(2)	Carbon/glass fiber/epoxy	3600	

Type of Service	Year put in Service	Design Const Code	Capacity	OD	Length	Material		Operating Press	Operating Temperature
			(liters)	(in.)	(in.)	Liner	Composite	(psi)	(°F)
Fuel tank		NGV2/METI		18	37	HDPE	Carbon/glass fiber/epoxy	3600	
Fuel tank		NGV2		18	49	HDPE	Carbon/glass fiber/epoxy	3600	
Fuel tank		NGV2/METI(3)		16	33	HDPE	Carbon/glass fiber/epoxy	5000	
Fuel tank		NGV2/METI		16	33	HDPE	Carbon/glass fiber/epoxy	5075	
Portable	1995	DOT-E-10945 [33]	9	7.2	22	Aluminum 6061-T6	Carbon fiber/epoxy	4250	-65 to 160
Portable	2002	DOT-E-10945	92	17	42	Aluminum 6061-T6	Carbon fiber/epoxy	5000	-65 to 160
Transport	2000	NGV2, EIHP	260	15.4	107	Aluminum 6061-T6	Glass fiber/epoxy	3625	
Storage	2002	Not Certified	165	16	70	Aluminum	Carbon fiber, epoxy	12,687	
Storage	2004	NGV2, EIHP	130	22.5	38.2	Aluminum	Carbon fiber, epoxy	10,150	
Storage	2000	NGV2, EIHP	150	16.3	60.4	Aluminum	Carbon fiber, epoxy	5075	
Storage	2000	NGV2, EIHP	93			Plastic	Carbon fiber, epoxy	3000	
Storage	2004	NGV2, EIHP	115			Plastic	Carbon fiber, epoxy	10150	
Storage	2001	NGV2, TUV(4)	205	18	68	Aluminum 6061-T6	Carbon fiber, epoxy	5000	-40 to 185

Type of Service	Year put in Service	Design Const Code	Capacity	OD	Length	Material		Operating Press	Operating Temperature
			(liters)	(in.)	(in.)	Liner	Composite	(psi)	(°F)
Storage	2004	DOT-E-10945	88	17	40	Aluminum 6061-T6	Carbon fiber, epoxy	5000	-40 to 185
Storage	2003	NGV2	305	18	80	Aluminum 6061-T6	Carbon fiber, epoxy	6500	-40 to 185
Storage		NGV2		12	36	HDPE	Carbon/glass fiber/epoxy	5000	
Storage		NGV2		16	33	HDPE	Carbon/glass fiber/epoxy	5000	
Storage		NGV2		22	50	HDPE	Carbon/glass fiber/epoxy	7000	
Storage		NGV2		19	38	HDPE	Carbon/glass fiber/epoxy	7250	

Notes:
(1) High Pressure Gas Safety Institute of Japan.
(2) HPDE = High density polyethylene.
(3) Ministry of Economy, Trade, and Industry (Japan).
(4) German certification body.

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PART III - A Study of Existing Data, Standards and Materials Related to Hydrogen Service for Piping Systems and Transport Pipelines

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1 INTRODUCTION

1.1 Background

The ASME B31 Piping Code Standards Committee has formed a project team to develop codes and standards for piping systems and pipelines to be used for hydrogen service. In order to support this effort, the ASME Standards Technology, LLC (formerly the Codes and Standards Technology Institute) is developing H_2 Standardization Interim Technical reports to address priority topics related to infrastructure applications.

1.2 Scope of Report

The scope of Part III of this report is to:

(a) review the design margins in existing piping/pipeline codes

(b) generate successful service data for H_2 piping systems and pipelines

(c) recommend design factors for systems with and without in-service inspection requirements

(d) recommend design rules for new H_2 piping and pipeline codes

(e) review effects of hydrogen on commonly used piping/pipeline materials

(f) make recommendations for design for cyclic service, and

(g) address special topics including performance of leak-tight joints, heat treatment of stainless steel, effects of surface finish, and pipe/tube bending.

The report will address only metallic materials. Piping fabricated from nonmetallic material such as plastic or composite material is outside the scope of this document.

1.3 Service Conditions

Only gaseous dry hydrogen with the following service conditions is within the scope of this report:

	Piping Systems		Pipelines
Pressure (psig)	15-3,000	3,001-15,000	15-3,000
Temperature (°F)	-20 to +500$^{(1)}$	-20 to +300$^{(1)}$	-20 to +300$^{(1)}$
Purity (%H_2)	99+	99+	99+

Note: (1) +200°F for aluminum and copper alloys.

The pressure is limited to internal pressure, and the design criteria are limited to the pressure design of piping and pipelines. Loadings due to external conditions (impact, live and dead loads, seismic, wind, thermal and thermal gradient, vibration, and support) are not considered in this report.

Note that temperatures above 300°F are not considered for piping systems above 3,000 psig, and pressures above 3,000 psig are not considered for pipelines.

Mixtures of hydrogen with other gases are outside the scope of this report. The presence of the other gases has various effects (both positive and negative) on the hydrogen compatibility of materials.

1.4 Executive Summary

Piping codes for up to 15,000 psi and pipeline codes for up to 3000 psi hydrogen service will need to account for the challenges of both high pressure and hydrogen compatibility.

Four existing design codes were evaluated (ASME B31.1, B31.3, B31.8, and 49 CFR 192). Although none have an upper pressure limit, only B31.3 has a separate chapter devoted to pressures above 6,000 psi. The design margins for carbon steel in these standards range from 4.0 (for allowable stresses based on the ratio of ultimate stress/allowable stress (S_u/S_a) to 1.25 (for allowable stresses based on the ratio of yield stress/allowable stress (S_y/S_a).

Pipe and fittings will need to be constructed of materials that are resistant to hydrogen embrittlement. 316L stainless steel is recommended for piping systems at 15,000 psi. There are limited data on commonly used carbon steel alloys, but the existing data support limitations on tensile strength. The harmonized EIGA/CGA 121/04/E recommendations should be followed for pipelines. New research is needed to expand the recommended materials to other alloys.

When carbon and alloy steels are used for piping systems, ultrasonic, or other NDE evaluation for inclusions and inner surface cracks is critical. The limited data available indicates that hydrogen can accelerate crack growth 50 to 150 times faster than an inert gas. Critical stress intensity (K_H) values and crack growth data must be established for higher pressures. By expanding research, fracture mechanics can be used to set limits on initial crack size, estimate rate of crack growth, and determine safe intervals for in-service inspections.

Careful evaluation of mechanical joints will be needed to ensure leak-free operation. Current reliance on flanges, straight thread O-ring seals or tapered threads may need to shift to welded, cone-and-thread, or new designs. Welded joints will need to be defect free, and post-weld heat treatment may be required to relieve residual stresses and ensure a favorable microstructure in the heat-affected zone (HAZ).

Both hot and cold tube or pipe bending is acceptable for hydrogen service, as long as wall thinning is limited to 5 to 15% (depending on material and bending process), and the hardness in the area of the bend is limited to HRC 22.

The recommended design margin for high-pressure hydrogen piping systems is consistent with the current B31.3 Chapter IX design margin. No in-service inspections (beyond basic visual and leak tests) are required when materials such as 316L stainless steel are used. 316L is not susceptible to hydrogen embrittlement and accelerated crack growth. When carbon and alloy steels are selected for piping systems, then in-service inspections capable of detecting critical cracks is mandatory.

There is some precedent for reducing design margins further (pipelines in isolated areas and large, seamless, forged transportation vessels have lower margins), but there is little incentive to drop them below the B31.3 Chapter IX margins.

For pipelines, successful service data of Class 1 pipelines may justify reducing margins in Class 2, 3, or 4 locations.

Existing piping standards have been used successfully and safely at hydrogen pressures as high as 10,000 psi (3,000 psi for pipelines). Increasing piping system pressure to 15,000 psi will require diligence in material selection, expanded hydrogen compatibility research, new mechanical joining methods, and in-service inspection methods capable of detecting critical cracks.

2 EXISTING DESIGN PHILOSOPHY/EXPERIENCE

2.1 Piping Design Philosophy

2.1.1 ASME B31.1

The scope of ASME B31.1 [1] is to prescribe requirements for the design, materials, fabrication, erection, test, and inspection of power and auxiliary service piping systems for electric generation stations, industrial and institutional plants, central and district heating plants and heating systems.

B31.1 does not limit its usage to any specific pressure value. Hence this standard covers the high-pressure (15,000 psi) piping in the scope of this study. There are no separate rules for the design of high-pressure piping and components, and there are no additional design criteria for cyclic pressure service conditions.

The elevated temperature limit of the standard is dependent on the material being used, typically:

(a) 800º F for carbon steel

(b) 1,200º F for alloy and stainless steel

(c) Less than 500º F for nonferrous alloys

The lower temperature limit of the materials is generally -20°F.

2.1.1.1 Design Margin

Table 19 in Appendix A provides the design margin for a few common B31.1 piping material specifications at temperatures ≤ 100º F and at 450º F. The temperature was limited to 450º F for comparison with B31.8 [2].

Design margin is based on either ultimate stress or yield stress. In cases where a fraction of ultimate stress governs as the allowable stress, the design margin is defined as the ratio of ultimate stress (Su) to allowable stress (S_a). In cases where a fraction of yield stress governs as allowable stress, the design margin is defined as the ratio of yield stress (S_y) to allowable stress (S_a).

2.1.1.2 Allowable Stress (S_a)

S_a is the allowable stress value in tension at temperature for a specified material. S_a values are listed in Appendix A of B31.1. Allowable stress values for B31.1 were established using the same basis as the ASME Boiler and Pressure Vessel Code, Section II, Part D, Appendix I [3]:

S_a is the lowest of:

(a) The lower of specified minimum tensile strength at room temperature (SMTS) divided by 3.5 and tensile strength at temperature divided by 3.5[5]

(b) The lower of 2/3 of specified minimum yield strength at room temperature (SMYS) and 2/3 of yield strength at temperature.

For austenitic steels and nickel alloys, two sets of allowable stress values are provided. The higher alternate allowable stress exceeds 2/3 of yield at temperature, but does not exceed 90% of yield strength at temperature. The higher stress value should only be used when slightly higher deformation is not objectionable.

[5] Although B31.1 states that allowable stress is based on Section II ratios (3.5:1 tensile: allowable), the actual allowables listed in Appendix A of B31.1 are based on a ratio of 4:1.

Note that since temperature is limited to 500º F (200°F for aluminum and copper alloys) for this study, creep and stress rupture strength basis are not considered in this report.

2.1.1.3 Ultimate Stress (S_u) and Yield Stress (S_y)

The ultimate stress and yield stress (at ambient temperature) for each material specification are also listed in B31.1 Appendix A. For elevated temperatures, these values are taken from ASME Section II Part D, Tables U and Y-1.

2.1.1.4 Other Factors Affecting Design Margin

In addition to the design margin based on the allowable stress, B31.1 provides for a weld factor to be included in internal design pressure calculations when the pipe is not seamless. The weld factor varies from 0.6 to 0.85, depending on the type of welding. For electric resistance welded pipe (ERW), the most common type of pipe welding, the weld factor is 0.85. The weld factor will increase the design margin of ERW pipes by about 18%.

Another factor (Y) is included in design pressure calculations. This factor affects design margin only for non-ductile materials or thick-walled pipe when the wall thickness exceeds 1/6 of the outside diameter of the pipe.

The design margins are unchanged for systems with and without in-service inspections. The standard makes no reference to any changes in design criteria for systems with in-service inspections.

2.1.1.5 Test Pressure

The hydrostatic test pressure is 1.5 times the design pressure. If a pneumatic test is selected as an alternative, the test pressure shall be between 1.2 and 1.5 times design pressure.

2.1.2 ASME B31.3

The scope of ASME B31.3 [4] is to prescribe requirements for the design, materials, fabrication, erection, test, and inspection of piping typically found in petroleum refineries, chemical, pharmaceutical, cryogenic, and related processing plants and terminals.

This standard separates the scope according to the service pressure and other service conditions.

(a) *Category D*: For pressure ≤ 150 psi, temperature ≤ 366º F, and nonflammable, nontoxic service.

(b) *Normal fluid service*: Fluid service pertaining to most piping covered by this standard. Fluids not subject to category D, category M (toxic service) or high-pressure service.

(c) *High-pressure service*: Fluid service for which the owner specifies the use of Chapter IX of this standard. Recommended for pressure in excess of Class 2500 flange rating for the specified design temperature and material group per ASME B16.5 [5]. Typically this would be for systems operating above 6,000 psi at ambient temperatures.

Hydrogen piping subjected to 15,000 psi pressure could be categorized under normal service or high-pressure service per the B31.3 code.

The elevated temperature limit of B31.3 is dependent on the material being used, typically:

(a) 1,100º F for carbon steel

(b) 1,500º F for alloy and stainless steel

(c) 1,650º F for nickel and nickel alloys

(d) 400º F for copper and for aluminum and its alloys

2.1.2.1 Normal Fluid Service

(a) Design Margin for Normal Fluid Service

Table 19 in Appendix A provides the design margin for a few common B31.3 piping material specifications at temperatures ≤ 100º F and at 450º F. The temperature was limited to 450º F for comparison with B31.8.

Design margin is defined the same as for B31.1 (see Paragraph 2.1.1.1).

(b) Allowable Stress (S_a)

S_a is the allowable stress value in tension at temperature for a specified material. S_a values are provided in Appendix A, Table A-1 of B31.3. The basis for establishing allowable stress values for various piping specifications is the lowest of:

(1) The lower of 1/3 of SMTS and 1/3 of tensile strength at temperature

(2) The lower of 2/3 of SMYS and 2/3 of yield strength at temperature

(3) For austenitic steels and nickel alloys, the lower of 2/3 of SMYS and 90% of yield strength at temperature

For structural-grade materials, the allowable stress is 0.92 times the allowable determined as above, which will further increase the design margin by 8.7%.

(a) Ultimate Stress (S_u) and Yield Stress (S_y)

The ultimate stress and yield stress (at ambient temperature) for each material specification are also provided in Appendix A, Table A-1 of B31.3. For elevated temperatures, these values are taken from ASME Section II Part D, Table U and Y-1.

(b) Other Factors Affecting Design Margin

Like B31.1, B31.3 provides for a weld factor to be included in internal design pressure calculations when the pipe is not seamless. The weld factor varies from 0.6 to 0.85, depending on the type of welding. For electric resistance welded (ERW) pipe, the most common type of pipe welding, the weld factor is 0.85. The weld factor will increase the design margin of ERW pipes by about 18%.

B31.3 also includes factor (Y) in design pressure calculations. This factor affects design margin only for nonductile materials or thick-walled pipe when the wall thickness exceeds 1/6 of the outside diameter of the pipe.

The design factors are unchanged for systems with and without in-service inspections. B31.3 makes no reference to any changes in design criteria for systems with in-service inspections.

The normal fluid section of the standard applies to all pressure ranges with no pressure limit set on any design parameter. However, for pressures exceeding a class 2500 flange rating, the owner has the option to specify design conforming to high-pressure fluid service, Chapter IX of B31.3. No additional design criteria for cyclic pressure service conditions are defined in the normal fluid service section.

(c) Test Pressure

The hydrostatic test pressure is 1.5 times the design pressure. If a pneumatic test is selected as an alternative, the test pressure is 1.1 times design pressure.

2.1.2.2 High-Pressure Service (Chapter IX)

(a) Design Margin for High-Pressure Service

Table 19 in Appendix A provides the design margin for a few common B31.3 high-pressure piping material specifications at temperatures ≤ 100º F and at 450º F. The temperature was limited to 450º F for comparison with B31.8.

Design margin is defined the same as for B31.1 (see Paragraph 2.1.1.1).

The design margins for high-pressure service differ from normal fluid service as follows:

(1) The allowable stress value is provided by B31.3, Appendix K, Table K-1

(2) The pressure design formula is modified

(3) No size factor (Y) is considered in the calculations.

(4) The weld factor is always 1 (weld acceptance criteria is different).

(b) Allowable Stress (S_a)

The basis for establishing allowable stress values for various piping specifications is the lowest of:

(1) The lower of 2/3 of SMYS and 2/3 of yield strength at temperature.

(2) For austenitic steels and nickel alloys, the lower of 2/3 of SMYS and 90% of yield strength at temperature

(c) Other Factors Affecting Design Margin

Additional design criteria for cyclic pressure service conditions are defined in this high-pressure section. Allowable values for alternating stress must be in accordance with Section VIII, Division 2, Appendices 4 and 5 [6].

The weld joint quality factor has to be 1 for welded pipes based on the acceptance criteria in Paragraph K341.3.2 of Chapter IX of B31.3.

The design factors are unchanged for systems with and without in-service inspections. The standard makes no reference to any changes in design criteria for systems with in-service inspections.

Chapter IX of B31.3 applies to piping designated by the owner as high-pressure fluid service, considered to be pressure in excess of a B16.5 2,500 lb flange class rating. However, there are no specified pressure limitations for the application of rules of this section.

(d) Test Pressure

The test pressure is 1.5 times the design pressure, regardless of whether the test is hydrostatic or pneumatic.

2.2 Pipeline Design Philosophy

2.2.1 ASME B31.8

ASME B31.8 covers the design, materials, fabrication, installation, inspection, and testing of pipeline facilities used for transportation of gas.

This standard does not limit its usage to any specific pressure value. The upper temperature limit of this standard is 450º F.

2.2.1.1 Design Margin

Table 19 in Appendix A provides the design margin for a few common B31.8 pipeline material specifications at temperatures ≤ 100º F and at 450º F. Two design margins are given for each material. The minimum value represents the design margin for a Class 1 location, and the maximum value represents the design margin for a Class 4 location.

2.2.1.2 Allowable Stress (S_a)

Three individual factors, depending on location, type of weld joint, and service temperature, are applied to the SMYS to arrive at the allowable stress for design calculations.

(a) *Basic design factor* (Location Class factor) depends on the number of buildings intended for human occupancy; varies from 0.80 for a Class 1 location to 0.40 for a Class 4 location.

(b) *Longitudinal joint factor* depends on the type of weld joint; varies from 1.0 in seamless pipe to 0.6 in furnace butt-welded pipe.

(c) *Temperature derating factor* varies from 1.0 for temperatures ≤ 250º F to 0.867 for 450º F.

2.2.1.3 Other Factors Affecting Design Margin

The design factors are unchanged for systems with and without in-service inspections. The standard makes no reference to any changes in design criteria for systems with in-service inspections.

B31.8 design guidelines apply to all pressure ranges, with no pressure limit set on any design parameter. No separate criteria are specified for design of high-pressure pipeline facilities, and there are no additional design criteria for cyclic pressure service conditions.

2.2.1.4 Test Pressure

The test pressure factor varies according to the location of pipeline, from 1.25 times maximum allowable operating pressure (MAOP) in a Class 1 location to 1.4 in Class 3 and 4 locations.

2.2.2 DOT Standard CFR Title 49 Part 192

Table 19 in Appendix A provides the design margin for a few common pipeline materials installed per CFR Title 49 Part 192 [7].

The pressure design criteria, limitations, and design are identical to ASME B31.8, except for the basic design factor for a Class 1 location, which is 0.72 instead of 0.80. Also, the DOT standard has a higher test pressure factor of 1.5 times MAOP for Class 3 and 4 locations.

2.2.3 Summary of Piping And Pipeline Standards

Table 15 - Summary Comparison of Piping and Pipeline Standards

Standard	B31.1	B31.3 (Normal Service)	B31.3 (High Pressure)	B31.8	49 CFR 192
Pressure limit	None	None (but a separate high-pressure section is provided)	None (intended for systems exceeding B16.5 Class 2500)	None	None
Temperature limit	Material dependent	Material dependent	Material dependent	450°F	450°F
Allowable stress basis	Lowest of: - SMTS/3.5 - S_u at temperature/3.5 - 2/3 of SMYS - 2/3 of S_y at temperature	Lowest of: - 1/3 of SMTS - 1/3 of S_u at temperature - 2/3 of SMYS - 2/3 of S_y at temperature	Lower of: - 2/3 SMYS or - 2/3 of S_y at temperature	Three factors applied to SMYS: - Location class factor (0.8- 0.4) - Weld joint factor (1.0 to 0.6) - Temperature derating factor (1.0-0.867)	Three factors applied to SMYS: - Location class factor (0.72 - 0.4) - Weld joint factor (1.0 to 0.6) - Temperature derating factor (1.0 - 0.867)
Allowable stress basis for austenitic stainless steels	Alternate S_a that exceeds 2/3 of S_y at temperature, but ≤ 90% of S_y at temperature	Lower of: - 2/3 SMYS or - 90% of S_y at temperature	Lower of: - 2/3 SMYS or - 90% of S_y at temperature	Same	Same
Source of ultimate and yield stress (ambient temperature)	B31.1 Appendix A	B31.3 Appendix A, Table A-1	B31.3, Appendix K, Table K-1	Material specification	Material specification
Source of ultimate and yield stress (elevated temperature)	ASME Section II, Part D, Tables U and Y-1	ASME Section II, Part D, Tables U and Y-1	ASME Section II, Part D, Tables U and Y-1	N/A	N/A
Weld factor	0.6 - 0.85	0.6 - 0.85	1.0 (strict acceptance criteria)	0.6 to 1.0 (for seamless)	0.6 to 1.0 (for seamless)
Cyclic service design rules	No	No, but states that cyclic loadings "shall be considered"	Yes, reference to Section VIII, Division 2	No	No
Hydrostatic test pressure	1.5 x DP	1.5 x DP	1.5 x DP	1.25 - 1.4 x MAOP	1.25 - 1.5 x MAOP
Pneumatic test pressure	1.2 - 1.5 x DP	1.1 x DP	1.5 x DP	1.25 - 1.4 x MAOP	1.25 - 1.5 x MAOP

2.3 Piping Experience and Data

2.3.1 Design Criteria

Much of the existing hydrogen gas piping in North America conforms to ASME B31.3. In Europe, although there are local codes in many countries, B31.3 is still frequently followed. Of late, there have been some instances in Europe, where EN 13480 "Metallic Industrial Piping" [8] was followed as this is a harmonized standard to European Pressure Equipment Directive (PED) [9].

2.3.2 Service Data

Appendix C provides some successful service data for H_2 piping systems. Table 22 lists data for piping systems that are operated by Air Products, but the materials are representative of those used throughout the industry. Carbon steel is the material of choice for hydrogen plants operating from 400 to 3,000 psig at ambient temperature. The large number of high-pressure piping systems located outside hydrogen plants are primarily those attached to storage and transport tubes for hydrogen (ranging from 2,450 to 7,000 psig MAWP). Older assemblies use red brass pipe and copper tubing. Newer assemblies use 304 stainless pipe and socket welded joints. The highest pressure and most recent systems (7,000 to 13,300 psig MAWP) use cold-drawn 316 stainless tubing and cone-and-thread fittings to support fueling systems for hydrogen-powered vehicles.

2.3.3 In-Service Inspection and Safety

In-service inspections of piping systems are based on a mechanical integrity program that establishes the testing interval, types and methods of inspection, pass/fail criteria, and documentation requirements.

Most of the existing hydrogen systems operate at pressures below 3,000 psig and temperatures below 200º F. Hence, the following in-service inspection procedures are for piping systems operating within these conditions.

For pure dry hydrogen, internal corrosion is not considered a factor, and hence the piping systems are only visually inspected periodically. These periodic inspections are carried out at various frequencies (quarterly, semiannual, and annual inspection schedules).

For carbon steel systems, in pressures above 1,000 psi, a one-time hardness check of the welds was carried out for piping that was not already checked for hardness during installation. (i.e., for older piping on which no hardness check was performed after welding during the installation of the piping). In more recent piping systems, this weld hardness check is completed at the time of fabrication/installation. The maximum allowable hardness in this examination is limited to 225 BHN. If hardness exceeds this value, the piping is either replaced or heat-treated (annealed).

In piping locations where high stresses or cyclic stresses are expected, such as the outlet of a compressor, magnetic particle tests are performed on critical locations on the piping. In addition to the piping checks, leak tests of all piping joints are performed periodically.

Mechanical integrity programs for monitoring hydrogen systems have been in place for many years. The results of these programs indicate a failure-free operating period for hydrogen service pressures and temperatures mentioned above. In addition to other critical factors, hydrogen embrittlement has direct relation to hydrogen pressure, and hence for future 15,000 psi hydrogen piping systems, a mechanical integrity program based on fracture mechanics is recommended when materials resistant to hydrogen embrittlement are not used.

2.4 Pipeline Experience and Data

2.4.1 Design Criteria

Hydrogen gas pipelines in North America conform to ASME B31.8 and 49 CFR Part 192. In Europe, although there are local codes in many countries, pipelines also commonly conform to ASME B31.8.

2.4.2 Service Data

Appendix D provides successful service data for H_2 pipelines. Table 23 lists data for hydrogen pipelines operated by Air Products. The materials are representative of those used throughout the industry, although API 5L X52 and A106 Gr B are underrepresented in the sample. The existing pipelines are up to 60 years old, operate up to 2,220 psig (with the majority in the 800 to 1,000 psig range), and range in size from 2 to 18 inches (with 6 to 10 inches being the most popular sizes). Figure 11 through Figure 13 in Appendix D display this information graphically.

2.4.3 In-Service Inspection and Safety

In-service inspections of pipelines are based on a pipeline integrity management program. This program is based on the requirements of Title 49 CFR, Part 192, Pipeline Safety Regulations, Subpart O. These requirements pertain to High Consequence Areas (HCA), which are defined in Subpart O. An operator must first identify the HCA segments along their pipelines and determine the threats associated with the pipe segment. Subpart O refers to ASME B31.8S [10] for a list of potential threats. The common threats to a pipeline are external corrosion, stress-corrosion cracking, and internal corrosion. Depending on the threats, capable technology is then selected for assessing the HCA segment. Subpart O indicates four acceptable technologies for assessing the integrity of pipelines. They are as follows:

(a) Internal inspection tool or tools capable of detecting corrosion, and any other threats to which the covered segment is susceptible. ASME B31.8S, Section 6.2 must be followed in selecting the appropriate internal inspection tools.

(b) Pressure test conducted in accordance with Title 49 CFR, Part 192, Subpart J using the test pressures specified in Table 3 of Section 5 of ASME B31.8S, to justify extended reassessment intervals.

(c) Direct assessment to address threats of external corrosion, internal corrosion, and stress corrosion cracking.

(d) Other technology demonstrated by an operator to provide an equivalent understanding of the condition of the line pipe.

Prior to the publication of the DOT integrity management program, hydrogen pipeline in-service inspection was restricted to external corrosion monitoring. No internal corrosion, embrittlement, or crack investigation were performed. Proper material selection and limiting tensile stress were the key factors preventing hydrogen embrittlement in pipelines. Internal corrosion in hydrogen was never a concern since pure dry hydrogen gas is not corrosive.

In-service external corrosion was monitored basically by cathodic protection and wrapping and coating evaluation.

3 EFFECT OF HYDROGEN ON COMMON MATERIALS

3.1 High-Pressure Hydrogen Exposure Degradation

3.1.1 Types of Hydrogen Embrittlement

Hydrogen gas embrittlement is a generic term that includes all of the different effects that engineering alloys might experience in hydrogen-gas or hydrogen-forming environments. There are three main categories of hydrogen embrittlement:

(a) Hydrogen reaction embrittlement

(b) Internal reversible hydrogen embrittlement

(c) Hydrogen environment embrittlement

3.1.1.1 Hydrogen Reaction Embrittlement

Hydrogen reaction embrittlement deals with the absorption of atomic or molecular hydrogen into the material, which then reacts to form a new phase. Such reactions may form CH_4 within low-alloy steels or hydrides in zirconium, titanium, and tantalum.

Hydrogen attack and decarburization are two other types of hydrogen reaction embrittlement. Hydrogen attack occurs in carbon steel or low-alloy steels at elevated temperatures higher than the scope of this document. Carbon within the alloy reacts with atomic hydrogen to form methane, which results in crack formation. The "Nelson Chart," which can be found in API 941 [11], shows the operating limits for carbon and low-alloy steels. Decarburization is very similar to hydrogen attack, except that the reaction occurs at the surface of the material. It can occur in high-temperature hydrogen environments, as well as oxidizing environments.

3.1.1.2 Internal Reversible Hydrogen Embrittlement

Internal reversible hydrogen embrittlement is also referred to as slow strain rate embrittlement. This type of embrittlement occurs when atomic hydrogen is trapped within voids around nonmetallic inclusions. High gas pressure, from the combination of hydrogen atoms trapped around the inclusion, can generate highly localized stresses that may initiate a crack parallel to the rolling direction. As the cracks link up, stepwise cracks will form. To be reversible, the embrittlement must occur without the hydrogen reacting within the lattice. This type of embrittlement can occur with the electroplating of high-strength steel with cadmium, with processing treatments such as melting and pickling, during welding of high-carbon steels with wet electrodes or in a moist environment, and with corrosion-produced hydrogen. Hydrogen embrittlement due to corrosion-produced hydrogen is also referred to as hydrogen-induced cracking or hydrogen stress cracking.

3.1.1.3 Hydrogen-Environment Embrittlement

Hydrogen-environment embrittlement deals primarily with embrittlement of a material exposed to room-temperature hydrogen. Surface adsorption has been shown to be the overall rate-controlling step during hydrogen-environment embrittlement. The embrittlement in a hydrogen environment is immediate once a stress level greater than the yield strength is reached. In other words, the tensile strength/ductility is reduced. This type of embrittlement is often called hydrogen-assisted cracking.

Degradation in fatigue limits has been observed in susceptible materials during testing in dry hydrogen gas environments. Carbon steels, low-alloy steels, and stainless steels show such degradation, even at low pressures in hydrogen. The fatigue crack growth is more pronounced at ambient temperatures than when the materials are exposed to elevated temperatures. The degradation in fatigue properties in dry hydrogen gas service is due to the reduction in ductility of the material at the crack tip.

3.1.2 Metallurgical and Process Factors Affecting Hydrogen Embrittlement

3.1.2.1 Metallurgical Factors

Material variables that affect susceptibility to hydrogen embrittlement include composition, microstructure, and strength level. Large amounts of carbon and manganese have been found to increase the susceptibility of steels to hydrogen embrittlement [12]. Several alloying elements have either a neutral or beneficial affect on hydrogen embrittlement. Silicon and titanium offer some benefit, but they are not used in large quantities due to their effect on weldability. Nickel is believed to increase the austenitic stainless steels' resistance to hydrogen embrittlement, since nickel increases the stability of austenitic stainless steels [13].

Grain orientation of the material can also influence its susceptibility to hydrogen embrittlement. A random grain orientation improves resistance. The presence of brittle second phases such as martensite and delta ferrite can increase a material's susceptibility to hydrogen embrittlement. Forming or thermo-mechanical processing can result in a microstructure change that can also increase susceptibility to hydrogen embrittlement. For example, grinding of 304 stainless steel will result in the formation of a martensite phase on the surface, in which a crack may form when the surface is stressed in a dry hydrogen environment.

The strength level of a material is very important for resisting hydrogen embrittlement. Iron-based alloys with a ferritic or martensite structure have been restricted to a hardness of less than 22 HRC when exposed to atomic hydrogen. Steels having a similar strength often have different resistances to hydrogen embrittlement, since the heat-treatment process might have been different, resulting in different microstructures.

3.1.2.2 Process Factors

The hydrogen embrittlement resistance for materials prone to hydrogen embrittlement decreases with increasing hydrogen pressure. The rate of increasing severity with pressure is dependent on the alloy. For medium-strength steels, hydrogen effects are rarely encountered below 1,000 psi [14]. Above 1,000 psi and with other alloys, each case must be addressed separately.

A material's ability to resist hydrogen embrittlement decreases as the purity of the hydrogen gas increases. Several impurities will help inhibit hydrogen embrittlement; CO, CS_2, N_2O, and SO_2 are examples of inhibitors, but they are pollutants. Oxygen is another inhibitor, but it is undesirable due to safety implications. The effectiveness of these inhibitors decreases as the pressure of the system increases [15].

3.2 Hydrogen Embrittlement Literature Review

It has been shown that high-pressure hydrogen can seriously degrade the mechanical properties of many commonly used engineering alloys. During the late 1960s and early 1970s, extensive research was conducted to determine suitable materials for high-pressure hydrogen service.

Walter and Chandler [16] exposed various alloys to hydrogen gas to determine the alloys' susceptibility to hydrogen embrittlement. They exposed notched and unnotched cylindrical tensile specimens to 10,000 psi helium and 10,000 psi hydrogen. Triplicate tests were conducted in the hydrogen gas, while duplicate tests were conducted in helium gas. By comparing the ultimate strength and elongation obtained in the helium with the values obtained in hydrogen, they ranked the alloys as having extreme, severe, slight, or negligible embrittlement. A definition of each category and the materials in the categories are listed below:

(a) Extreme embrittlement (large reduction in notched and unnotched strength and ductility): high-strength steels and high-strength, nickel-base alloys.

(b) Severe embrittlement (considerable reduction in notched strength and unnotched ductility): lower strength steels, Armco iron, pure nickel, and the titanium-base alloys.

(c) Slight embrittlement (small reduction in notched strength): nonstable 300 series stainless steel, beryllium-copper, pure titanium.

(d) Negligible embrittlement: aluminum alloys, stable austenitic stainless steels, copper.

Table 16 provides complete results of the tests conducted in helium and hydrogen.

Fidelle et al. [17] performed experiments with disks shaped like rupture disks to determine a material's susceptibility to hydrogen embrittlement. They exposed disks to helium and hydrogen at a rate of 942 psi/min. The results of the helium tests were divided by the results of the hydrogen tests to determine susceptibility to hydrogen embrittlement. They grouped the materials into several categories similar to the categories described by Walter and Chandler. The categories and the materials follow:

(a) High or very high sensitivity ($pHe/pH_2 > 2$):

- Haynes 25
- 60Cr-40Fe
- Medium- and high-strength steels
- Badly processed, high - temperature, tempered steels
- Rolled or machined 304 stainless steel
- Electroformed nickel
- Annealed Ti-13V-11Cr-3Al alloy
- Ti-6Al-6V-2Sn ($\alpha + \beta$) alloy treated 1 hour at 750°C.

(b) Moderate sensitivity (pHe/pH_2 from 1.25 to 1.83):

- Pure rolled cobalt
- 0.18C ferro-pearlitic steel
- Rolled nickel
- Ti-6Al-4V ($\alpha + \beta$) alloy treated 1 or 2 hour at 800°C

(c) Little or no sensitivity (low pHe/pH_2):

- 7075-T6 Al
- Haynes 188
- Beryllium copper
- Austenitic stainless steels 304,[6] 316, 310
- A286 age-hardened austenitic steels

[6]Rolled and machined 304 stainless steel had a ratio of $pHe/pH_2 = 4.62$ due to the formation of martensitic stainless steel. Sensitization of stainless steel caused intergranular hydrogen cracking.

- 430 ferritic steel
- Ti-5Al-2.5Sn, Ti-6AL-6V-2Sn ($\alpha + \beta$) treated 2 hours at 860°C, quench and tempered 4 hours at 595°C.

Loginow and Phelps [18] ran tests using wedge-opening-loading (WOL) specimens to obtain a critical stress intensity level at which crack propagation spontaneously arrests (K_H). They conducted tests from 3,000 to 14,000 psi. For each combination of steel and hydrogen pressure, at least two and often five samples were exposed. The load on the sample was provided by a bolt, and the load exerted was recorded at least once a day. At the end of the exposure period, the test specimens were removed, broken open, and the initial and final crack lengths were measured on the fracture surface. K values (initial K_o and final K_t) were calculated according to the following relationship:

$$K = \frac{EBVC_3}{C_6\sqrt{BB_N a}}$$

where E = modulus of elasticity, B = total specimen thickness, B_N = net specimen thickness (in the notch), V= crack opening displacement, a = crack length, and C_3 and C_6 are functions of relative crack length.

The critical stress intensity in hydrogen (K_H) for a given steel was defined as the lowest K_t value obtained at the test pressure. Values of K_H for several material and hydrogen pressure combinations are shown in Table 17.

Through fracture mechanics, the critical stress intensity was used to calculate a critical size for a given shape of flaw under specific loading conditions. The crack shape and loading used was a semi-elliptical crack in bending. Table 17 shows the calculated critical flaws based on a maximum fiber stress equal to 40% of the measured tensile strength. For the various materials tested, the critical flaw depths ranged from 0.02 to 0.5 inches.

Loginow and Phelps concluded that the susceptibility of steels tested increased with yield strength. For steels with intermediate yield strengths (85 to 113 ksi), K_H tended to decrease as pressure was increased.

ISO 11114-1 [19] states that for 34 CrMo 4 quenched and tempered steel, the maximum ultimate tensile strength should be 138 ksi (950 MPa) when the steel is exposed to gases that can cause hydrogen embrittlement. The equivalent ASTM material for 34 CrMo 4 is ASTM A372 Grade F Class 70.

Alloys can also suffer accelerated fatigue crack growth rates in H_2 gas compared to air or inert gas. In order to determine if a material is acceptable for use in cyclic service, fracture mechanics must be used. Hydrogen accelerates the rate of fatigue crack growth, which varies with the magnitude of applied fracture stress intensity factor range, dK. At low values of dK, the effect is usually small or negligible. Higher values of dK can accelerate growth by 50 to 150 times the rate in an inert environment. Detailed crack growth data of fracture stress intensity factors for subject steels is not available.

In 2002 the hydrogen-producing companies developed a joint EIGA/CGA Document 121/04/E [20] pertaining to hydrogen transportation pipelines. The document covers design philosophy, equipment selection, cleaning, construction, operation and monitoring, and general protective measures. The document describes in detail which materials are suitable for pipelines operating below 3,000 psig. The primary materials discussed are carbon steels, microalloyed steels, and stainless steels. Nickel alloys are covered, but the document indicates that they are susceptible to hydrogen embrittlement and that they should be avoided unless the user verifies the alloy is suitable for hydrogen gas service by testing.

The document indicates that steels used in hydrogen pipeline service should have a maximum hardness of approximately 22 HRC or 250 BHN. This hardness limit is approximately equivalent to a tensile strength of 116 ksi (800 MPa). Welds should also have a similar hardness. To achieve an acceptable weld zone hardness, it may be necessary to use a lower strength steel (72.5 ksi). Pre- and postweld heat treatment may be another approach to lower the hardness at welds.

The most commonly used materials for pipelines are carbon steels. The common carbon steel piping grades such as API 5L X52 (and lower strength grades) and ASTM A106 Grade B have been widely used with very few problems [20]. Due to the low strength of these steels, they are resistant to hydrogen embrittlement. The Product Specification Level 2 (PSL2) for API 5L pipe is advantageous for hydrogen piping, since it incorporates desirable requirements such as minimum notch toughness energy, maximums for tensile strengths, and carbon equivalents. These requirements help ensure that base metal and weld hardness are maintained. A complete list of carbon steels used for hydrogen pipelines is provided below:

- ASTM A53, Type S Grade A
- ASTM A53, Type S Grade B
- ASTM A106, Grade A
- ASTM A106, Grade B
- ASTM A333, Grade 1[7]
- ASTM A333, Grade 6
- API 5L Grade A PSL1
- API 5L Grade B PSL1 and PSL2
- API 5L Grade X42 PSL1 and PSL2
- API 5L Grade X46 PSL1 and PSL2
- API 5L Grade X52 PSL1 and PSL2

EIGA/CGA Document 121/04/E also indicates that microalloyed line pipe in the API 5L grades has been used to transmit hydrogen gas at pressures exceeding 1,000 psi since the early 1990s. The document describes in detail what additional chemistry and property requirements should be added to the API 5L X42 and X52 specifications. The additional requirements for microalloys are summarized below:

(a) Sulfur content shall not exceed 0.01%.

(b) Phosphorous content shall not exceed 0.015%.

(c) Use of sulfide shape control agents such as calcium is permitted, but must be reported.

(d) Maximum carbon equivalent is 0.35.

(e) Concentration of any intentionally added element such as rare earths and any element that affects the carbon equivalent must be reported.

(f) Final ferrite grain size shall be ASTM 8 or finer.

(g) Samples of seam weld shall be examined for proper fusion.

[7]Toughness testing required by specification or PSL2 requirement.