

HIGH-PRESSURE CONFORMABLE HYDROGEN STORAGE FOR FUEL CELL VEHICLES

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Abstract

On-board high-pressure hydrogen fuel storage presents unique challenges for the commercialization of fuel cell-powered motor vehicles. Vehicle range, storage system weight, cost, durability, and compatibility of component materials are all key issues. Thiokol Propulsion, with support from the U.S. Department of Energy, is in the midst of a program to apply and extend its conformable composite pressure vessel capabilities to address these fundamental issues.

High-strength carbon fiber composite pressure vessels with plastic liners offer a lightweight solution to the high-pressure and low-permeation requirements for on-board storage. At the same time, the conformable storage concept addresses the range issue by more efficient packaging on the vehicle; conformable tanks can provide up to 50% more storage within available vehicle space compared to conventional cylindrical tanks.

Design, analysis, materials and process optimization, and tank fabrication and testing are being performed to ensure high-pressure capability and to minimize cost and material requirements. Extensive testing is in progress to select liner materials with the low hydrogen permeability and long-term durability required in the demanding motor vehicle environment. The latest safety and performance standards for high-pressure vehicle storage are being applied to ensure safe operation over the tank's 15-20 year design life. Pressure cycling, extreme temperature testing,

and damage tolerance testing are being performed on full-scale storage systems. The current status of these efforts will be described, along with prospects for commercialization of the technology developed under the program.

Introduction

The U.S. Department of Energy (DOE) has identified fuel cell-powered motor vehicles as a potential solution both to the nation's air quality problems and to its dependence on foreign fuel sources. A fuel cell combines hydrogen with oxygen from the air to produce electricity to power the vehicle, with water vapor as the primary by-product. A key issue is the availability of hydrogen on-board the vehicle. This can be provided either as compressed hydrogen, liquid hydrogen, or metal hydride storage. Alternatively, an on-board reformer can generate hydrogen from gasoline, diesel, natural gas, or methanol. Of these alternatives, compressed hydrogen storage is perhaps the best near-term solution due to its relative simplicity, rapid refueling capability, excellent dormancy characteristics, low infrastructure impact, and low development risk.¹

Despite these advantages, on-board high-pressure hydrogen storage is not without its challenges. The energy density of gasoline is approximately 12 times that of hydrogen compressed to 5,000 psi. Even with the high efficiencies projected for fuel cell vehicles (up to three times the current fuel efficiencies for internal combustion engines), a larger volume of storage is required for acceptable vehicle range.

With increased volume requirements, packaging of the fuel storage system becomes an issue. Liquid fuels such as gasoline and diesel can be stored in tanks that closely conform to the available space on the vehicle without reducing cargo capacity. For a gaseous fuel, the added requirement of pressurized storage constrains the geometry of the fuel tank. Because cylindrical tanks provide near-optimum pressure vessel structural efficiency, current practice employs one or more fuel storage cylinders. However, the cylindrical geometry often does not lend itself to efficient use of the substantially rectangular volumes available on the vehicle. In a rectangular envelope with an aspect ratio (width/height) equal to an integer, cylinders provide less than 75% of the available storage volume. For non-integer aspect ratios, this figure can be as low as 50%.

The twin issues of energy density and packaging efficiency combine to exact a significant range penalty for hydrogen-fueled vehicles. On the one hand, a lower energy density means that a larger volume of fuel is required for the same range as a conventional vehicle; on the other hand, the requirements of pressurized storage dictate that a smaller volume of fuel can be stored in the same envelope used for a conventional fuel tank. The most common solution to this problem in current practice is to locate additional cylinders in the vehicle's cargo areas, thereby sacrificing payload for range.

The weight of the storage system can also influence the vehicle fuel efficiency and handling characteristics. Plastic-lined, carbon fiber overwrapped pressure vessels currently provide the

most weight-efficient designs, but hydrogen permeation, sealing, and durability issues are critical to their successful application. In addition, cost is always a primary issue in the commercialization of vehicle technologies. As a point of reference, high-pressure compressed natural gas (CNG) storage systems account for approximately 50% of the cost premium for natural gas vehicles over their gasoline-powered counterparts.

In light of the above discussion, vehicle tankage represents a critical technology for fuel cell vehicles that should ideally be addressed at the earliest stages of vehicle design. Thiokol is currently working with DOE to address the most critical issues confronting high-pressure on-board hydrogen storage. This paper discusses design, material, and process considerations for hydrogen tanks, with particular attention paid to the development of conformable tanks for use with fuel cell vehicles.

The Conformable Storage Concept

The problem of maximizing on-board fuel storage is being addressed through the development of conformable pressurized tanks. Based on the physical principle that cylinders efficiently contain internal pressure via membrane response, the fundamental concept for the conformable tank consists of adjoining cylindrical segments with internal web reinforcements. The general approach is shown in cross-section in Figure 1. The result is a multi-cell pressure vessel. The number of internal cells is optimized for volume and pressure capacity and depends in large part on the aspect ratio of the envelope.

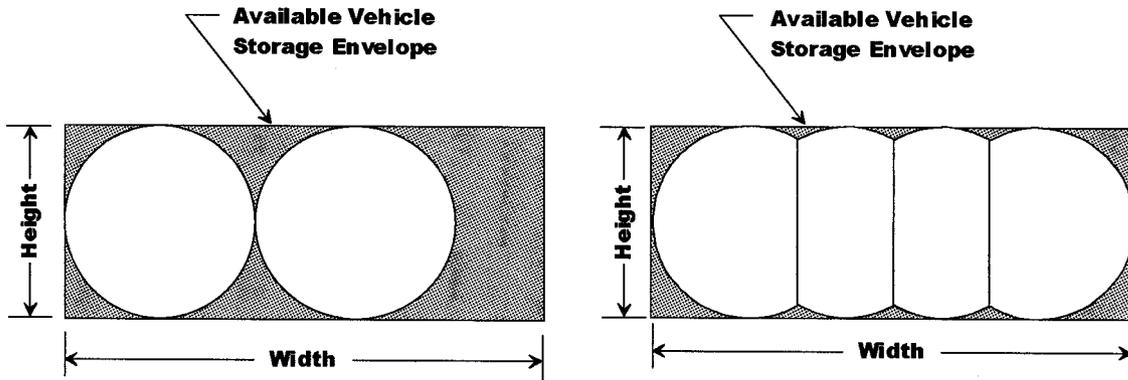


Figure 1. Cylinders vs. a Conformable Tank in a Rectangular Envelope

The expected benefits in volumetric efficiency of this conformable tank concept compared to multiple cylinders in a rectangular envelope are shown in Figure 2. Regardless of aspect ratio, the internal volume of the multiple cylinders never exceeds 70% of the envelope volume; except for aspect ratios close to 1.0, the conformable tank provides significantly increased storage volume.

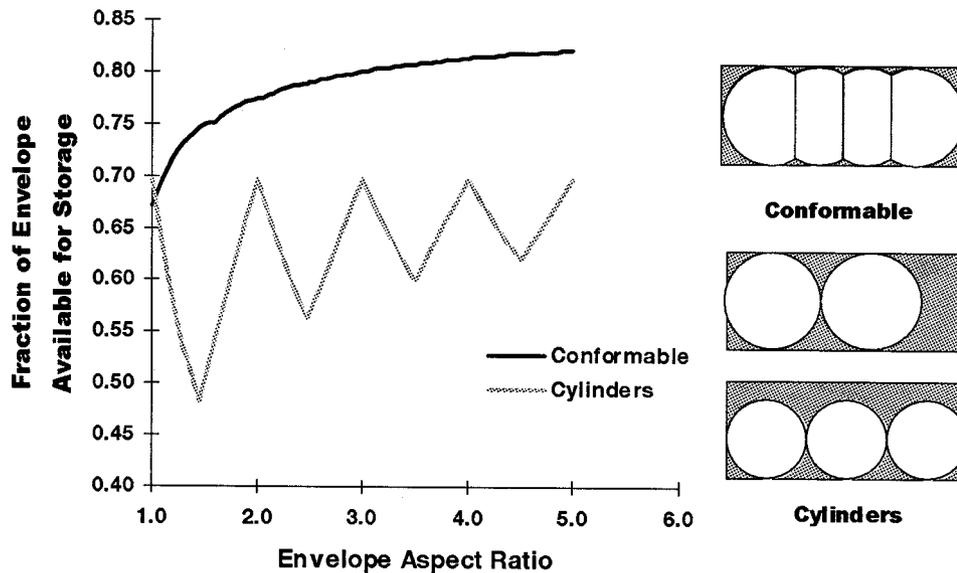


Figure 2. Comparison of Volumetric Efficiencies in a Rectangular Envelope

A Low-Pressure Application

Thiokol's initial application of the conformable tank concept for pressurized fuel storage was a full-scale welded aluminum liquefied petroleum gas (LPG, or propane) tank for Chrysler Canada, Ltd. The tank was designed, developed, and demonstrated to fit into the same location as the current gasoline tank on the Dodge Ram Van, replacing two conventional steel propane cylinders. The conformable tank increases the storage capacity by 40% and decreases the tank weight by 50%. The aluminum LPG tank when filled with propane weighs the same as the gasoline tank filled with gasoline. The tank was also easily integrated into the current vehicle assembly line. Figure 3 shows the conformable tank used in the Dodge Ram Van. This tank has a capacity of 30 gallons of propane and fits into a 36 in. x 23 in. x 14 in. envelope.

Thiokol has continued to improve aluminum conformable LPG tank technology by developing, demonstrating, and patenting an interlocking welded joint. This joint features extruded aluminum sections to reduce the loads carried in the longitudinal welds, and makes the welded material a secondary load-carrying member. ASME



Figure 3. Chrysler Conformable LPG Tank

certification was obtained for the basic interlocking welded joint. Several subscale prototype tanks were built and tested to demonstrate the technology, which was then moved to a full-scale 30-gallon LPG tank that fits into a 66 in. x 15.5 in. x 12 in. envelope. This tank was designed, developed, and demonstrated for Ford Vans with the Bi-Phase Technologies liquid propane electronic fuel-injection system. Several more configurations are in various stages of design and demonstration for large commercial customers (original equipment manufacturers or OEMs), indicating Thiokol's interest and commitment to this technology.

Extension to High-Pressure Applications

To sustain the higher service pressures required for conformable hydrogen storage, material, and process trade studies dictate substantial modifications to the design and construction of the conformable LPG tank. Due to the required increase in wall thickness, tank weight, cost, and fabrication limitations preclude an all-metal tank for hydrogen applications. These studies give a clear edge to carbon fiber composite material to meet structural, cost, weight, and volume requirements. The high strength-to-weight ratio and directional tailorability of continuous fiber carbon composites provides the potential for meeting tank requirements. The filament winding process was selected for fabrication of the tanks due to its proven history for pressure vessel construction as well as its capability for automation and avoidance of fiber discontinuities.

To prevent permeation of the stored gas through the structural composite, an impermeable liner is required which must also serve as the mandrel for filament winding. From both weight and cost considerations, a plastic liner molded using the rotational molding process was selected as the preferred approach. Rotational molding provides the dual benefits of relatively low-cost tooling requirements for prototype development as well as the capability for molding non-symmetrical shapes.

As with any significant material and process change, design modifications are required to exploit the advantages of the new material while avoiding its weaknesses. The tailorability of filament-wound composites offers the opportunity to minimize wall thickness by applying less material in the lower-stressed axial direction, and more in the higher-stressed hoop direction. However, the sharp corners at the transition between the outer cell walls and the internal webs (Figure 4) are not compatible with the filament winding process. Furthermore, the low through-thickness strength of the composite requires the virtual elimination of bending and peel stresses prevalent at the intersection between cells.

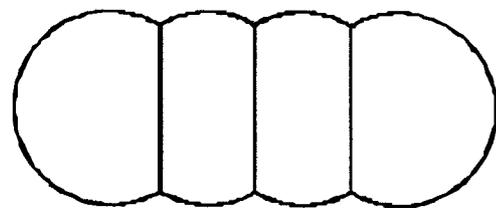


Figure 4. Metal Tank Configuration

Through application of design optimization and finite element analysis, along with consideration of winding requirements, a design and fabrication approach for the composite conformable tank was developed. Individual cells comprising the tank are wound with a combination of hoop and helical layers, after which the cells are fixtured together and a hoop overwrap is wound. It was found that, by carefully controlling the transition radius between the curved outer wall and the

flat internal web, bending and peel stresses at the joint could be virtually eliminated. The geometry of the tank cross-section is shown in Figure 5; a U.S. Patent² has been obtained for the design and fabrication approach. The cross-sectional geometry of Figure 5 results in a 2.5% decrease in internal volume capacity compared to the metal tank design (Figure 4); however, this is partially offset by the reduction in wall thickness made possible by the elimination of bending stresses.

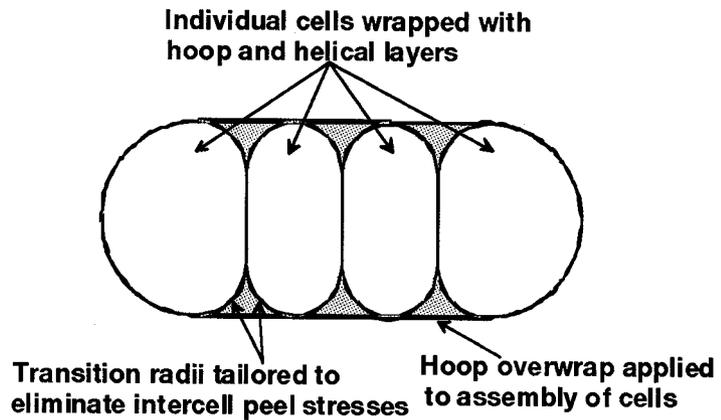


Figure 5. Conformable Tank Configuration

Prototype Fabrication and Testing

To demonstrate the structural capabilities of the resulting composite conformable tank design, a subscale, two-cell prototype design was developed. The prototype, pictured in Figure 6, fits into an envelope of 10.5 in. x 15.5 in. x 19 in. and has a capacity of 7.5 gallons; this is 50% more than the 5 gallon capacity of a cylinder within the same envelope. Mandrels for winding the individual cells were fabricated from sand mixed with a water soluble binder; the sand was cast and cured in a metal mold, and a thin layer of elastomeric material was applied to the surface of the mandrel for containing the pressurizing fluid. Following winding of the carbon/epoxy hoop overwrap and oven cure of the tank, the sand was washed out of the interior. The finished prototype tank had a weight of 23 lb, including 15 lb of composite.

Prototypes were fabricated using Toray's M30S carbon fiber with Thiokol's TCR[®] prepreg resin system. Considerable trial and error was required to develop filament-winding procedures for the non-axisymmetric conformable geometry. The long out-life of the TCR resin has proved invaluable in optimizing winding processes.



Figure 6. Two-cell Prototype

The target burst pressure for the initial prototypes was 8,100 psi, corresponding to a safety factor of 2.25 for a 3,600-psi service pressure tank. This is consistent with current qualification requirements for CNG fuel tanks³. A burst pressure of 8,820 psi was achieved, with failure

initiating in the overwrap and tank sidewalls. Although the current tank specification does not require a specific failure mode, Thiokol is designing all pressurized tankage to fail away from the dome ends to minimize variations in burst pressure. The successful burst test demonstrates that the composite conformable tank concept can meet the strength requirements for a CNG fuel tank. A subsequent prototype was designed to the higher pressure requirements for hydrogen storage, resulting in a burst pressure of 10,950 psi with structural failure also occurring in the hoop overwrap and cell sidewalls as designed.

To demonstrate the flexibility of the composite conformable tank to accommodate different geometric envelopes by the incorporation of interior cells, a three-cell prototype (Figure 7) was also developed. Although the two flat sides of the interior cell introduced significant design and fabrication challenges, burst capability in excess of the 8,100-psi target for CNG was demonstrated.



Figure 7. Three-cell Prototype

Composite Processing Issues

Filament winding the non-cylindrical tank geometry presents several processing challenges. The key to optimizing tank performance is to maintain fiber alignment and tension during wind and cure. When winding helical layers on individual cells, there is a tendency for the tows to slip, particularly at the transition between the dome and the flat side. This slipping is most pronounced when winding the internal cells with two flat sides. The tackiness of the TCR prepreg aids in reducing slipping compared with wet winding the cells. In addition, the cell geometry affects the severity of slipping; cell cross-sections with higher width-to-height ratios exhibit less slipping.

A catenary effect is also observed in winding the cell domes. This occurs when tows fail to lay flat on the domes, resulting in de-tensioning the outer fibers. Providing individual rollers on the delivery head has been effective in reducing catenary.

In the hoop layers on individual cells and the overwrap, there is a tendency for roping of the individual tows when traversing the flat sides. Modifications to the rollers have reduced this tendency. Care must be taken to avoid hoop fiber waviness and wrinkling both in the cells and in the overwrap.

Liner Material and Processing Issues

As previously noted, composite hydrogen tanks require a liner to form an impermeable barrier to the stored natural gas. The liner also serves as a mandrel for winding the composite wrap. In metal-lined tanks, the liner is designed to carry a portion of the pressure load; plastic liners, on the other hand, are designed as permeation barriers alone with the composite wrap carrying virtually the entire structural load.

Compatibility with the stored hydrogen gas is a critical consideration for liner material selection. Steel liners are subject to hydrogen embrittlement, which severely limits fatigue life. Aluminum liners, although commonly used in CNG storage, may be limited in their application to hydrogen storage; there are reports that aluminum ions can poison fuel cells, rendering them inoperable. Plastic-lined tanks offer significant weight advantages over metal-lined tanks. In addition, for the non-cylindrical geometry required of liners for conformable tanks, the flexibility of plastic molding processes afford substantial cost reductions compared to their metal counterparts. For these reasons, rotationally molded plastic liners are currently under development for the composite conformable hydrogen tank.

There are significant technical issues that impact the selection and development of plastic liners for hydrogen tanks, influencing cylinders as well as conformable systems. Clearly, the permeability of the liner material to hydrogen gas is a primary material selection criterion. The operating temperature range is also a key consideration in the choice of a material. The nominal design temperature range for the tank materials is -40° to 180°F^3 ; however, local temperatures in the vicinity of the inlet port may be outside this range, particularly during fast fill and discharge. The liner must also survive the cure process of the composite overwrap. A reliable, leak-free seal between the liner and metal end fittings, or polar bosses, is required for the life of the tank. Compatibility of the various materials (metal boss, plastic liner, and composite wrap) in the vicinity of the interface when subject to extremes of temperature and pressure over thousands of cycles is critical to the success of the design.

These issues are being addressed through the systematic integration of configuration design, analysis, material selection and characterization, and process control. AeroTec Laboratories (ATL, Ramsey, NJ) is teamed with Thiokol, with the primary responsibility for liner material selection and rotational molding of the liners. After an extensive survey of available polymers candidate liner materials selected for evaluation included polyethylene, nylon, PVDF, and PEEK. Key selection criteria included permeability, processability, material compatibility, cost, and mechanical properties.

Since hydrogen permeation is a key liner issue, coupon testing for permeation of candidate materials was performed at Southern Research Institute (Birmingham, AL) in a test facility specifically designed for this program (Figure 8). The facility permits coupon permeation measurements with a pressure drop of up to 5,000 psi at ambient, high, and low temperatures. The fixture also permits permeation testing of samples under biaxial strain. Based on this testing, Nylon was selected as the primary candidate for liner development, with polyethylene as a backup.

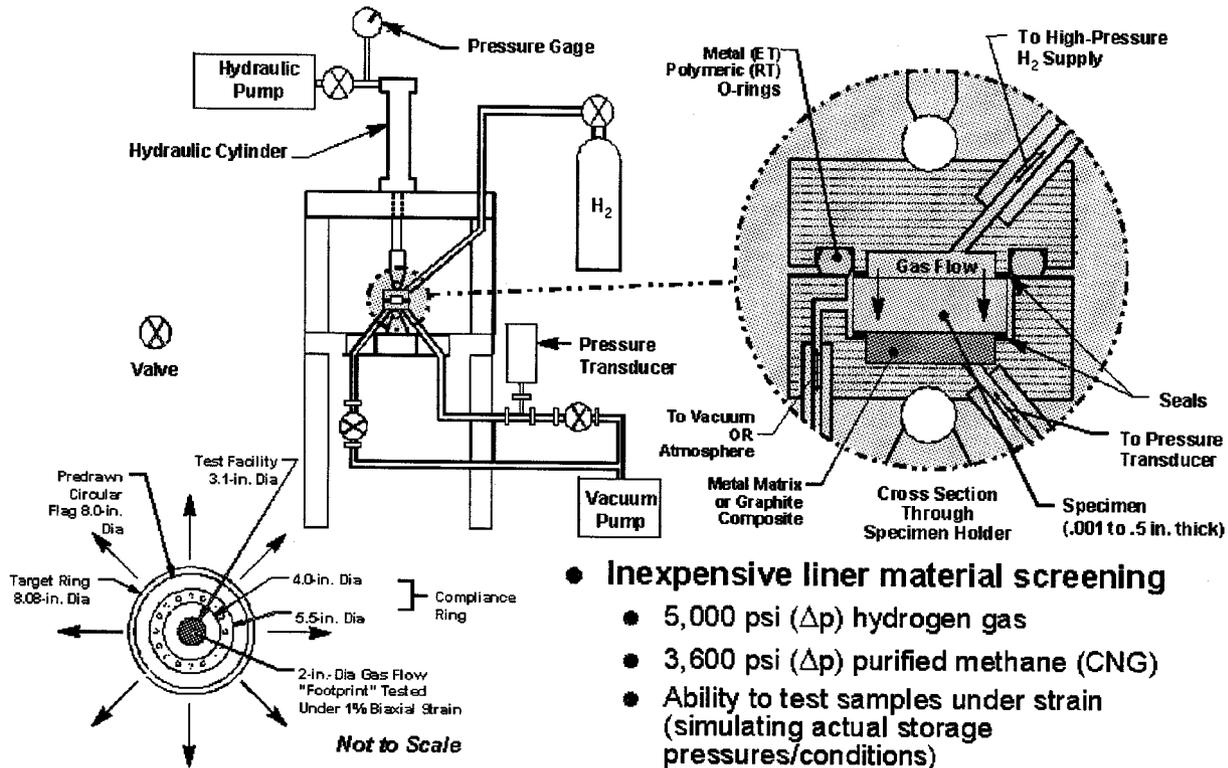


Figure 8. Schematic of Permeation Test Fixture at Southern Research

Options for the sealing configuration between the liner and polar bosses are being investigated at Thiokol. Critical issues include long-term durability under cyclic pressurization, and high- and low-temperature capability, particularly at the gas inlet region. An analog test fixture has been designed to permit rapid pressure cycling at high, low, and ambient temperatures for evaluation of sealing configurations and materials. In addition, material characterization testing, accelerated aging testing, and analytical modeling of liner and sealing materials and configurations are being performed to address life-cycle concerns. The results of all these efforts have been incorporated in the development of a full-scale liner for prototype testing.

Full-Scale Two-Cell Tank Development

Directed Technologies, Inc. and Ford Motor Co. provided storage envelope requirements for a full-scale hydrogen tank consistent with available space on Ford's P2000 advanced fuel cell vehicle. Based on this information, Thiokol designed a two-cell conformable hydrogen tank with overall dimensions of 12.8 in. x 21.2 in. x 27.9 in. The tank has a water volume of 17.9 gallons and a capacity of 3.4 lb of hydrogen at a service pressure of 5,000 psi. As an alternative configuration, it can be expanded to a three-cell configuration by incorporation of a center cell; this would increase tank width from 21.2 in. to 29.6 in., and the hydrogen storage capacity to 4.8 lb.

Based on this configuration, liner molds were designed and fabricated, and liners were rotationally molded by ATL with both polyethylene (Figure 9) and Nylon. Two tanks were fabricated with polyethylene liners using Toray's M30S carbon fiber with Thiokol's TCR prepreg resin system. The tanks were designed to a minimum burst pressure of 11,250 psi, consistent with a 5,000 psi service pressure and a 2.25 burst factor. Both tanks were hydroburst tested, and burst at 11,600 psi and 12,150 psi, respectively. As with the prototype tanks, structural failures initiated in the hoop overwrap and cell sidewalls (Figure 10).

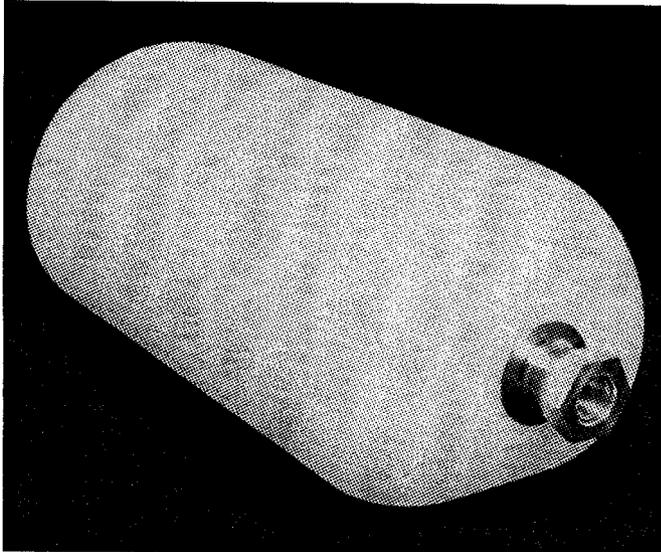


Figure 9. Full-Scale Plastic Liner

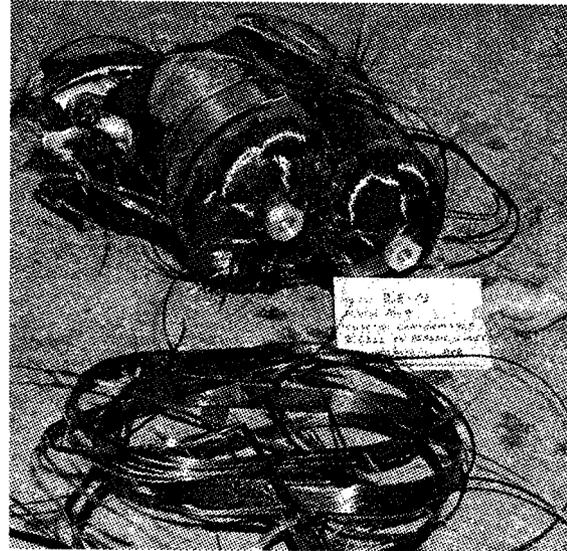


Figure 10. Full-Scale Burst Test

Refinements to the design and fabrication of the full-scale tanks are being developed to improve overall carbon fiber structural performance. Advanced analytical techniques are under development to more accurately predict structural response to pressure loading. This will lead to the ability to optimize the tank structure within the constraints imposed by the filament winding process.

Safety and Durability

The safe operation of the conformable hydrogen system over its 15- to 20-year life cycle in the demanding motor vehicle environment is of paramount importance. The current ANSI/ISA NGV2 industry standard³ for CNG vehicle fuel tanks addresses durability and safety issues through a comprehensive set of qualification tests. This standard has recently been revised to incorporate the results of field experience over the past several years.

There currently exists no comparable standard for hydrogen storage systems. The National Hydrogen Association has formed a Codes and Standards Work Group to develop safety standards for hydrogen storage containers, using the NGV2 standard as a point of departure. Prescribed safety testing under NGV2 includes hydrostatic burst testing; pressure cycling at ambient temperature; environmental testing to assess susceptibility to exposure to corrosive fluids and temperature extremes; flaw tolerance and drop testing to evaluate damage tolerance; bonfire

testing to evaluate the pressure relief system; and bullet impact testing to assess the potential for fragmentation failure.

Concurrent with the development of the full-scale conformable hydrogen system, selected qualification tests are being performed. This will enable the early identification and resolution of safety and durability issues during the development process. The issue of damage tolerance is of particular concern. Carbon fiber composites are known to be resistant to stress rupture and to attack by corrosive chemicals, but are susceptible to damage due to impact. The low flexural stiffness of the plastic liner adds to the concern over impact damage. Therefore, while high-strength carbon fibers and thin plastic liners minimize tank weight, damage tolerance is adversely affected. Preliminary testing has indicated areas of the tank that are particularly susceptible to impact damage. The need for, and potential development of, external protection from impact damage is being addressed as part of the development of the full-scale conformable system.

Economic Evaluation and Systems Analysis

Successful commercialization of the conformable hydrogen storage system depends on the trade-off between the cost of the system and the benefits that it offers. It is clear that, strictly on the basis of cost per unit of stored volume, a cylindrical tank will always be lower than a conformable tank. However, the potential for dramatically increasing vehicle range without reducing cargo capacity may offset the increased tankage costs. Although an exact cost estimate has not been generated for a specific vehicle envelope and design to date, a general rule of thumb is that one could expect a 30 to 50% increase in cost over cylinders for a 30 to 40% increase in fuel capacity for conformable storage systems.

Rather than simply comparing tank costs, it is important to consider the total installed costs of the fuel storage system when comparing cylinders to conformable tanks. If a single conformable tank can replace two or more cylinders, savings are realized in labor costs, mounting brackets, pressure relief devices, and manifold tubing. Experience with the Chrysler conformable LPG tank indicates that the installed cost per unit of storage for the conformable system can be comparable to cylinders. A significant goal of the development program for conformable hydrogen systems is to fully exploit potential savings in system integration to reduce total system costs. To this end, detailed cost models are being developed concurrently with the technical development efforts.

Material and process improvements are also being developed in an effort to reduce the cost of both cylinders and conformable tanks. Prepreg winding offers the capability for faster winding speeds and significantly reduced material waste and cleanup compared to wet winding. In addition, new, low-cost commercial grade carbon fibers are currently being pursued and evaluated in conjunction with the primary carbon fiber suppliers in an effort to reduce the most significant component of carbon composite tank cost.

Conclusions

Conformable high-pressure hydrogen storage has the potential for addressing tank packaging and range issues for fuel cell-powered vehicles. These unique designs will offer vehicle designers the

flexibility to package the desired amount of fuel into areas of the vehicle not typically suitable for storage. The fundamental composite and liner design and fabrication approach has been demonstrated to satisfy basic structural requirements. Additional challenges remain to optimize tank performance with respect to cost, weight, and durability requirements. Current programs at Thiokol are addressing these challenges with the goal of commercialization of high-pressure conformable tank technology.

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