III.7 Inexpensive Delivery of Cold Hydrogen in High Performance Glass Fiber Pressure Vessels

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Subcontractor:
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Project Start Date: April 30, 2005
Project End Date: September 30, 2012

Objectives

- Quantify economic performance advantages of cold glass composites.
- Develop delivery trailer capable of realizing most of those advantages.
- Demonstrate this delivery approach can surpass all significant technical risks.

Technical Barriers

This project addresses the following technical barriers from the Delivery section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(F) Gaseous Hydrogen Storage and Tube Trailer Delivery Costs
(G) Storage Tank Materials and Costs

Technical Targets

This project is expected to meet several of the 2012 DOE technical targets for hydrogen delivery. It addresses all the key targets relevant to a hydrogen infrastructure between centralized production and the filling station. Capacity targets it meets include a delivered hydrogen capacity over 1,000 kilograms, well above the 700 kilogram 2012 target, and delivered hydrogen pressure of 7,000 psi. The end-to-end cost of delivered hydrogen is minimized by a projected trailer capital cost below $140 per kilogram delivered. This detailed estimate for delivery trailer capital cost allows cold, compressed, glass composite pressure vessel delivery trailers to compete with and ultimately to beat the alternatives in minimizing delivery cost from identical hydrogen sources into identical vehicular hydrogen storage.

Table 1 shows that project's estimated capital costs (on a per-kilogram delivered basis) exceed DOE's Multi-Year Program Plan technical targets. Detailed capacity modeling shows both 200 K and 140 K designs can even surpass the 1,000 kg capacity target for 2017 while continuing to meet the capital cost target. Table 1 summarizes much more detailed costs from component-level modeling (based on DOE's H2A Delivery model) of our project's approach. The same detailed results show our approach's superiority over other compressed hydrogen delivery alternatives. Colder designs can deliver far more hydrogen in a volume limited trailer envelope. (Our project presumes an International Organization for Standardization standard twenty-foot equivalent unit shipping container.)

TABLE 1. Progress towards Meeting Technical Targets for Hydrogen Delivery

Characteristic	Units	2012 Targets	LLNL 2012 (Projected Cost)
Delivery Capacity	kg of H_2	700	1,000
Operating Pressure	psi	<10,000	7,000
Purchased Capital Cost	$/kg of H_2	<$428	$140

Accomplishments

- Designed a pressure vessel suitable for affordable development at full-scale which enabled the reduction of all technical risks when incorporated into a trailer capable of delivering hydrogen at a cost below $1.00 per kilogram (not including forecourt expenses). This design is proceeding to prove this delivery concept will work both technically and economically. The effort is on schedule, and makes use of prior Spencer-proprietary materials testing efforts and licenses.
- Subscale S-Glass fiber wound pressure vessels were successfully built and burst at 300 and ~170 K, failing within 2% of design at 20,000 psi.

- The first batch of full-scale S-Glass fiber vessels were built, demonstrating the manufacturability of all high technical risk trailer components and processes.
- Several novel manufacturing problems were found and fixed to achieve these results. Along the way various materials properties were investigated, including tensile strength, toughness, and thermal shock tolerance, and some beneficial changes were made to proprietary formulations.

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Introduction

We are currently conducting both research and development efforts aimed at delivering hydrogen by truck. Our system concept relies on composite pressure vessels to minimize delivery cost through an optimized combination of hydrogen properties and fiber characteristics. Preliminary H2A-based analysis indicated that our system concept has the potential to greatly reduce the cost of hydrogen delivery by taking advantage of increased strength in inexpensive glass fiber proven to be available at cold temperature.

LNLL embodied this concept to minimize the total cost of hydrogen delivery by reducing the cost of tube trailers. Information gained from ongoing experimental research is being applied to a full-scale hydrogen pressure vessel development program.

Approach

- Optimization of operating pressure and temperature: Today's hydrogen delivery technologies (compressed and liquid) are restricted to single points at extremes of the hydrogen phase diagram. Minimum cost of delivering hydrogen from centralized production (or pipelines) to filling stations can be found by exploring the entire phase diagram. Pressures and temperatures that minimize cost attain high storage density without the heavy thermodynamic penalty of hydrogen liquefaction. Cold hydrogen at high pressure (between ~140 K and 200 K, at up to 10,000 psi) appears most promising.
- Use of inexpensive glass fiber: Glass fiber is typically considered an inexpensive low-performance alternative to carbon fiber. However, glass fiber achieves higher strength in low-temperature operation, strengthening as much as 80% as it is cooled down from 300 K to 70 K. Our project confirmed this effect on one of the least expensive glass fibers in 2008, and found legacy published data on an even less expensive glass where the effect was even stronger. Cold glass fiber should maximize delivered hydrogen per dollar of delivery cost, maximizing capacity of the truck's trailer. The combination of higher density reducing trucking labor, fuel, and capital expense with direct reductions in trailer capital cost more than compensates for the increased capital and energy costs of refrigeration and compression (as demonstrated above in Table 1), keeping delivered cost projections well below $1/kg-hydrogen (excluding forecourt expenses).

Results

Experimental Program

LLNL is developing a hydrogen delivery solution that can function at various temperatures and pressures. However, design, manufacturing processes, and capital plus operating costs of this solution depend on currently unknown properties of fibers, plastics, and processed surfaces. The single most important unknown is the fiber strength versus temperature. Even if currently available glass fiber types show only half the cold strength gain LLNL has found in legacy data, the cold glass pressure vessel delivery option minimizes delivery cost per kilogram of hydrogen.

Last year we identified legacy data that shifted our projection of delivery-cost-optimal trailer storage temperature down to ~140 K. (At temperatures somewhat lower than this, the increasing costs of refrigeration would not be repaid.) Since 2006, LLNL has been experimentally pursuing the collection of new cold strength data for all the grades of commercially available glass fiber. In 2008, LLNL data confirmed experimentally that the cold strength effect was sufficient to give our concept the lowest projected hydrogen delivery cost. Since that time, it has become clear that neither proven plastic liners nor metal liners can serve as the vital hydrogen containing layer of a composite pressure vessel that would advantageously operate at cold enough temperatures.

Spencer Composites is collaborating with LLNL in pursuit of a fundamental advance in the manufacturing cost of large composite structures, including pressure vessels. That advance relies on the properties and manufacturing process savings implicit in a new category of plastics. This category will be termed "ROMP" catalyzed, which stands for Ring Opening Metathesis Polymerization. Spencer Composites intends to apply ROMP plastics in numerous aerospace and energy applications. Among the features of this advance are low thermal expansion and full properties retention at temperatures as low as 77 K. These plastics are expected to form both liner and matrix of a new generation of inexpensive pressure vessels. LLNL has sized vessels built with these advanced plastics for low temperature hydrogen delivery trailers.

Experimental research is underway to measure unknown properties of available cold glass composites. Additional experimental research centered on the toughness of high-performance ROMP plastics at low temperature is underway as a direct component of this project's development effort.

Subscale Vessel Development

Figure 1 shows several of the 3" diameter experimental test articles prototyped to affordably determine unknown properties and improve formulations. Roughly 40 of these articles began prototyping, and roughly 25 survived enough of the ~18 steps in a minimal process sequence to become hydroburst test articles. Another three process steps were added to the most successful prototypes, while three articles received post-prototyping steps intended to improve permeation. All 18 were burst tested to gain feedback for manufacturing process improvement. One of these was burst at ~170 K in acetone cooled by dry ice, a process Spencer had used before, while LLNL is setting up to burst with liquid nitrogen fill.

FIGURE 1. Subscale Pressure Vessels: 3" diameter tests articles photographed in a number of experimental configurations. In the photograph at top left, a metal-coated, glass composite vessel is shown at left with stainless steel bosses configured for permeation tests, next to a bagged advanced plastic composite matrix vessel, and a view into the blown out bottom of a failed vessel. In the photograph at lower left, a liner spin cast from advanced plastic awaiting filament winding and boss installation at its top end appears next to an attempt to use these 3" articles to test the strength of the liner only, inside a partial-coverage winding of graphite epoxy composite. The photograph at right shows the bottom of a sectioned, completed, and tested to failure vessel which has been sliced to examine failure in its boss-side dome form the inside, after "dog bone" tensile test specimens have been cut out of its side with a water jet.

The decision to proceed with subscale development was obvious given the development cost of full-scale tooling. Several iterations in 3" spin casting tools were conducted in Fiscal Year (FY) 2009. The small size proved convenient for storing and displaying the results of testing. However, the small size implied a factor of roughly 7 scale-up to transfer into a full-scale process. It also made it more difficult to observe defects, and imposed tolerances too tight to prototype Spencer's full-scale pressure vessel seal design.

Spencer has a proven seal design of the right size to specify the 3" liner tooling for ROMP plastic liner molding. That design was known to seal to 18,000 psi, and relied on a spring-compressed Teflon$^{\circledR}$ C-ring (similar in cross section to a square 'O-ring') whose excessive thermal coefficient of expansion and tendency to plastic deformation made it unlikely to survive thermal cycles below 200 K. Such a compromise turned out to be warranted because the full-scale seal design (which was computationally tested to withstand worst case thermal and pressure cycling to 77 K and 25,000 psi without exceeding 20% of the elastic limit of the advanced plastic) could not realistically be scaled down. Ultimately the expedient C-ring seal withstood 22,000 psi before leaking.

Three of the best 3" test articles survived hydroburst to greater than 20,000 psi, with one of these being nearly thermally equilibrated at ~170 K before its seal leaked. The winding design for the ambient test article that failed at slightly over 20,000 psi burst within 2% of its design value. The low temperature result did not fail structurally. Its leaking seal did not re-seat well enough to try a second cycle, but its strength exceeded 23,000 psi, at least 15% higher than the same design and fabrication process at ~300 K. In the course of the subscale test program, both graphite and S-glass fibers were wound with epoxy and ROMP catalyzed plastic matrixes. The two successful articles just mentioned were both made with epoxy matrix S-Glass.

Before achieving these successful subscale results, the development process had to go back to process development for ~4 months after the 2009 Annual Merit Review. An apparently well-formed ROMP liner that passed all visible and thickness inspections failed at unexpectedly low pressures in the earliest subscale burst tests. Cracks that were not apparent in the ROMP liners before they were wound were obvious in the end dome region. Some of these premature failures occurred at pressures that could not have strained liners in the regions that cracked more than 0.5%. Yet the same ROMP material, processed into flat specimens and cut into "dog bone" tensile test articles was stretching ~18% before failure! Figure 2 shows some of the expedients it took to solve this problem.

Over 60 round plaques of a standardized shape were cast with different formulations of ROMP plastic and broken by dropping an impactor from an ASTM-specified toughness test apparatus built to debug this problem. A large number of hypotheses emerged for what our project called the "anomalous toughness" problem, and a full matrix of seven plaques times seven formulations would not suffice to sort these out. Tensile test "dog bone" specimens were broken at room temperature and roughly dry ice temperature for original and candidate fix formulations. Ultimately our team decided that a slight decrease in strength was a good tradeoff for significant improvement in toughness, and the improved formulation liners sailed trough burst testing without cracks. Subsequent employment of the 3" subscale vessel test articles has been restricted to testing with less wound fiber in order to achieve strains anticipated in the full-scale design, since the materials we have developed withstood their worst case design stresses.

Full-Scale Development Program

A first generation of tooling for full-scale liner production was assembled in FY 2009. That tooling realized the liner and boss details that build a calibrated finite element design, which combines with already-measured ROMP plastic strengths to keep all structural components well within their elastic range during independent pressure cycles to 22,500 psi (maximum design burst pressure) and temperature cycles from 77 K to 365 K. LLNL enabled this design in 2007 by performing preliminary pressure optimization in order to size vessel diameter. This design resulted in an economic optimum of 8,000 psi maximum expected operating pressure (MEOP) for the delivery trailer at the time that tooling diameter was specified in May of

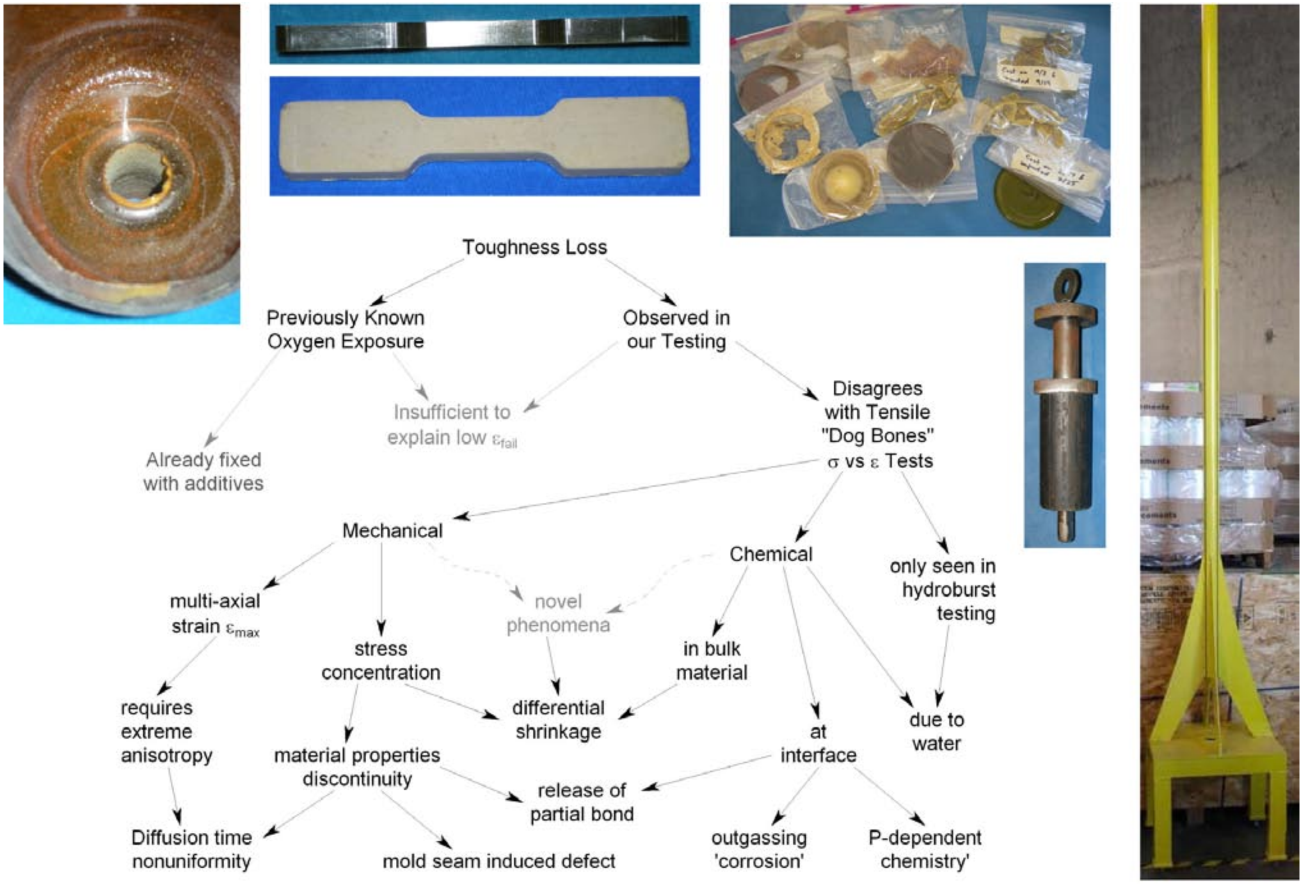

FIGURE 2. Toughness Loss Materials Research: A tree diagram of hypothesized toughness loss mechanism is surrounded by photographs of experimental hardware. Photographed clockwise from the upper left are a sliced interior view of a failed liner in a prematurely burst 3" vessel showing circumferential cracking, "dog bone' tensile test specimens in front and side view in different formulations, a collection of broken and bagged toughness test plaques, the variable weight drop test impactor, and the ASTM toughness test drop rig that impacts plaques.

2009. LLNL also made sure this full-scale design is robust enough to fit in our container when wound with sufficient fiber to preserve "Safety Factors" of 2.25 at any MEOP from 1,500 psi to 11,500 psi. This robustness allows the same tooling to minimize cost for stationary hydrogen storage applications (including filling station storage and renewable energy buffering).

The tooling for ROMP catalyzed spin casting is highly affordable compared to tooling for other plastic articles as big as our full-scale design. This affordability was put to the test through a series of mechanical redesigns. Conventional rotational molding tooling is very similar in degrees of freedom, but needs to operate inside an oven, which means every potential change must be designed to withstand thermal cycling. Several rounds of drive alignment changes were needed just to achieve sufficient rotational symmetry in molded liners, and those drive mechanism alterations could be bought out of catalogs because they need not run at high temperature. Other unexpected phenomena emerged at full-scale that could not have been noticed at the 3" subscale, and affirmed our strategic assertion that only full-scale development proves that a technology really works.

The most alarming encounter our development effort had on the way to achieving its Go/No-Go milestone of full-scale component production came the first time a full length liner emerged from the tooling. The surprise is shown in Figure 3 – the full length wasn't full length even though two shorter length vessels had been built from liners made 'successfully' in the same tooling. Full diameter turned out not to be full-scale because of the effect of the greater mass of plastic resin that had to be introduced and spun up to mold the same diameter liner at full length. The part that emerged had an incomplete cylindrical section because most of the resin had solidified in a flat-topped lump at the bottom of the mold before it had a chance to spin up. Yet this same formulation had a 20 minute "pot life" in the 3" tooling, and it didn't take even a minute to spin up the tool. The answer has to do with the rate of catalysis that solidifies the ROMP resin, and the reconfiguration of the tooling (to introduce the resin progressively after the tooling was already spun up) rendered subsequent liners acceptable.

Trailer Integration Design and Field Test Program

Figure 4 shows our first batch of full-scale pressure vessels. The first produced was a 'shortie' with a 5" cylindrical section of the liner and S-Glass epoxy overwrap. It was designed to burst at 18,000 psi,

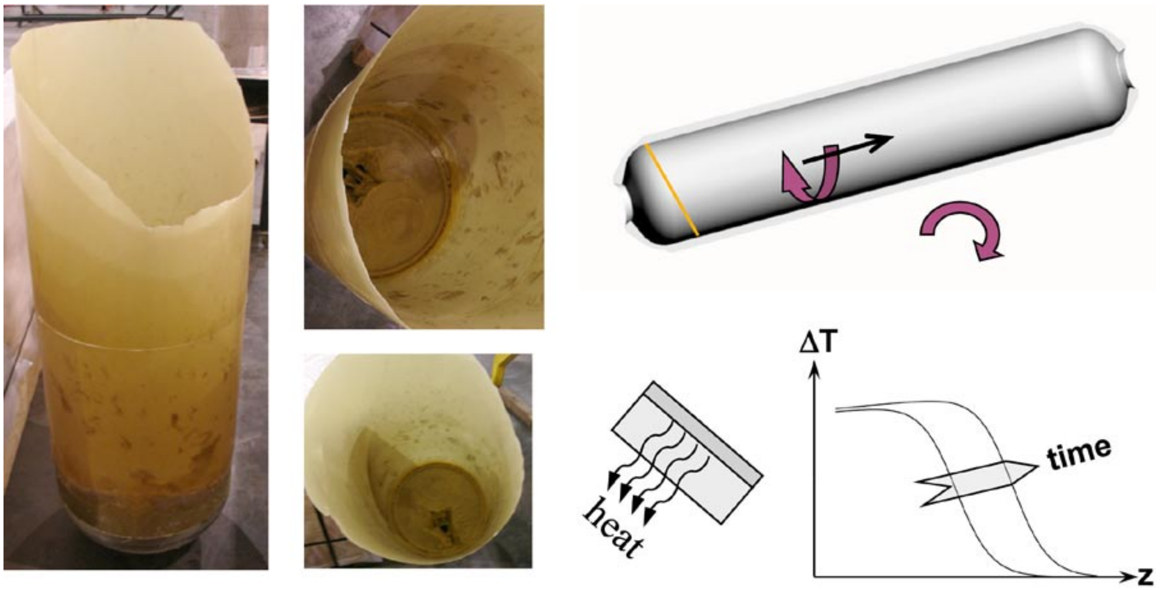

FIGURE 3. Surprising Failed Liner Prototype: Photographs at the left show the incomplete cylindrical section that emerged from the first attempt to cast full-length, full-diameter liners. The same mold had previously cast liners successfully with 5" and 35" long cylindrical sections, but this first attempt to achieve full length led to an unpleasant surprise when the mold was opened. Nearly 100 pounds of plastic resin had solidified in the lower end of the mold before it was spun up. The sketch at the upper right shows a notional cross section of the full-scale, spinning mold, which rocks similarly to conventional rotational molding. The additional mass was almost triple that used to cast the cylindrical section on this molds previous use, and it must have solidified in a far shorter time than the 20 minute pot life of the catalyzed resin observed in subscale tooling. Sketches at lower right show the wave of catalysis sweeping though the wall of spun liquid resin, where evolved heat is removed by thermal diffusion. This explains the faster solidification of the 100-pound puddle observable at the bottom of the failed article. Success in subsequent full-length liner molding operations was enabled by progressively introducing resin.

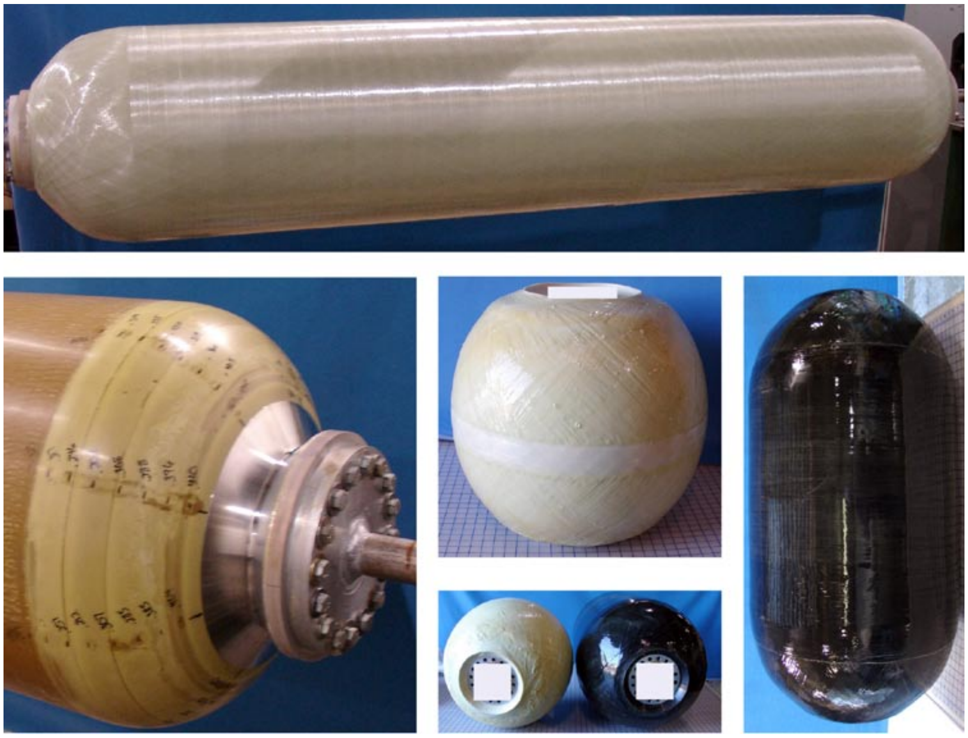

FIGURE 4. Full-Scale Test Articles: The photograph at top shows the first completed full-scale, full-length pressure vessel developed by this project, wrapped with S-Glass fiber in an epoxy matrix, over a ROMP catalyzed plastic liner sealed into 316L stainless steel bosses at either end. The photograph at lower left shows that vessel's liner dome with thickness markings reflecting quality control of its molding, mounted on one end boss and bolted to a removable winding spindle. Middle and right photographs in the lower row show the first (short white) and second (48" long, graphite composite wound) test articles produced on the same tooling.

and was produced before slight eccentricities in the tooling spin axis drive were corrected. It therefore had asymmetric liner thicknesses, which were not noticed in the customary inspection (with bright internal lamination) before wrapping. This unit was intended to survive as a souvenir small enough to keep after being exercised as a seal test unit through pressure cycling and then subsequent thermal cycling. Its relatively small size makes it less expensive in time and refrigerant to cycle. In hindsight, it was too short to be a fully representative example of the stresses in a wound high-pressure vessel of this diameter because the spreading out of the transition between cylinder and dome that accompanies the fiber trajectories of an 18,000 psi burst design built from S-Glass meant that it has no truly cylindrical section far enough from the domes to obtain the most accurate strain gage readings.

The other short pressure vessel that appears in Figure 4 was almost 48" from boss to boss, and proved that finished liners could be extracted from the mold. Even though drive eccentricity had been fixed, there were still many pounds of liquid resin inside the mold before it spun up, and this eccentric mass was enough to cause one spin axis bearing to seize. In order to prevent this partially solidified liner from slumping, its molding was completed on a large lathe. Bubbles in that liner were 'fixed' by a subsequent spin in the lathe, but this part was not considered to have full quality, and was intended to be a permeation rig debug article and showpiece. Given these intended roles, it was wrapped with 700 ksi graphite fiber epoxy composite to illustrate the relevance of this technology for vehicular applications. The third article shown was full length, making use of the progressive resin introduction step described above, and was the first to have a full-scale S-glass fiber overwrap (with epoxy) matrix, thereby completing the promised milestone.

Building more of these full-scale test articles is only the beginning of a test program that is intended to remove all significant technical risks form this advanced, inexpensive pressure vessel technology. That test program has been planed to make the best use of the extended development timeline of 4 years, culminating with cycling of pressure and temperature as its final milestone. All of the risk reduction testing we have planned was presented in our FY 2009 progress report. In the last year, a test site has been selected for the dangerous permeation and cycle testing. We are in the process of designing and building a second generation transport case capable of carrying full-scale and full-length test vessels weighing up to 900 pounds. (Our current heaviest design weighs 650 pounds, but it is conceivable that more fiber can be wound on liners from this tooling to burst over 36,000 psi.) This next generation of case will be gas tight to sense hydrogen permeation and ventilate with chilled nitrogen.

Complete plans for addressing the remaining significant technical risks in our vessel technology will be complete by mid-FY 2011 with the exercise of full-scale vessels in the new transportable case. This case raises the issue of shifting vessel mass during transport, which is already undergoing preliminary design to handle atypical mounting requirement of these vessels inside our delivery container design. The cold strength effect enables vessels that use it to stretch perhaps twice as much as conventional plastic lined (Type IV) composite pressure vessels, and as much as 8 times more than metal or Type III pressure vessels. The accommodation of this stretching must be accompanied by the ability with withstand significant vehicle acceleration loads in a design that favors spreading these external loads over several bands around each delivery vessel.

LLNL's diameter specification and length margin budgets provide sufficient room for this design to expand in routine service without its vessels touching, even assuming the most extreme likely cold strength effect. One other unavailable component is necessary to make these geometric budgets feasible, and its technical risks are moderate. Our team has begun designing and prototyping a hollow tile (made from cast plastic and metal foil) to provide planar vacuum insulation in a thin form inside the delivery container's walls. A second generation of trailer thermal management design indicates that two layers of such tiles could provide more than seven days of durability for a stranded delivery trailer before hydrogen would need to be vented to avoid any safety decrease due to diminished cold strength. Variants of this design have been modeled for three layers with nearly three weeks durability, and for single cylindrical tank delivery configurations. A development pathway that can affordably prove single tank configurations is also being considered for a follow on development effort that can make best use of the next generation of (larger) full-scale tooling.

Conclusions and Future Directions

- Subscale S-Glass fiber wound pressure vessels were successfully built and burst at 300 and ~170 K, bursting within 2% of design at 20,000 psi.
- The first batch of full-scale S-Glass fiber vessels were built, demonstrating the manufacturability of all high technical risk trailer components and processes.
- Several novel manufacturing problems were found and fixed to achieve these results. Along the way various materials properties were investigated, including tensile strength, toughness, and thermal shock tolerance, and some beneficial changes were made to proprietary formulations.
- Designed a thermal management system for containerized and single cylinder delivery trailer that preserves trailered hydrogen for more than a week before needing to vent. This effort included planning an affordable development pathway for single large pressure vessel delivery.
- Future work culminates development of full-scale pressure vessels with a test program that eliminates all unique risks of this technology. Planned proof-of-concept tests include hydrostatic burst of a statistically significant number of full-scale vessels, pressure and temperature cycling of one such article before bursting it, and hydrogen permeation testing. A site has been selected for these dangerous tests, and will be prepared to safely mitigate the explosion risks of testing experimental vessels filled with hydrogen.
- Materials research and further development efforts are planned to extend our improved understanding of toughness to lower temperature, and to improve permeation of hydrogen through ROMP materials with mitigation layers.
- Design and modeling efforts planned for our future trailer integration efforts include the full specification for insulating tiles containing thin vacuum layers, suspension for vessels that isolates them from worst case trailer acceleration loads, and suspension design that also isolates the container and its insulation from the significant length and diameter expansion under pressure expected due to the cold strength effect on glass composites.
- Spencer Composites and other industrial partners will assist LLNL's formulation of realistic production cost models. In future years we anticipate adding a tube-trailer-integration-capable subcontractor to form a team of industrial partners with the capability and incentive to prototype advanced hydrogen delivery trailers.
- Future work includes initiatives to prepare federal regulators in other agencies to consider cold hydrogen systems pressure safety, funding initiatives with potential Department of Transportation collaboration to demonstrate a full hydrogen delivery container in the field, and initiatives to partner with gas vendors.

Special Recognitions & Awards/Patents Issued

1. Storage of H2 by Absorption and/or Mixture within a Fluid, Gene Berry and Salvador Aceves, US Patent 7,191,602, March 20, 2007.

2. Four patents in process.

FY 2010 Publications/Presentations

Publications in Books and Technical Journals

1. **Delivery of Cold Hydrogen in Glass Fiber Composite Pressure Vessels,** Salvador M. Aceves, Andrew H. Weisberg, Francisco Espinosa-Loza, Elias Ledesma-Orozco, Blake Myers, International Journal of Hydrogen Energy, Vol. 34, pp. 9773-9780, 2009.

2. **High-density automotive hydrogen storage with cryogenic capable pressure vessels**, Salvador M. Aceves, Francisco Espinosa-Loza, Elias Ledesma-Orozco, Timothy O. Ross, Andrew H. Weisberg, Tobias C. Brunner, Oliver Kircher, International Journal of Hydrogen Energy, Vol. 35, pp. 1219-1226, 2010.

Invited Presentations

1. Hydrogen Storage in Cryogenic Capable Pressure Vessels, Salvador Aceves, Invited Presentation, **Spanish National Hydrogen Research Center**, Puerto Llano, Spain, March 2010.

2. Hydrogen Storage in Cryogenic Capable Pressure Vessels, Salvador Aceves, Invited Presentation, **International Conference on Hydrogen Production and Storage**, Istanbul, Turkey, June 2010.

3. Hydrogen Storage in Cryogenic Capable Pressure Vessels, Salvador Aceves, Invited Presentation, **AICHE Topical Symposium on Hydrogen Production and Storage**, Salt Lake City, October 2010.