III.12 Inexpensive Delivery of Cold Hydrogen in High Performance Glass Fiber Composite Pressure Vessels

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Objective

- Build and test high-performance vessels for delivery truck applications.
- Test performance of glass fiber at low temperature.

Technical Barriers

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

(F) Gaseous Hydrogen Storage and Tube Trailer Delivery Cost

(G) Storage Tank Materials and Costs

TABLE 1. Progress towards Meeting Technical Targets for Hydrogen Delivery in Tube Trailers

Hydrogen Delivery in Tube Trailers Characteristic	Units	2012 Target	LLNL trailer (projected)
Tube trailer delivery capacity	kg	700	1,000
Tube trailer operating pressure	psi	<10,000	7,000-10,000
Purchased capital cost (700 kg trailer)	$	<$300k	$200-300k

Accomplishments

- Successfully demonstrated process to produce subscale (3” diameter) liners from new plastic.
- Designed and analyzed (finite element) full-scale (22” diameter) vessel dome and boss using verified codes.
- Demonstrated low temperature strength of new plastic that remains elastic over temperature and pressure cycles.
- Built full-scale tooling to implement finite element analysis design (in liners of several lengths).
- Designed new specimen profile and clamp fixturing to vanquish multiple failures per specimen in cold strength tensile experiments.

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Introduction

Delivering hydrogen in today’s low capacity compressed hydrogen tube trailers is expensive. Substantial cost reductions appear possible with development of advanced pressure vessels and a broadened range of thermodynamic conditions under which hydrogen is trucked and delivered. We have identified and confirmed synergies that promise to considerably reduce the cost of hydrogen delivery and dispensing to a vehicle. Our ongoing experimental project will test the practical feasibility of our proposed approach to inexpensive hydrogen delivery.

Approach

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:

- **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 (140-200 K and 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 strengthens as much as 100% as it is cooled down from 300 K to 140 K. Cold glass fiber maximizes delivered hydrogen per dollar by increasing trailer capacity. The combination of higher density reducing trucking labor, fuel, and capital expense more than compensates for the increased capital and energy costs of refrigeration and compression, keeping delivered cost projections below $1/kg-$H_2$.

Our Fiscal Year 2009 effort is proceeding to prove that this delivery concept will work both technically and economically. Information gained form the experimental research will be applied to an ongoing full-scale hydrogen pressure vessel development project. This report describes results from the first 8 months of a three-year project.

Results

LLNL is pursuing a fundamental advance in the manufacturing of large inexpensive pressure vessels. This advance relies on the properties and manufacturing process savings implicit in a new category of plastics. These plastics are expected to form both liner and matrix of a new generation of inexpensive pressure vessels sized for low-temperature hydrogen delivery trailers. Many of the materials properties of this family of plastics have already been shown superior at very low temperatures. In collaboration with Spencer Composites, we have produced 3" diameter experimental test articles (Figure 1) to affordably determine unknown properties and improve formulations.

Tooling for full-scale liner production has just been completed. Tooling incorporates a calibrated finite element design and already measured plastic strengths sufficient to keep all structural elements well within the elastic range during independent pressure cycles to 22,500 psi (design burst pressure) and temperature cycles from 77 K to 365 K. LLNL enabled this design by performing preliminary pressure optimization in order to size vessel diameter, resulting in an economic optimum of 8,000 psi maximum expected operating pressure (MEOP) for the delivery trailer. LLNL has also made sure this full-scale design is robust enough to fit in our container design when wound with sufficient fiber to preserve safety factors of 2.25 at any MEOP from 1,500 psi to 11,500 psi. This allows the same tooling to minimize cost for stationary hydrogen storage applications (including filling station storage and renewable energy buffering).

FIGURE 1. Photographs of early test articles built and destroyed to test new matrix and liner plastic formulations and manufacturing processes. Dozens of 3" subscale pressure vessels have been built and burst tested. The figure shows a liner test article with partial graphite overwrap intended to test liner burst strength (left), a sectioned fully overwrapped vessel designed to burst at 3,000 psi with dog bone tensile test specimens cut from as-built walls (center), and a liner with 3,000-psi boss design ready for overwrapping (right).

Although we are developing a solution that can function at various temperatures and pressures, the manufactured and operating costs of this solution depend on currently unknown properties of fibers, plastics, and processed surfaces. (Overall delivery costs also depend on currently uncertain projections for the costs of refrigeration and compression, especially as functions of scale and temperature.) 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 [1,2], the cold glass pressure vessel delivery option minimizes delivery cost per kilogram of hydrogen.

Figure 2 shows a crucial piece of legacy data [2] that is of interest because it indicates the potential for *doubling* the strength of glass fiber composite when cooled down to ~140 K. Much of the lack of repeatability in cold glass fiber strength in the legacy data (leading to large error bars) is likely due to monolayers of water on the glass fiber surface, and our experiments have been redesigned several times to control this variable.

The highly significant unknown that we expect will depend on moisture control is glass fiber strength versus time, where we believe almost all previous data is corrupted by moisture-driven 'corrosion'. At the moment, there is absolutely no data on "strength aging" of glass fiber at low temperature. Water vapor effects can be routinely controlled on a trailer, especially if the ambient gas (e.g. CO_2) outside the pressure vessels is chosen to maximize the sensitivity of hydrogen leak detection, and the hydrogen inside is cold enough to precipitate water in sorption "cold traps". The lack of strength aging of much more defect-ridden plate glass

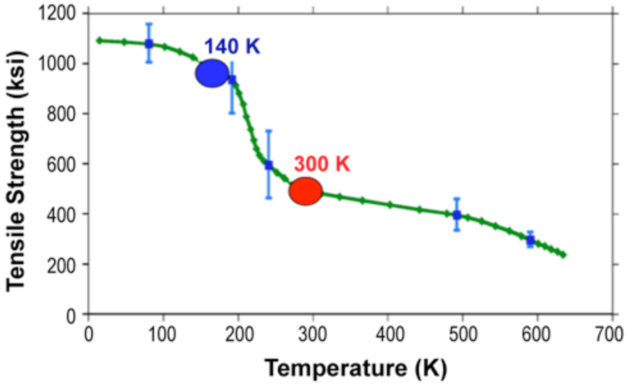


FIGURE 2. Legacy data showing the potential for great (2X) glass fiber strengthening at low temperature [2].

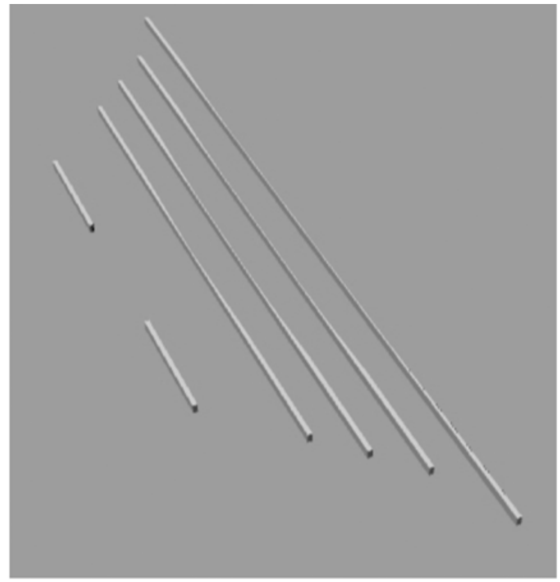
when tested in nitrogen, argon, or vacuum argues that our trailers can be designed for long capital life.

Measuring the cold strength effect is a challenge. If glass fiber strength indeed doubles at low temperature, there are very few materials that could stretch enough to hold on to tensile test specimens up to their failure strain. In previous experiments, we attempted to reuse a design developed at LLNL more than a decade earlier that sufficed to hold onto the strongest graphite fibers at 98% of their failure strain by gluing samples into metallic fixtures.

Our attempts to scale that design up led to high variability in the results. Special data reduction techniques (Weibull) sufficed to prove the cold strength effect in currently available glass fiber, with a measured strength gain of ~41% at liquid nitrogen temperatures. However the 10% variation in the low temperature strength was likely due to inconsistent temperature histories between cold tests. We subsequently concluded that there might be a diffusion time for water vapor in micro-cracks that considerably exceeds the thermal equilibration time. Another major concern was that many of the 'early' failure stresses (which were sorted out on our data reduction) were due to subsurface damage by machining a "reduced area section" and that the undamaged volume might vary considerably between specimens.

This year we have come up with major improvements in specimen and fixture design. Figure 3 shows a new set of specimen profiles that maintain a relatively long stretch of constant cross section between profiles designed to produce only one failure per specimen. We have developed a new machining process that appears to be holding 0.001" tolerances on this profile, and expect its testing will make the Weibull-method data reduction complexities unnecessary.

Figure 4 shows new specimen fixtures whose stress and strain predictions work (on paper) to hold composite rods up to ~4% strain. The replacement



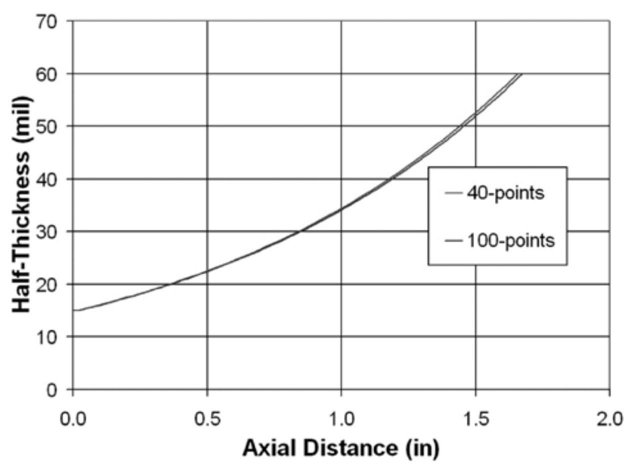


FIGURE 3. Design of machined rods for a better approach to tensile testing limits the maximum shear stress experienced by the composite matrix material in a tapered neck whose profile (bottom) is much more gradual than the conventional "dog bone" test articles. The two curves shown confirm convergence of the numerical solution for this profile. These profiles, including relatively long (4") tests sections of constant area have been successfully machined with very little surface damage using single point diamond tool (numerically controlled) milling.

of bonded fixturing with friction means that days of precisely filling fixtures with glue are replaced by minutes clamping set screws with a torque wrench. The fixtures and specimens as shown might pull out at 500,000-psi tension. However, both machining on the perpendicular axis and diluting the fiber with more matrix appear to be routine approaches to test fiber up to ~2,000,000 psi. The specimen holder has been designed to fit inside a 2.5" Dewar, and various improvements in the tensile testing apparatus have also been planned. Although we have recently discovered two ways to affordably test single fibers, these have

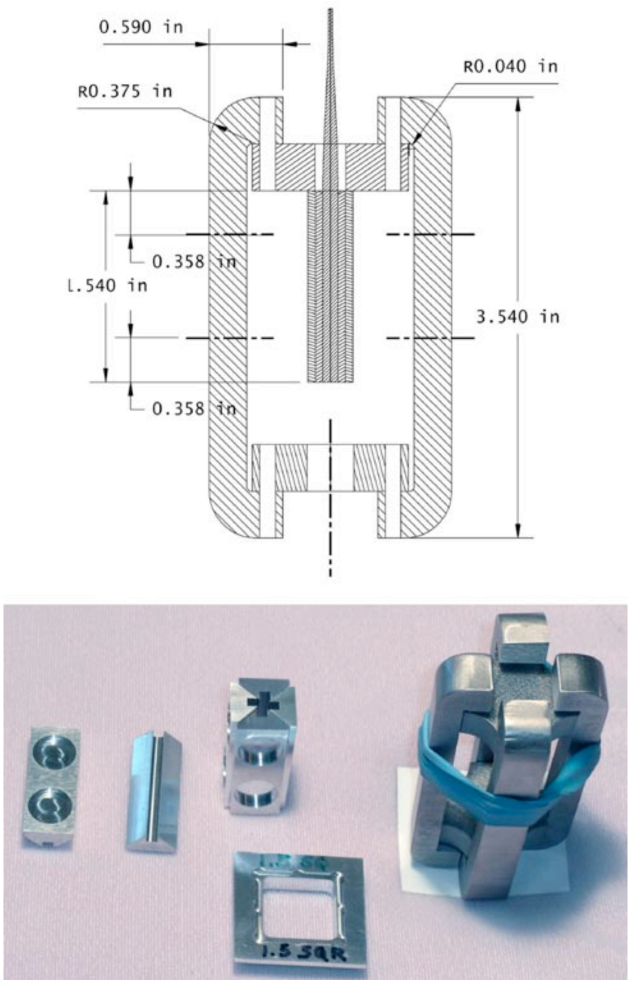


FIGURE 4. New test fixture under construction provides the savings in skilled labor familiar from more conventional tensile testing where clamping by friction substitutes for bonding. This approach would not work for holding the strongest composites in metal jaws, which would fail to stretch sufficiently to clamp composite at several percent strain, except that these metal jaws mount inserts of the same composite rod (visible in the photograph at right as the cross in the center of the jaws).

been rejected from our immediate plans due to their significant risks of false positive results (since many of the failure onset phenomena could be at the fiber matrix interface).

Conclusions and Future Directions

We are prototyping various novel glass composites. These test articles (rods, 3" liners, and full-scale vessels) should exhibit structural and hydrogen storage properties similar to those resulting from future mass production. Spencer Composites (and other industrial partners in a different DOE composite pressure vessel manufacturing technology award) will assist our formation of realistic production cost models. We have sufficient reason to expect that LLNL and its industrial partners can achieve new lows in hydrogen storage and delivery costs with an informed understanding of the significant technical risks that remain in the design and implementation of cold glass fiber composite pressure vessels.

References

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2. Metcalfe, A.G., and Schmitz, G.K., Glass Technology, Vol. 13, 1972. Reprinted in Lowenstein's "The manufacturing Technology of Continuous Glass Fibers," Elsevier, 1983.

FY 2009 Publications/Presentations

1. High Density Hydrogen Storage in Cryogenic Capable Pressure vessels, Salvador Aceves, Invited presentation, Purdue Hydrogen Symposium, April 2009.

2. Hydrogen-Fueled Carbon-Free Transportation, Salvador Aceves, Invited Presentation, Engineering Solutions for Sustainable Development: Materials and Resources, an international workshop organized by AIME and ASCE, Lausanne, Switzerland, July 22–24.