III.8 Inexpensive Delivery of Cold Hydrogen in High Performance Glass Fiber Composite Pressure Vessels

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Objectives

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

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	700
Tube trailer operating pressure	psi	<10,000	7,000-10,000
Purchased capital cost (700 kg trailer)	$	<$300,000	$200-300k

Accomplishments

- Performed cryogenic tensile testing of a favorable ($4.50/kg, chemically tolerant) high performance glass (basalt) fiber. This structural material is projected to be the best for minimum cost hydrogen delivery in composite pressure vessels.
- Demonstrated that glass fiber strengthens considerably (in our initial experiments by ~41%) when cooled from 300 K to 77 K, proving the synergy between cold hydrogen and glass fiber.
- Developed a reference design which packages cold compressed hydrogen storage 'tubes' in shipping containers. This design can likely withstand almost all truck accidents, protects insulation, and is ideal for off-board storage (at filling stations).
- Designed and procured all components for a refrigerated tensile test apparatus capable of testing pultruded composite specimens at a spectrum of cold temperatures (from ~140 K to ambient), under precisely controlled sates of humidity trapped in the composite under test.

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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 work will test the practical feasibility of our proposed approach to inexpensive hydrogen delivery.

Approach

Our pressure vessels minimize delivery cost through a synergistic optimization 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 the extremes of the hydrogen phase diagram. We can minimize hydrogen delivery cost by exploring the entire phase diagram and finding pressures and temperatures that result in high storage density without the heavy thermodynamic penalty of hydrogen liquefaction. Cold high-pressure hydrogen (~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 is synergistic with low-temperature operation, strengthening ~50% as it cools down from 300 K to 200 K [1]. Cold glass fiber delivers unequalled performance per unit of cost; expanding weight-limited trailer capacity and reducing capital expense. We are experimenting with the likely most cost-effective, currently-available forms of glass fiber, including basalt, S-Glass, and several grades of E-Glass.

Further advantages come from delivery of cold hydrogen, transferring it through 'off-board' storage at the filling station, and dispensing it to a vehicle. These advantages show up in equipment cost, weight and safety, but cannot be currently captured by the performance targets of either infrastructure or onboard storage: delivering 200 K compressed hydrogen avoids overheating and overpressurizing of both onboard and off-board storage vessels, increasing the fill speed and potentially reducing the cost of storage. Vessel designs can be simplified if their operating pressure and temperature never exceed the nominal rating, and the safety of operations is improved without a filling pressure transient above rated pressure. This collection of advantages is likely to provide considerable additional savings in vehicle and filling station capital costs, beyond the direct (per-kilogram dispensed) cost savings from inexpensive delivery.

Results

We have conducted an H2A-based analysis of hydrogen delivery cost for metallic and composite compressed hydrogen tanker trucks. The analysis compares the results from delivering ambient temperature hydrogen in metallic and graphite composite tanks to the cost of delivering cold (200 K) compressed hydrogen in the best-projected glass composite tanks. The results are presented in Figure 1, and can be summarized as follows:

- Hydrogen liquefaction is expensive, pushing the cost of liquid hydrogen delivery to over $2/kg. Future progress on efficient liquefaction plants may address this issue and make liquid hydrogen an inexpensive delivery solution. Liquid hydrogen delivery is not shown in Figure 1.
- Delivery of compressed hydrogen in metallic tube trailers is expensive due to their low capacity (300 kg) that magnifies the impact of labor cost.
- Carbon fiber composite tanks operating at 10,000 psi and ambient temperature have potential to deliver up to 1,000 kg, compensating for the high capital cost of the truck ($430,000). The balance is favorable, and these vessels can deliver inexpensive hydrogen at large (1,000 kg/day) fueling stations where they can be cycled daily. Issues remain, however. Fast refueling with ambient temperature gaseous hydrogen is challenging due to the compression heating and the over-pressurization necessary for a complete fill. Hydrogen cooling at the station may be necessary to deliver hydrogen to the vehicle in practical filling times.
- Inexpensive glass fiber composite tanks operating cold (200 K) deliver the highest performance per unit of dollar. Hydrogen can be delivered at low cost (~$1/kg) even at relatively small stations (500 kg/day or less).

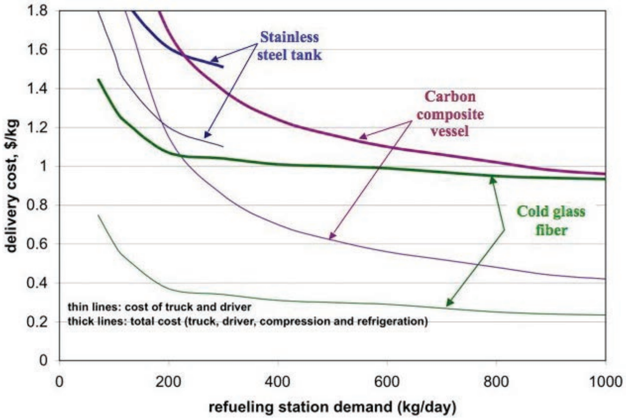

FIGURE 1. Cost of hydrogen delivery for metallic tube trailers, carbon composite tanks, and glass fiber tanks storing cold (200 K) compressed hydrogen, as a function of refueling station demand. Thin lines show truck and driver cost, and thick lines show total cost, which also includes the cost of compression and (possibly) refrigeration (both energy and capital). The costs plotted do not include other costs associated with the rest of the delivery infrastructure (terminal, refueling site, etc.).

The costs plotted in Figure 1 are only those for truck transport (including the capital and energy costs of both cooling and compression), and they do not include the other costs associated with the rest of the delivery infrastructure (terminal, refueling site, etc.).

The results in Figure 1 assume that glass fiber strengthens by 50% when cooled down to 200 K. This assumption is supported by legacy research [1]. Whether minimum-cost, cold glass containers are optimal or not could depend on the actual tensile strength versus temperature curve of the best composite materials, as well as the capital and operating costs of refrigeration. We do not know if the legacy data apply to our current best-economics glass fiber for 'tube' trailer applications (pultruded volcanic basalt glass, Figure 2), which was not available in the twentieth century. This key presumption of significant cold glass fiber strength gain was proven true by our initial experiments on pultruded basalt specimens in early 2008, wherein we observed consistent >40% strength gained at reduced (liquid nitrogen) temperature.

The legacy research data on cold glass strength is notable for its lack of repeatability. Other old hypotheses (explaining plate glass strength in the 1960s) attribute a variety of gaseous ambient effects on strength to very low levels of humidity. Therefore we designed and began building an apparatus capable of tensile testing under precise control of both temperature and humidity. Our intent was to make 1-2% accurate measurements on 2% repeatable specimen production processing in a repeatable environment to achieve perhaps 5% repeatable cold strength data. Such data might be good enough to assert an optimal delivery pressure and temperature, whereas 20% unrepeatable legacy data was too inaccurate to justify new pressure vessel products.

The precise control of humidity demands more than control of gas in the envelope around the specimen. It also requires the ability to remove the moisture already in the microscopic defects of the fiber surface. Therefore we designed a refrigerator apparatus with the capability to bake moisture out of specimens in hard vacuum, dial its temperature throughout the region we expect to be optimal, and introduce our choice of gaseous ambient to sort out how much moisture control a real 'tube' trailer might need. This future apparatus was designed for installation, shake-down, and affordable operation in a particular tensile testing machine (Figure 3) where we could begin experiments with existing temperature control equipment that limited our initial experiments to liquid nitrogen (at –162°C). This tensile testing machine and its operators provide over 30 years of unique composites testing expertise.

Affordable testing of a full matrix (four materials, at least five temperatures, or five samples each to acquire variance) of structural specimens in a controlled environment (both temperature and 'atmosphere') will be conducted in 2009 as our ability to collect good data

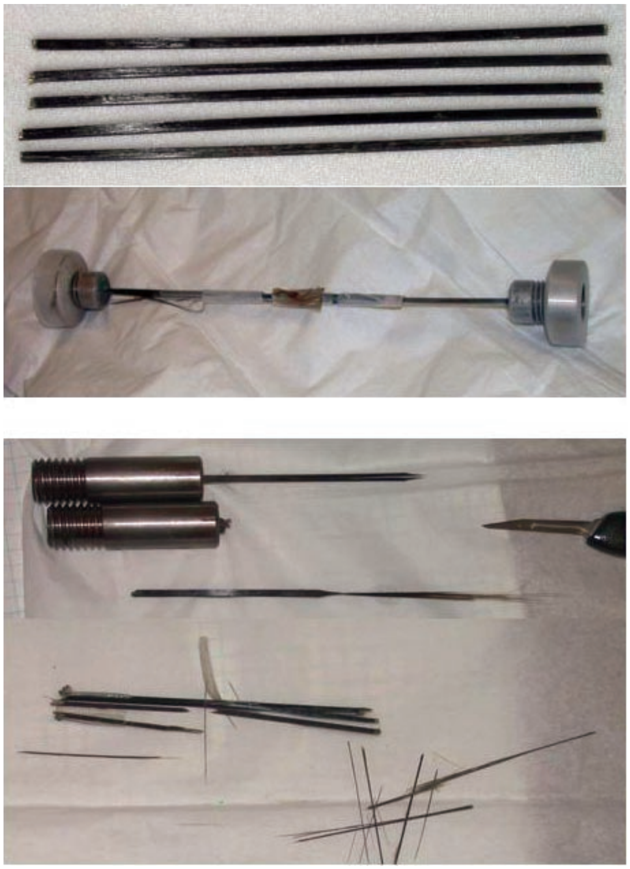

FIGURE 2. Glass composite specimens in various stages of the experimental campaign. Top: pultruded volcanic basalt glass fiber specimens as procured for the experiment. Middle: basalt rod glued into third generation Invar 36 tensile mounting fixtures. Bottom: specimen fragments after tension tests. These fragments were observed microscopically to analyze failure mechanisms.

FIGURE 3. Experimental apparatus and procedure for testing campaign that broke pultruded glass fiber (basalt) composite specimens. Testing to failure occurred under pure uni-axial tension at constant (liquid nitrogen and ambient) temperatures, but uncontrolled atmosphere. Upper left: liquid nitrogen Dewar mounted into tension testing machine. Upper right: basalt rod mounted inside Dewar with invar fixtures into tension test machine. Lower left: Operator filling Dewar with liquid nitrogen in preparation for tension test. Lower right: Temperature stabilization in the basalt rod ahead of the tension test.

improves. Currently the ability to collect good data is limited to very few samples per day by the thermal equilibration time of the liquid nitrogen setup. The refrigerator apparatus designed to replace liquid nitrogen was designed for rapid thermal equilibration and vacuum pump-down, to minimize costly operator attention by the deliberate choices of push-a-button-and-walk-away vacuum pumping and thermoelectric refrigeration. However, the duration of a pump-down sufficient to reverse the "glass fatigue" (strength decrease due to exposure to humidity over time) in order to achieve repeatable results remains to be seen. In the worst case, only five specimens per week might be broken. A matrix of test conditions has been designed to sort out the mechanisms responsible for strength lost in the baseline of specimens tested under normal laboratory conditions, to find out how to preserve maximum structural performance by residual moisture and thermal control in a hydrogen delivery container.

Our first experimental campaign (in early 2008, Figure 4) used the tensile test machine, its liquid nitrogen tension-path Dewar, and expert operator. It tested straight glass fiber composite specimens under tension to failure, at one of two tightly controlled temperatures. While the atmosphere was not deliberately controlled, room temperatures were stable within ~1°C. An essential result (a consistent 41% strength gain in basalt) is shown in the form of a reduced data plot in Figure 4. Although per-specimen testing costs were severe, the learning of how to test straight composite articles was necessary to achieve good data. Our plans to be able to afford to break hundreds of test articles rely on pultrusion, the lowest cost, highest consistency composites manufacturing process, to produce straight test articles that cost 2-3 orders of magnitude less than pressure vessels.

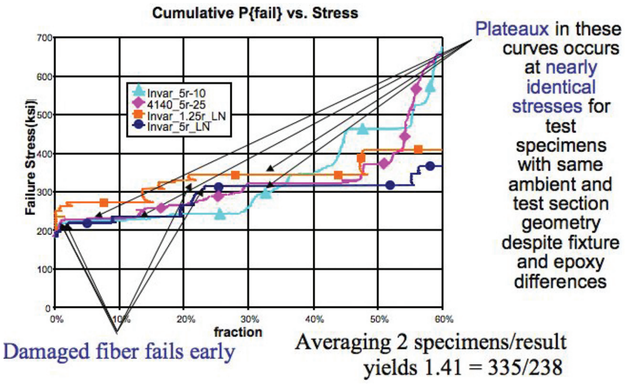

FIGURE 4. Results from cold tension experiments reduced using Weibull cumulative probability of failure plots. Data reduction presumes the fraction of surviving fiber is proportional to area, and linear elasticity of the surviving composite cross section. The results showed consistent average 'core' fiber failure stress that was 41% higher at -162°C (lines marked 'LN') than at -10°C.

Conclusions and Future Directions

- We have identified glass fiber vessels as capable of delivering hydrogen at ~$1/kg H_2 in small- to large-scale (200-1,000 kg/day) fueling stations. This cost only includes truck transport, hydrogen compression, and hydrogen cooling, but does not include other costs associated with the rest of the delivery infrastructure (terminal, refueling site, etc.). This cost is much lower than any possible metallic tube trailer design, and it is obtained by taking advantage of the high density of hydrogen at 200 K, the relatively low cost of cooling down the hydrogen, and the high strength of glass fiber at low temperature.
- We are building unprecedented experimental apparatus and affordable test articles (straight pultruded composite specimens in Invar 36 fixturing mounts) for tensile testing of glass fiber composite specimens at low temperature (and in 2009 under vacuum and controlled humidity ambient) to verify the fundamental hypothesis that glass fiber strengthens when cooled down or when adsorbed water is removed. Preliminary testing at ambient and liquid nitrogen temperatures will expand to five glass composite materials in 2008, and continue into investigation of glass fiber capital life in 2009. The components for the cost-saving refrigerator apparatus have been procured, its assembly is on hold awaiting final dimensions of specimen mounts, and we anticipate shaking its operations out in 2009.

Special Recognitions & Awards/Patents Issued

1. Storage of H_2 by Absorption and/or Mixture within a Fluid, Gene Berry and Salvador Aceves, US Patent 7,191,602, 2007.

FY 2008 Publications/Presentations

1. Cryogenic Hydrogen Storage, Salvador Aceves, Invited Presentation, *Materials Science and Technology 2007 Conference and Exhibition*, September 2007.

2. Setting a World Driving Record with Hydrogen, Salvador Aceves, *Science and Technology Review*, June 2007, http://www.llnl.gov/str/June07/Aceves.html.

3. H_2 Going for Distance, Salvador Aceves, *Mechanical Engineering*, December 2007, p. 16.

4. Inexpensive delivery of compressed hydrogen with advanced vessel technology, Salvador Aceves, Andrew Weisberg, Gene Berry, Proceedings of the National Hydrogen Association Conference, San Antonio, TX, 2007.

Reference

1. Reed, R.P., and Golda, M., 1994, "Cryogenic properties of unidirectional composites," Cryogenics, Vol. 34, pp. 909-928.