III.D.1 Inexpensive Delivery of Compressed Hydrogen with Advanced Vessel Technology

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Objectives

- Evaluate and build high-performance containers for delivery truck applications
- Test performance of glass fiber at low temperature

Technical Barriers

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

(A) Lack of Hydrogen/Carrier and Infrastructure Options Analysis

(F) Gaseous Hydrogen Storage and Tube Trailer Delivery Cost

Technical Targets

TABLE 1. Progress Towards Meeting Technical Targets for Hydrogen Delivery in Tube Trailers and for Off-Board Gaseous Hydrogen Storage Tanks

Hydrogen Delivery in Tube Trailers	Units	2012 Target	LLNL Advanced Vessel (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

TABLE 1. Progress Towards Meeting Technical Targets for Hydrogen Delivery in Tube Trailers and for Off-Board Gaseous Hydrogen Storage Tanks (Continued)

Off-Board Gaseous Hydrogen Storage	Units	2010 Target	LLNL advanced vessel (projected)
Off-Board Tank Cost	\$/kg H_2	300	300-400
Off-Board Tank Volumetric Capacity	kg H_2/l	>0.035	0.040

Accomplishments

- Identified cold (200 K) high-pressure (up to 10,000 psi) hydrogen as economical for hydrogen delivery due to its high density leading to high carrying capacity (up to 1,000 kg per trailer) and the relatively low cost of cooling the hydrogen.
- Identified a synergy between cold hydrogen and glass fiber that considerably reduces the cost of delivery trucks: glass fiber strengthens considerably (by ~50%) when cooled from 300 K to 200 K.
- Identified a favorable ($4.50/kg, chemically tolerant) high-performance glass (basalt) fiber as the best structural material for composite containers that may minimize capital cost in hydrogen delivery truck trailers.
- Designed a tensile test apparatus for fibers at a variety of (cold + ambient) temperature and precisely controlled humidity conditions.

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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/or a broadened range of thermodynamic conditions under which hydrogen is trucked and delivered. We have identified 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

Our pressure vessels minimize delivery cost through a synergistic optimization of hydrogen properties and fiber characteristics:

1. **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. 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.
2. **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.

An extra synergy exists between delivery of cold hydrogen and hydrogen dispensing to a vehicle: delivering 200 Kelvin compressed hydrogen avoids overheating and overpressurizing of automobile storage tanks, increasing the fill speed and potentially reducing the cost of automotive storage (i.e., vessel designs can be simplified if pressure and temperature never exceed the nominal rating). This synergy provides considerable additional savings in vehicle vessel cost beyond the direct savings from inexpensive delivery.

We are researching hydrogen storage in through-strut macrolattice containers that promise optimum utilization of the vessel structure (all struts work under pure tension). However, the tests and synergies described here apply equally well to more conventional filament wound pressure vessels made of glass fiber.

Results

Last year we conducted an H2A-based analysis of hydrogen delivery cost for metallic and composite compressed hydrogen tanker trucks and compared the results to the cost of delivery of cold (200 K) compressed hydrogen. The results are presented in Figure 1 and can be summarized as follows:

1. Hydrogen liquefaction is expensive, pushing the cost of liquid hydrogen (LH_2) delivery to over $2/kg. Future progress on efficient liquefaction plants may address this issue and make LH_2 an inexpensive delivery solution. Liquid hydrogen delivery is not shown in Figure 1.
2. Delivery of compressed hydrogen in metallic tube trailers is expensive due to their low capacity (300 kg) that magnifies the impact of labor cost.
3. Carbon fiber composite tanks operating at 10,000 psi and ambient temperature increase the mass of hydrogen delivery and 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 overpressurization necessary for a complete fill. Hydrogen cooling at the station may be necessary for practical filling times.
4. Inexpensive glass fiber composite tanks operating cold (200 K) deliver the highest performance per dollar. Hydrogen can be delivered at low cost (40 cents or less without including refueling station cost) even at relatively small stations (500 kg/day or less).
5. The costs plotted in Figure 1 are only those for truck transport (and possibly cooling) and do not include the other costs associated with the rest of the delivery infrastructure (terminal, refueling site, etc.).

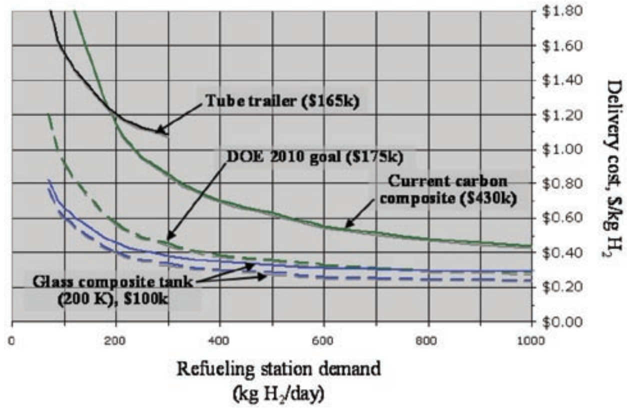

FIGURE 1. Hydrogen delivery cost as a function of fueling station size for: 1) metallic tube trailers, 2) current carbon composite tanks, 3) carbon composite tanks achieving costs comparable to the DOE 2010 hydrogen storage capital expense goal for automotive onboard storage on a kg H_2 capacity basis, and 4) glass fiber vessels at 200 K and 10,000 psi without including (dotted line) and including (solid line) estimated costs of cooling the hydrogen to 200 K. The costs plotted are only those for truck transport (and possibly cooling) and do not include the other costs associated with the rest of the delivery infrastructure (terminal, refueling site, etc.).

The results in Figure 1 are based on the key assumption (supported by legacy research [1]) that glass fiber strengthens considerably when cooled down. 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 also do not know if the legacy data apply to our current optimal glass fiber for container applications (pultruded volcanic glass, Figure 2), which was not available in the twentieth century.

We have collected more legacy data, noticed its lack of repeatability, and read decades-old hypotheses attributing a variety of ambient effects on strength to very low levels of humidity. We therefore designed and are building an apparatus capable of tensile testing under precise control of both temperature and humidity (Figure 3). The precise control of humidity demands the ability to remove the moisture already in the microscopic defects of the fiber surface, so the apparatus we built was given the capability to bake moisture out of specimens in hard vacuum. The apparatus of Figure 3 will be installed in a tensile testing machine (Figure 4). We will use a scanning electron microscope (Figure 4) to analyze failure mechanisms.

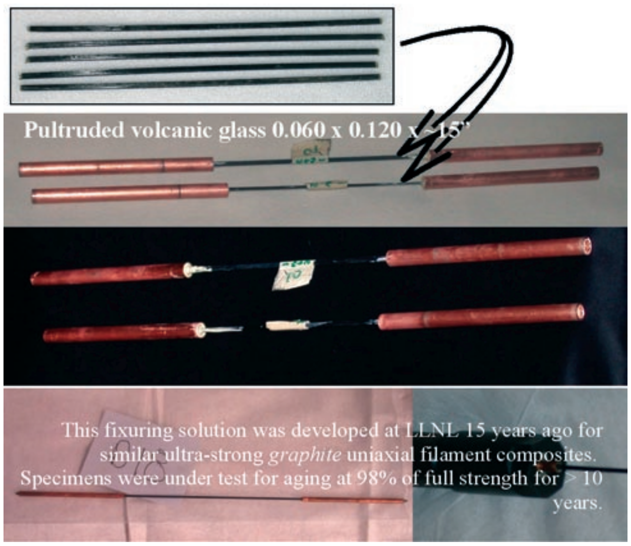

FIGURE 2. Pultruded Volcanic Basalt Glass Fiber Samples Attached to Copper Supports to be Tested to Failure in Tension Machine

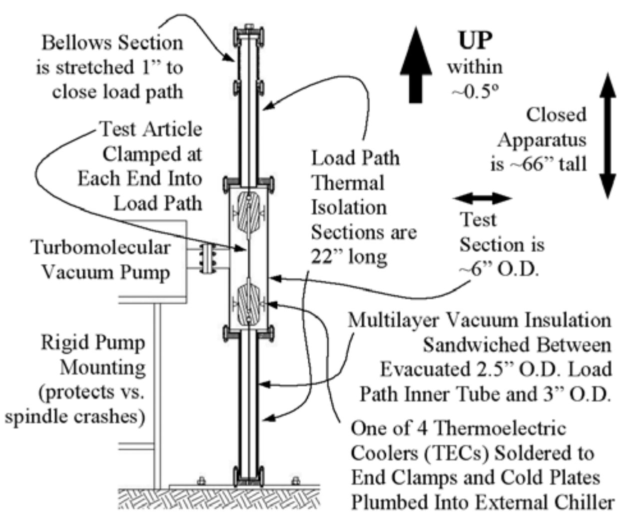

FIGURE 3. Experimental Apparatus for Testing Glass Fiber Samples under Tension at a Controlled Temperature and Atmosphere

Testing of the full matrix of structural specimens in a controlled environment (both temperature and 'atmosphere') will be conducted in the near future. The apparatus (Figure 3) has been designed for rapid pump-down, and costly operator attention has been minimized by deliberate choices of push-a-button-and-walk-away vacuum pumping and thermoelectric refrigeration. However, the duration of a pumpdown 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. This 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.

The experimental device (Figure 3) tests the glass fiber samples under tension at a controlled temperature and atmosphere. The test sample (pultruded volcanic glass rods) is attached to copper supports (Figure 2) and held in place in an environmental chamber. The sample can be cooled down to 140 K with four thermoelectric coolers. The test sample is wrapped with multiple layers of shiny plastic to reduce radiation heat transfer. The bellows section located at the top of the apparatus permits expansion of the test sample during the tension test. The apparatus is rather long (1.67 m) to reduce conduction heat transfer losses and enable cold operation within the power constraints of the thermoelectric coolers.

All large or expensive parts of the apparatus are now on order, and we are planning to start testing glass specimens during the summer and continuing into the next fiscal year, when we will be able to deliver an experimental evaluation of environmental (low

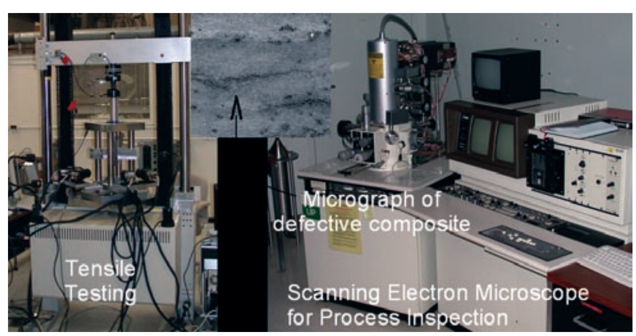

FIGURE 4. Experimental Equipment for Tension Testing of Glass Fiber Samples Located Inside Apparatus (Figure 3) and Scanning Electronic Microscope to Evaluate Failure Mechanisms

temperature and humidity) effects on tensile strength of pultruded glass composite struts and determine the effect of these parameters on the delivery cost of cold compressed hydrogen.

Conclusions and Future Directions

- We have identified glass fiber replicant vessels as capable of delivering hydrogen at a cost of ~$0.30/kg H_2 to large-scale (1,000 kg/day) fueling stations. This cost only includes truck transport and hydrogen cooling and does not include the other costs associated with the rest of the delivery infrastructure (terminal, refueling site, etc.). The cost is much lower than that possible with metallic tube trailers (~$1/kg H_2). This low cost 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 an experimental device for testing glass fiber at low temperature and vacuum or low-humidity environmental conditions to verify the fundamental hypothesis that glass fiber strengthens when cooled down or when adsorbed water is removed. The components for this device are on order and we anticipate initiating the testing in the near future.

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, March 20, 2007.

FY 2007 Publications/Presentations

1. Advanced Concepts for Vehicular Containment of Compressed and Cryogenic Hydrogen, Salvador M. Aceves, Gene D. Berry, Andrew H. Weisberg, Francisco Espinosa-Loza, Scott A. Perfect, Proceedings of the 16^{th} World Hydrogen Energy Conference, Lyon, France, June 10–15, 2006.

2. Vehicular Storage of Hydrogen in Insulated Pressure Vessels, Salvador M. Aceves, Gene D. Berry, Joel Martinez-Frias, Francisco Espinosa-Loza, International Journal of Hydrogen Energy, Volume 31, pp. 2274-2283, 2006.

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

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

5. Inexpensive Delivery of Compressed Hydrogen with Advanced Vessel Technology, S. Aceves, A. Weisberg, G. Berry, Proceedings of the National Hydrogen Association Conference, San Antonio, TX, March 2007.

Reference

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