

IV.D.2 Thermomechanical Cycling of Thin Liner High Fiber Fraction Cryogenic Pressure Vessels Rapidly Refueled by Liquid Hydrogen Pump to 700 Bar

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Project Start Date: January 2014
Project End Date: January 2017

Technologies Office Multi-Year Research, Development, and Demonstration Plan.

- (A) System Weight and Volume
- (D) Durability/Operability
- (N) Hydrogen Venting

Contribution to Achievement of DOE Hydrogen Storage Milestones

This project will contribute to achievement of the following DOE milestones from the Hydrogen Storage section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan.

- Milestone 2.6: Transportation: Develop and verify onboard storage systems achieving capacity of 5.5% by weight and an energy density of 0.04 kg H₂/L. (4Q, 2020)

FY 2016 Accomplishments

- Built and commissioned hydrogen test facility.
- Built and hydraulically cycle tested six thin lined pressure vessels rated for 700 bar.
- Built a seventh thin lined vessel and cycle tested it with hydrogen.



INTRODUCTION

Storing cryogenic hydrogen in a pressurized, insulated system has many benefits in terms of safety, volumetric and gravimetric densities, and ownership cost that have been studied and demonstrated by LLNL [1-3] and external parties [4-7]. High utilization (>1,500 kg H₂/d) commercial-scale fueling stations will likely require the use of LH₂ by means of a fast, energy efficient LH₂ pump. Until now, the development of cryogenic pressure vessels by LLNL has used off the shelf pressure vessels with an aluminum liner, a maximum operating pressure limited to 350 bar with large capacity (151 L, equivalent to 10.7 kg H₂) and large diameter (25 in). We believe that system densities (both volumetric and gravimetric), cycle life, and manufacturability could be improved by developing pressure vessels specifically tailored towards cryogenic utilization, even at a 5.6 kg H₂ scale, by exploring thin liner design (especially important for 12-in

Overall Objectives

- Develop ultra-light cryogenic pressure vessels with a 12-in diameter up to 700 bar.
- Optimize metallic liner thickness, composite fiber fraction, and ultra-thin vacuum jacket.
- Quantify liquid hydrogen (LH₂) pump durability to 700 bar over 6,000 refuelings.
- Demonstrate full-scale system density of 50 g H₂/L_{system} and 9 wt% H₂, and a cycle life of at least 1,500 refills.

Fiscal Year (FY) 2016 Objectives

- Complete construction and commission LLNL's hydrogen test facility.
- Analyze, design, and fabricate full-scale (65 L) 700 bar cryogenic pressure vessel prototypes with long cycle life.
- Demonstrate minimum pressure vessel life of 1,500 thermomechanical (pressure and temperature) cycles at LLNL's hydrogen test facility,

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section (3.3.5) of the Fuel Cell

diameter), non-Al liner materials, high fiber fraction for the composite overwrap, 700 bar operating pressure, and ultra-thin vacuum jacket designs.

APPROACH

Within this project, we are designing, manufacturing and cryogenically pressure testing full-scale (65 L) 700 bar pressure vessels with a thin (<2 mm), non-Al liner and high fiber fraction. Our primary goal is to assess the *cryogenic* strength of those prototype composite vessels after 1,500 thermomechanical hydrogen cycles, while other secondary objectives will be accomplished in parallel: (1) measure LH₂ pump performance at 700 bar after 6,000 refuelings (~24 tonnes of LH₂), (2) demonstrate lightweight vacuum jackets for cryogenic hydrogen pressure vessels, and (3) design and fabricate an experimental cryogenic hydrogen storage system with 5.6 kg H₂ capacity.

In order to achieve the thermomechanical cycling, the hydrogen test facility was constructed next to the existing 875 bar LH₂ pump, capable of rapidly cycling full-scale (65 L) non-certified cryogenic pressure vessels up to 700 bar and performing strength testing of those vessels up to 160 K and 1,300 bar. One to two vessels can be cycled at the same time in this single-manned, remotely operated facility that also includes a vent stack and will include a 40-kW heat exchanger.

RESULTS

Work in the reporting period focused on building and commissioning the hydrogen test facility, and on building and cycle testing thin-lined pressure vessels.

Hydrogen Test Facility

LLNL's hydrogen test facility, completed during the reporting period (Figure 1), offers a unique platform for testing hydrogen systems over a wide range of pressures, temperatures, volumes and flow rates.

The main component of LLNL's hydrogen facility is a liquid hydrogen pump. Manufactured by Linde, a leading supplier of cryogenic equipment, the pump takes liquid hydrogen from the station dewar at low pressure (2–3 bar) and very low temperature (23–25 K) and pressurizes it up to an 875 bar cryogenic fluid. The flow rate is very high (up to 120 kg of hydrogen per hour) enabling (future) 5-min refuels. The station dewar has 11,000-L capacity, sufficient to refuel ~150 vehicles. When empty, it is refilled by a liquid hydrogen truck.

Another key component of the facility is a containment vessel that enables testing of thin-lined experimental pressure vessel prototypes. These one-of-a-kind experimental vessels are not certified by current standards (American Society of Mechanical Engineers, International Organization for Standardization, Federal Motor Vehicle Safety Standards)



FIGURE 1. Hydrogen test facility at LLNL showing the main components and their performance metrics: liquid hydrogen pump, liquid hydrogen dewar, containment vessel, control room, insulated hydrogen tubes, and vent stack.

and are therefore unsafe to pressurize in manned areas. Made of 3.2-cm thick stainless steel 304 and weighing almost 5,000 kg, the containment vessel is rated for 65 bar maximum pressure and can contain the equivalent energy of 1.8 kg of trinitrotoluene, therefore enabling testing of full-scale vessels and hydrogen systems. The containment vessel can also hold high vacuum down to 0.1 Pa.

The test facility can be operated from a control room strategically located for maximum visibility and far enough from the dewar (23 m) to meet National Fire Protection Association (NFPA) standards. Full instrumentation is also available with sensors for temperature, pressure, flow, liquid hydrogen level, electricity, and vent rates. All sensors and system components are explosion-proof (Class 1 Division 1 Group B), as demanded by NFPA for systems that may be exposed to hydrogen.

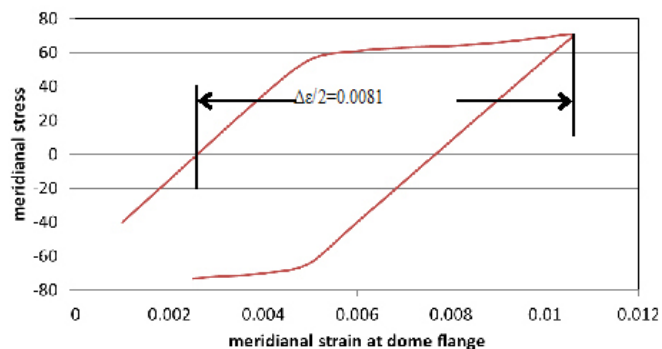
A 9-m high vent stack completes the facility, enabling rapid venting of hydrogen subsequent to pressure testing. High altitude venting of hydrogen is demanded by NFPA for rapid dispersion away from personnel at ground level.

Hydrogen, being so light and therefore buoyant, rapidly diffuses upward once it is released and warms up to ambient temperature.

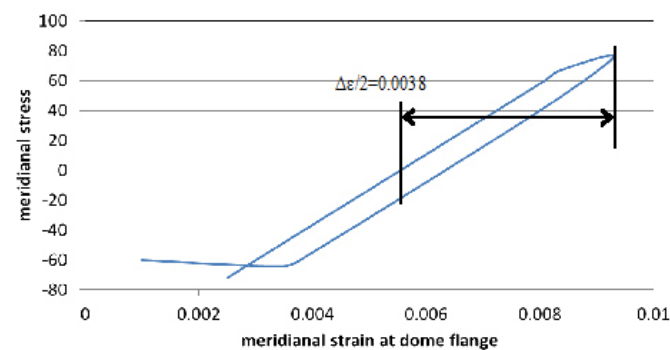
In the next quarter (fall of 2016), a 40-kW electric heater and heat exchanger will be added in order to provide varying hydrogen outlet temperature, from cryogenic to room temperature, enabling cost effective, rapid thermomechanical testing at high pressure and low (60 K) to elevated (360 K) temperature.

Thin-Lined Pressure Vessels

Following last year’s strength testing of a pressure vessel to 1,560 bar (2.23 safety factor for 700 bar operation), we dedicated this year to designing and producing a vessel that could be cryogenically cycled over 1,500 times. This demanded detailed finite element and fatigue analysis (Figure 2) to determine composite layer strength necessary to meet cyclability requirements. In collaboration with BMW, we also conducted linked thermo-fluid and stress analysis of the fill process to determine improved boss designs for

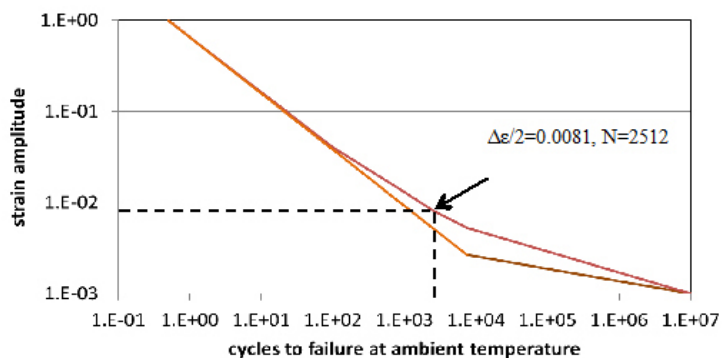


Cool-down cycle from 300 K to 80 K

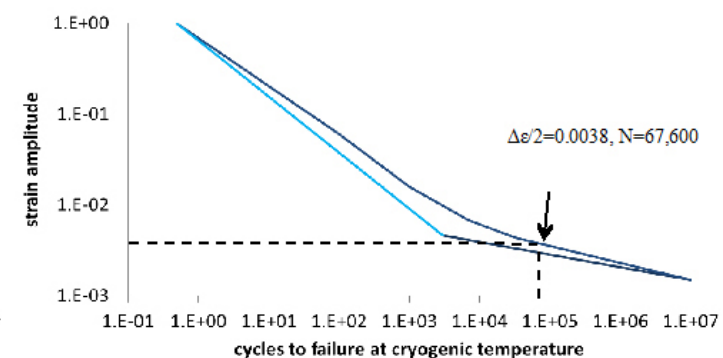


Cold fill cycle between 80 and 20 K

Finite element modeling of thin-lined vessel



Ambient temperature strain vs. cycle life



Cold (80 K) strain vs. cycle life

Fatigue life calculations for warm and cold cycles

FIGURE 2. Finite element and fatigue analysis of thin-lined cryogenic pressure vessels. Left: finite element model results indicating stress vs. strain for the metal liner during a cool-down and pressurization cycle (above) and a cold pressurization cycle (below). Right: Calculation of fatigue analysis based on strain amplitude vs. number of cycles to failure for both cool-down (above) and cold (below) cycles.

surviving thermal gradients that may result while filling an initially warm vessel with cryogenic hydrogen (Figure 3).

In total, we manufactured and tested seven vessels during the year (Table 1). The first two vessels failed during autofrettage. Research into this failure mode indicated that lack of roundness of the liner weakened the structure and resulted in premature failure at low pressure. Process modifications finally led to vessels that survived autofrettage and an increased number of water pressure cycles to 700 bar (except for Vessel 6 that failed during autofrettage while researching alternate resins). After partial success with water cycling, a final vessel was tested with cryogenic hydrogen, reaching 456 cycles, well short of the 1,500 cycle target.

CONCLUSIONS AND FUTURE DIRECTIONS

Research into the cause of the failure indicates that liner welds area the likely culprit. Hand tungsten inert gas welds are irregular by nature and introduce flaws that may initiate crack propagation during vessel cycling. Future work in this topic will demand new liner manufacture techniques such as e-beam welding, pulsed laser welding, or spin forming. The potential still remains to manufacture thin-lined vessels with long cycle life to demonstrate the ultimate performance limits of cryogenic pressure vessels.

After careful review of the experimental results, DOE decided to reduce the scope of the project eliminating vessel

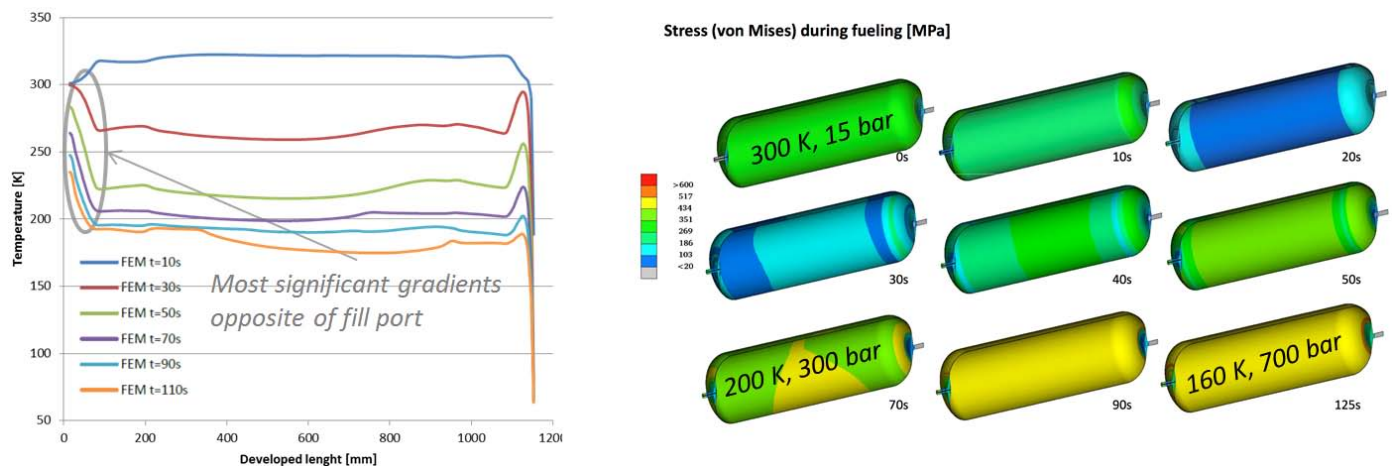


FIGURE 3. Linked thermo-fluid and stress analysis of the cryogenic fill process of an initially warm thin-lined pressure vessel indicating temperature distribution along vessel (left) and Von Mises stress distribution (right) as a function of time (from BMW).

TABLE 1. Experimental results from the testing of the seven thin-lined experimental pressure vessels built and tested for this project.

Date	#	Liner	Resin	Test result
Aug 15	1	1.3 mm Steel	High Fiber Fraction	Buckling then burst @ 8 ksi (during autofrettage)
Sep 15	2	1.5 mm Alternate	Epoxy	Buckling then burst @ 12 ksi (during autofrettage)
Oct 15	3	1.7 mm Alternate	Epoxy	Leak after 133 cycles, T-weld failure
Nov 15	4	1.5 mm Alternate	Epoxy	Leak after 247 cycles, root cause not found, NOT at T-weld
Jan 16	5	1.7 mm Steel	Epoxy	Leak after 468 cycles, longitudinal weld failure
Mar 16	6	1.7 mm Steel, annealed	High Fiber Fraction	Burst @ 10 ksi (during autofrettage)
May 16	7	1.7 mm steel	Epoxy	Leak after 456 cryogenic hydrogen cycles

development activities and instead testing pressure vessels supplied by BMW. This may initiate in the fall of 2016 once vessels are received, a test protocol is identified, and the electric heater (possibly necessary for vessel testing) is installed at LLNL's test facility.

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