

Performance and Durability Testing of Volumetrically Efficient Cryogenic Vessels and High Pressure Liquid Hydrogen Pump

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June 7, 2016

**Project ID #
TV029**

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Overview

Timeline and Budget

- **Start date: January 2014**
- **End date: December 2016**
- **Total project budget: \$5.5M**
- **Total recipient share: \$1.5M**
- **Total federal share: \$4M**
- **Total DOE funds spent: \$2.7M***

*As of 3/31/16

- **Funded jointly by Storage, Delivery, and Technology Validation**
- **Also presented as ST-111 Thursday AM in storage session**

Barriers

- **C. Hydrogen storage**
- **D. Lack of hydrogen infrastructure performance and availability data**

Partners

- **Spencer Composites Corporation custom cryogenic pressure vessels**
- **Linde LH₂ pump operation, maintenance & HAZOP**
- **BMW thermomechanical stress modeling, performance requirements, automotive perspective**



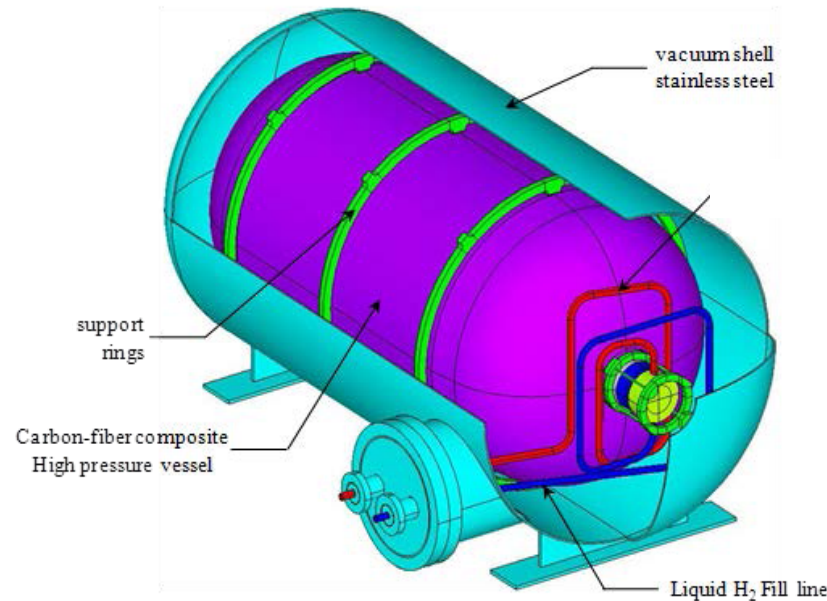
Relevance: Cryogenic pressurized H₂ storage and delivery provide safety, cost and weight advantages over alternative approaches to long-range (500+ km) zero emissions transportation

Cryogenic pressure vessels have the best performance:

- Highest system storage density (43 g/L)
- Highest hydrogen weight fraction (7.5%)
- Lowest cost of ownership (Argonne [1])
- Compelling safety advantages:
 - 20X less expansion energy vs. 300 K gas
 - Inner vessel protected by vacuum jacket
 - Gas expansion into vacuum jacket reduces thrust by 10X

Outstanding issues:

- Scalability to smaller diameters (35 cm)
- Vacuum stability
- Manufacturability



Relevance: Demonstrate performance limits (50 g/L, 9% H₂wt) of cryo-compressed technology by combining thin-walled vessels, thin insulation, and high density H₂ from LH₂ pump

New generation cryogenic pressure vessel

- 65 liters, 34 cm diameter, 100 cm long
- 700 bar
- 50 g/L, 9% H₂ weight fraction (3X and 2X better than 700 bar CGH₂)
- Thin lined (<2 mm), high fiber fraction (up to 80%)
- 80+% volumetric efficiency (inner vessel volume/outer vessel volume)
- Thin vacuum insulation (<1 cm)
- **Test strength (1600 bar new; 1300 bar cycled) and durability (1000 thermomechanical cycles)**

Liquid hydrogen pump

- Manufactured by Linde and installed at LLNL campus on FY13
- Rapid refuel of cryogenic vessels, even when warm and/or pressurized
- High fill density (80 g/L) and throughput (100 kg/h)
- LH₂ pump evaporation (1-3%) recycled into Dewar; not vented
- **Test pump degradation by pumping 24 tonnes of LH₂**

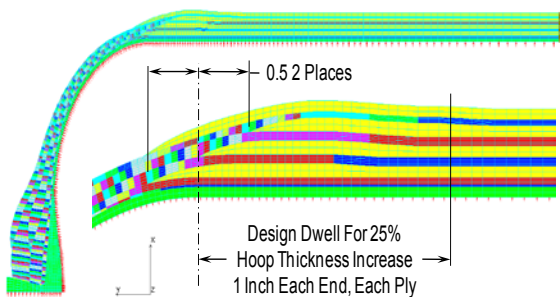


Approach: Combine finite element modeling and design expertise to demonstrate durable (1000 cycle) thin-lined (<2 mm) volumetrically efficient (80+%) 700 bar vessels

FY15: static pressure vessel strength test



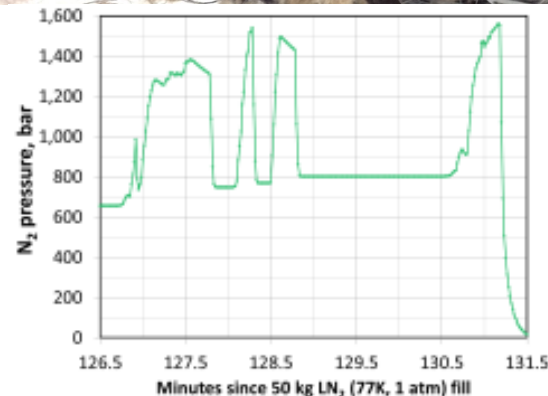
Cold strength test of candidate liner materials



Finite element modeling of thin-lined vessel



First thin-lined (1.8 mm) vessel, 81% volumetric efficiency (vs. 70% conventional vessels)

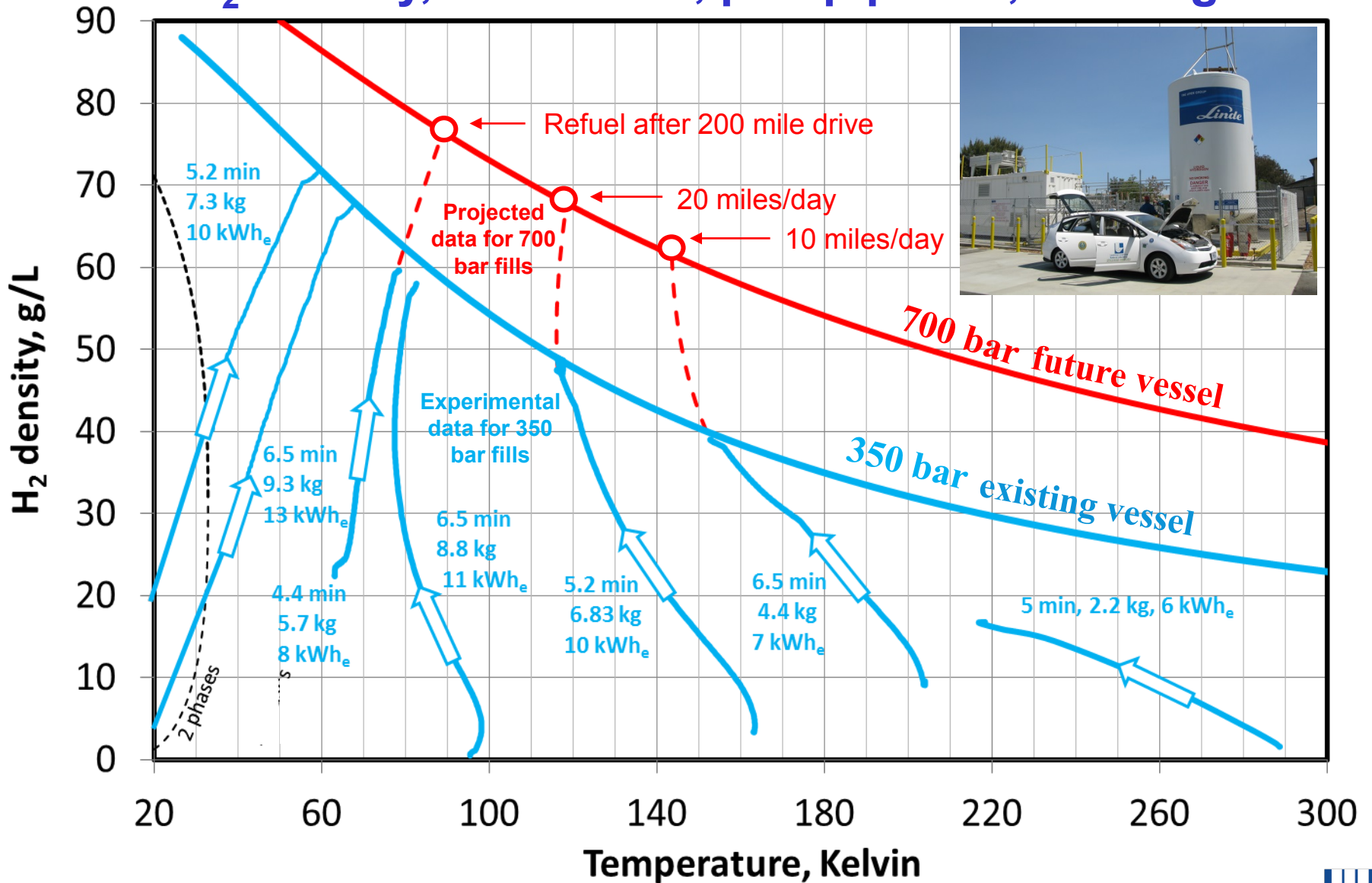


**Vessel pressure tested to 1560 bar
Preferred failure mode:
Hoop stress in cylindrical section
No failure in welds or domes**



Approach: Extend LH₂ refueling to 700 bar

Measure H₂ density, refuel time, pump power, and degradation

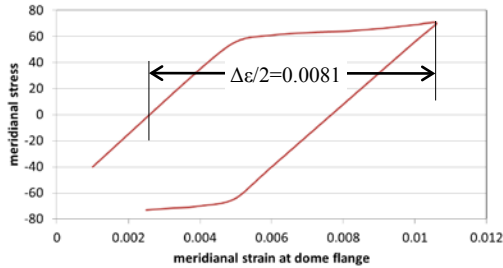


Up to 80g/L H₂ density possible at 700 bar

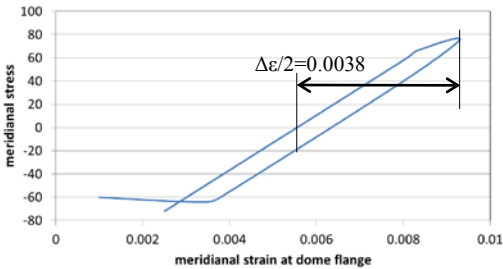


Accomplishment: Use finite element and fatigue analysis to design durable (1000 cycle) thin-lined (<2 mm) volumetrically efficient (80+%) pressure vessels

FY16: fatigue analysis of dynamically cycled vessel

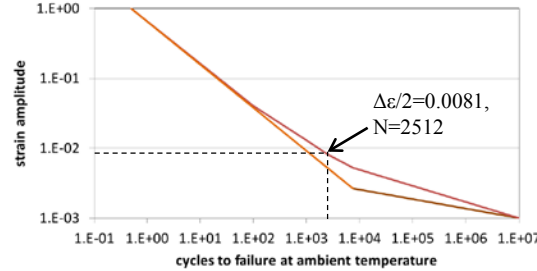


Cool-down cycle from 300 K to 80 K

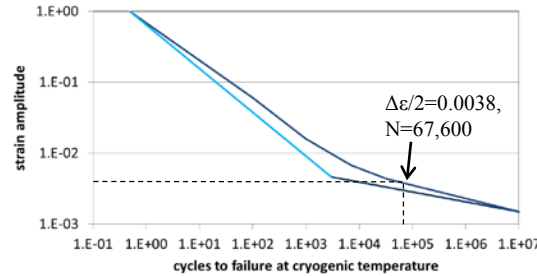


Cold fill cycle between 80 and 20 K

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



Cryogenic vessel designed for 6400 cycles (1600 cycles, safety factor=4)



Accomplishment: In collaboration with BMW, we have analyzed thermomechanical stresses caused by rapid fill of initially warm cryogenic pressure vessels

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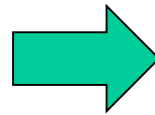
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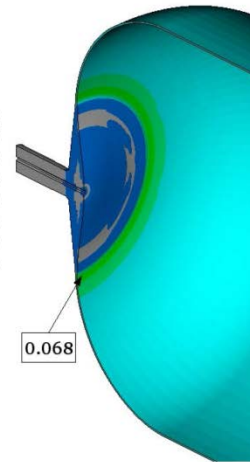
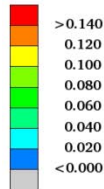
Velocity
10.00
7.50
5.00
2.50
0.00



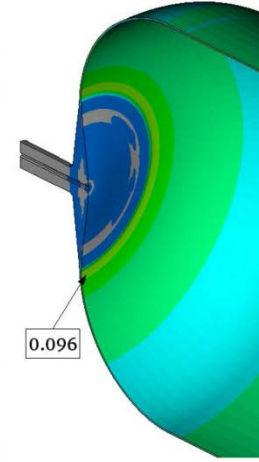
Temperature
320
270
220
170
120
70



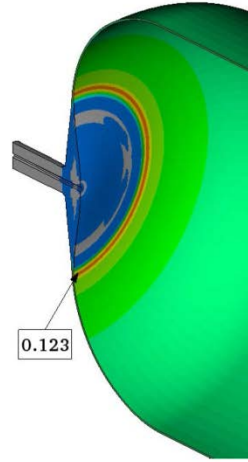
Equivalent plastic strain [-]
after autofrettage



after the first cycle



after the second cycle



Linked thermo-fluid analysis of warm vessel fill

Hand-off information to stress analysis code for calculation of fatigue life



Accomplishment: We have built and cycle tested five cryogenic vessels with continuously improving cycle life



(#1) initial prototype (32 kg)

1.7 mm SS 316 liner/epoxy

Modified neck, 1560 bar LN₂ burst

(#2) Aggressive design (28 kg)

1.3 mm SS liner/cryogenic resin

buckled during autofrettage

(H₂O burst at 8,000 psi)

(#3) Conservative design

1.5 mm liner/epoxy

buckled during autofrettage

(H₂O burst at 11,000 psi)

(#4) Conservative design

1.7 mm liner/epoxy

pinhole leak after 133 cycles @ 700 bar

(6,000 psi H₂O leak at T-weld by X-Ray)

(#5) Vessel Dome

1.5 mm liner/epoxy

Analyzed by Optical, X-ray, Dye Penetration

(T-weld ruled out, but root cause not found)

(#5) Conservative design

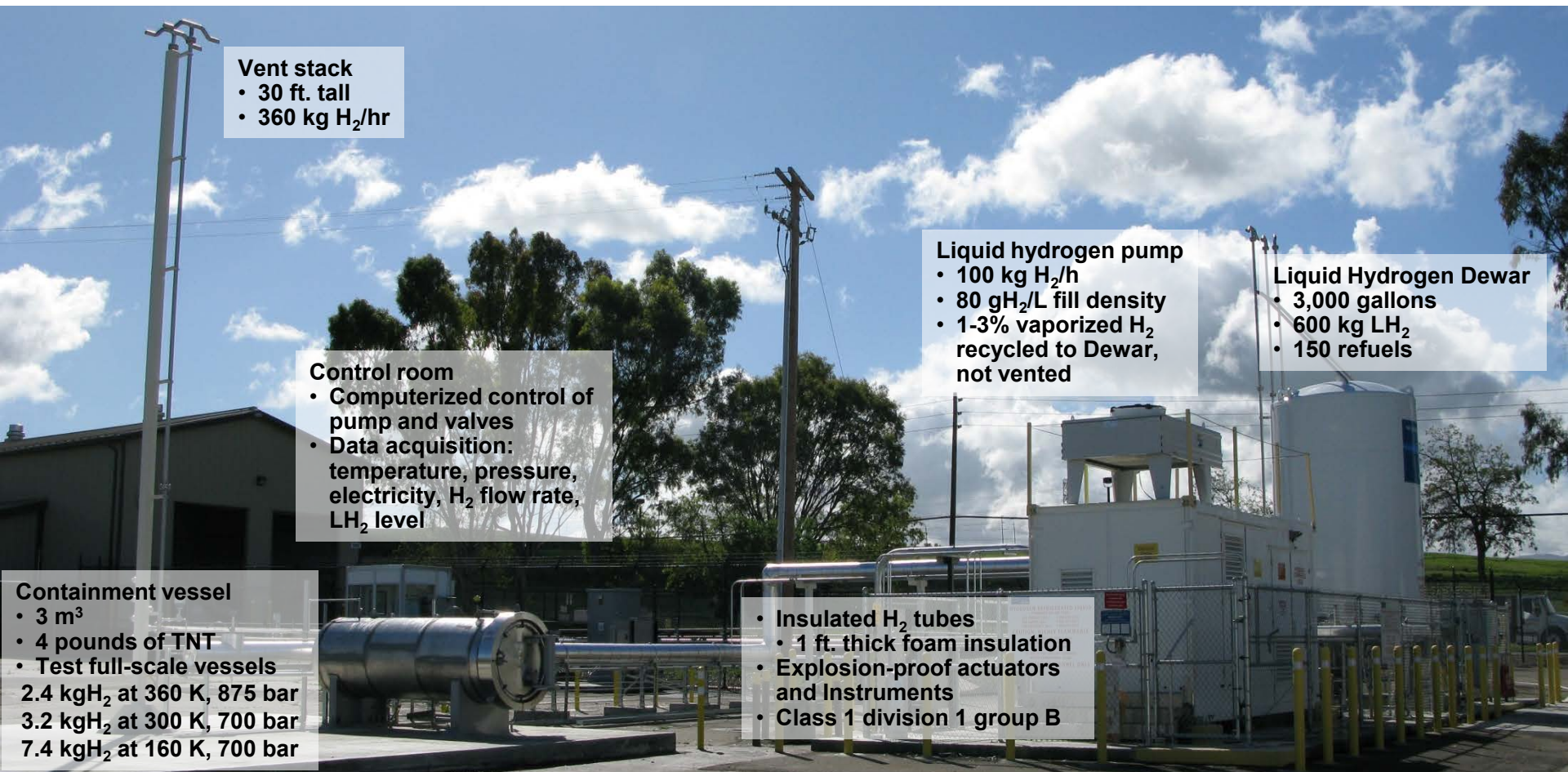
1.5 mm liner/epoxy

pinhole leak after 247 cycles @ 700 bar

(8,000 psi H₂O leak NOT at T-weld)



Accomplishment: We have built a Hydrogen Test Facility for cost effective durability, cyclic, thermomechanical, permeation, leak, and burst testing



Vent stack
• 30 ft. tall
• 360 kg H₂/hr

Control room
• Computerized control of pump and valves
• Data acquisition: temperature, pressure, electricity, H₂ flow rate, LH₂ level

Containment vessel
• 3 m³
• 4 pounds of TNT
• Test full-scale vessels
2.4 kgH₂ at 360 K, 875 bar
3.2 kgH₂ at 300 K, 700 bar
7.4 kgH₂ at 160 K, 700 bar

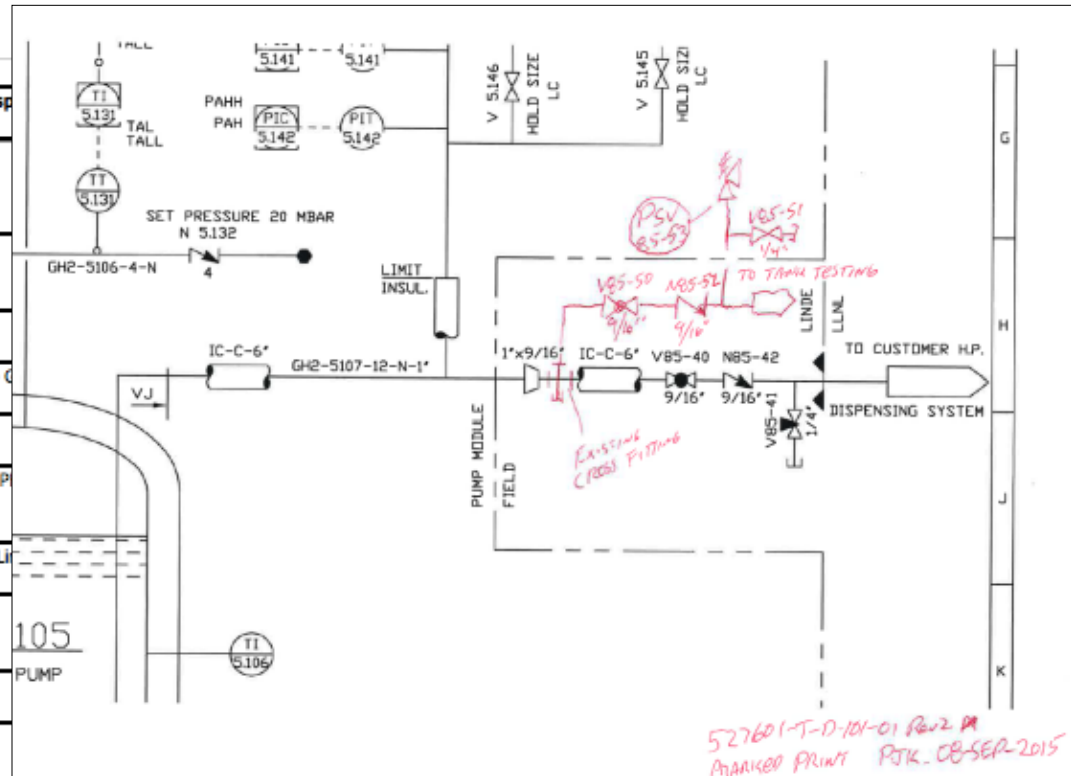
Liquid hydrogen pump
• 100 kg H₂/h
• 80 gH₂/L fill density
• 1-3% vaporized H₂ recycled to Dewar, not vented

Liquid Hydrogen Dewar
• 3,000 gallons
• 600 kg LH₂
• 150 refuels

• Insulated H₂ tubes
• 1 ft. thick foam insulation
• Explosion-proof actuators and Instruments
• Class 1 division 1 group B

Accomplishment: In collaboration with Linde, we conducted extensive HAZOP review of Hydrogen Test Facility

Action	Notes	Status	Resp
LLNL to ensure Linde staff are not allowed onsite during strength testing.	Delivers to be schedule outside of test dates. Gates will be closed with signage.		LLNL
Change setpoint for PRD4 to 13,920 PSIG or lower if MAWP of E-001 is less than 13,920 PSIG.	LLNL Agrees. Setting is 13,400 P&ID to be changed.		LLNL
Change PRD0 to 13,920 PSIG.	LLNL Agrees. Setting is 13,400 P&ID to be changed.		LLNL
Linde Gas to acquire data sheet for E-001 to confirm MAWP of heat exchanger.	Linde to contact LHS		Linde-C
Confirm PRD4 is sized for full flow through E-001.	LLNL to provide calculation sheet.		LLNL
Update P&ID to show tie in point for Cyclic vessel testing connection.	Need to verify location with pictures of current installed branch fitting.		Linde-P
Install manual isolation valve at tie point.	Eric to witness installation of manual valve.		LLNL/Li
Ensure LLNL provides allowance for pipe stresses at tie-in due to thermal expansion and contraction.	LLNL to provide pipe layout drawings showing VJ Expansion joints		LLNL
Ensure valves in field are tagged to match the P&ID.			LLNL
Ensure LLNL has a procedure which specifies correct valve lineup for each use point from the LH2 supply scheme.			LLNL
Add a thermal relief valve between new manual isolation valve at tie in point and 1-CV-0.			LLNL
Linde site staff to create energy isolation procedure for tie in work to LLNL cyclic pressure testing.			Linde-ET
Ensure insulation is replaced after tie in connection is made.			LLNL
LLNL consider adding a purge supply and outlet connection on distribution manifold for high pressure storage cycling system.(Downstream of isolation valve at tie in point)			LLNL
If LLNL requires remote access to control/monitor LH2 pump, then a review meeting must occur before this activity (Linde)	Linde to review hookup and software for remote access with LHS		LLNL/Linde-PK



1.1 High pressure — LLNL Tie In Point
1.13 Deviation During Startup — LLNL Tie In Point
1.13 Deviation During Startup — LLNL Tie In Point
1.13 Deviation During Startup — LLNL Tie In Point 1.15 Deviation During Maintenance — LLNL Tie In Point
1.13 Deviation During Startup — LLNL Tie In Point



Responses to reviewers' comments

The project is a logical extension of a storage concept that has been under development for many years. The goals of the project are relevant but may be obsolete if industry (beyond BMW) does not pick up the technology. While it is obviously important to obtain buy-in from stakeholders, cryogenic H₂ storage has fundamental advantages (safety, driving range, ownership cost, and weight) over all existing alternatives that makes this project valuable beyond individual company strategies. In this project we are exploring the limits of the technology with a new generation of cryogenic vessels that may demonstrate 3X higher volumetric capacity and 2X higher H₂ weight fraction over 700 bar CGH₂, in addition to being safe and cost effective. It is our opinion that these results will be valuable to the future of hydrogen transportation regardless of near-term corporate decisions.

The convincing demonstration for the need for cryogenic storage is not evident. It is not clear whether 10%–20% is adequate to justify the additional cost and complexity of cryogenic containment. According to analysis by Argonne, compressed gas vessels can achieve 17-18 gH₂/L and 4-5.5% H₂ weight fraction. This project is aiming at 50 gH₂/L and 9% H₂ weight fraction. This would be 3X and 2X higher performance than compressed gas – not 10-20%. These advantages are obtained simultaneously with an overall reduction in cost of ownership and safety advantages.



Responses to reviewers' comments

A project weakness is the lack of a broader liquid hydrogen research community and stakeholders to share and build knowledge to advance the technology. The dispensing of liquid hydrogen would need additional investments that would be difficult to expect in the short term. Niche markets within the hydrogen FCEV (already) niche market would need to be found. While it is true that today's vehicles use compressed gas vessels, most of today's fueling stations store liquid H₂. When LH₂ is available at the station, a LH₂ pump followed by a heat exchanger is the most economic option to refuel compressed gas vehicles (Argonne). *The same pump* would then be available for cryogenic refueling, only the heat exchanger is bypassed.

The specific performance benchmarks can be more fully specified. For instance, acceptable/anticipated heat leaking into the thinly insulated vessel is not specified. We did set an insulation performance target as a part of this project (4 Watts). This will result in good dormancy considering the maximum operating pressure of the vessel (700 bar), enough to contain the hydrogen for a long time even if the vehicle is seldom driven.

The cost of the system is not addressed. We are currently collaborating with Argonne for a cost analysis of the technology. See AJ Simon's PD134 at Delivery session on Thursday PM.



Long standing collaborations with Industry Leaders

- ***Spencer Composites (Sacramento, CA)***: Long expertise in custom composite pressure vessel development. Long-standing collaboration with LLNL on cryogenic vessels for H₂ storage and delivery
- ***Linde***: World class cryogenics experience. Manufactures maximum efficiency LH₂ pump. Delivered first commercial LH₂ pump to BMW in 2009 (300 bar). Conducted extensive HAZOP review of LLNL's Hydrogen Test Facility
- ***BMW***: Long standing collaboration with LLNL through two cryogenic pressure vessel CRADAs. Contributing detailed thermofluid/stress analysis, automotive perspective, and expertise. Advancing cryogenic pressure vessel technology & demonstration vehicles



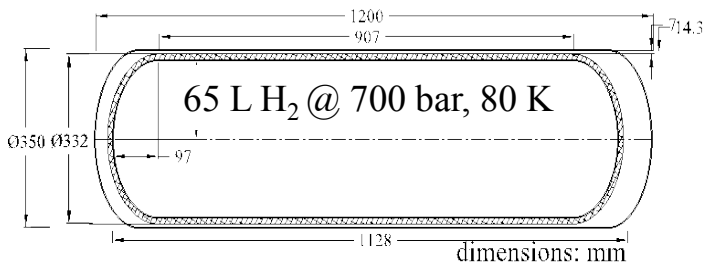
Remaining Challenges and barriers:

- ***Demonstrate cryogenic cyclability of thin-lined, high fiber fraction pressure vessels:*** Next two prototypes will be cycled 1000 times in temperature and pressure, then pressure tested
- ***Demonstrate high refuel density & durability of LH₂ pump:*** Need 80+ gH₂/L cold refuel density and no degradation by pumping 24 tonnes of LH₂
- ***Demonstrate compact, lightweight system with adequate dormancy:*** thin (<1cm) vacuum insulation with volumetrically efficient vacuum jacket necessary for small diameter onboard storage

**Durability of vessel (1000 cycles) and pump (24 tonnes LH₂)
Light, compact insulated vessel with acceptable dormancy**



Future work: demonstrate rapid refueling of 700 bar cryogenic H₂ vessels with high system density, small diameter (~35 cm), & cryogenic durability (1000 refuels)



Volumetric efficiency at 65 L capacity

- Up to 5.2 kg H₂ peak H₂ storage
- Thin metal liner (<2 mm)
- High fiber fraction (70+%)
- Thin vacuum insulation (<1 cm)
- Final system demo: 50 gH₂/L_{sys}, 9 wt%H₂
- Characterize heat transfer, vacuum, & dormancy

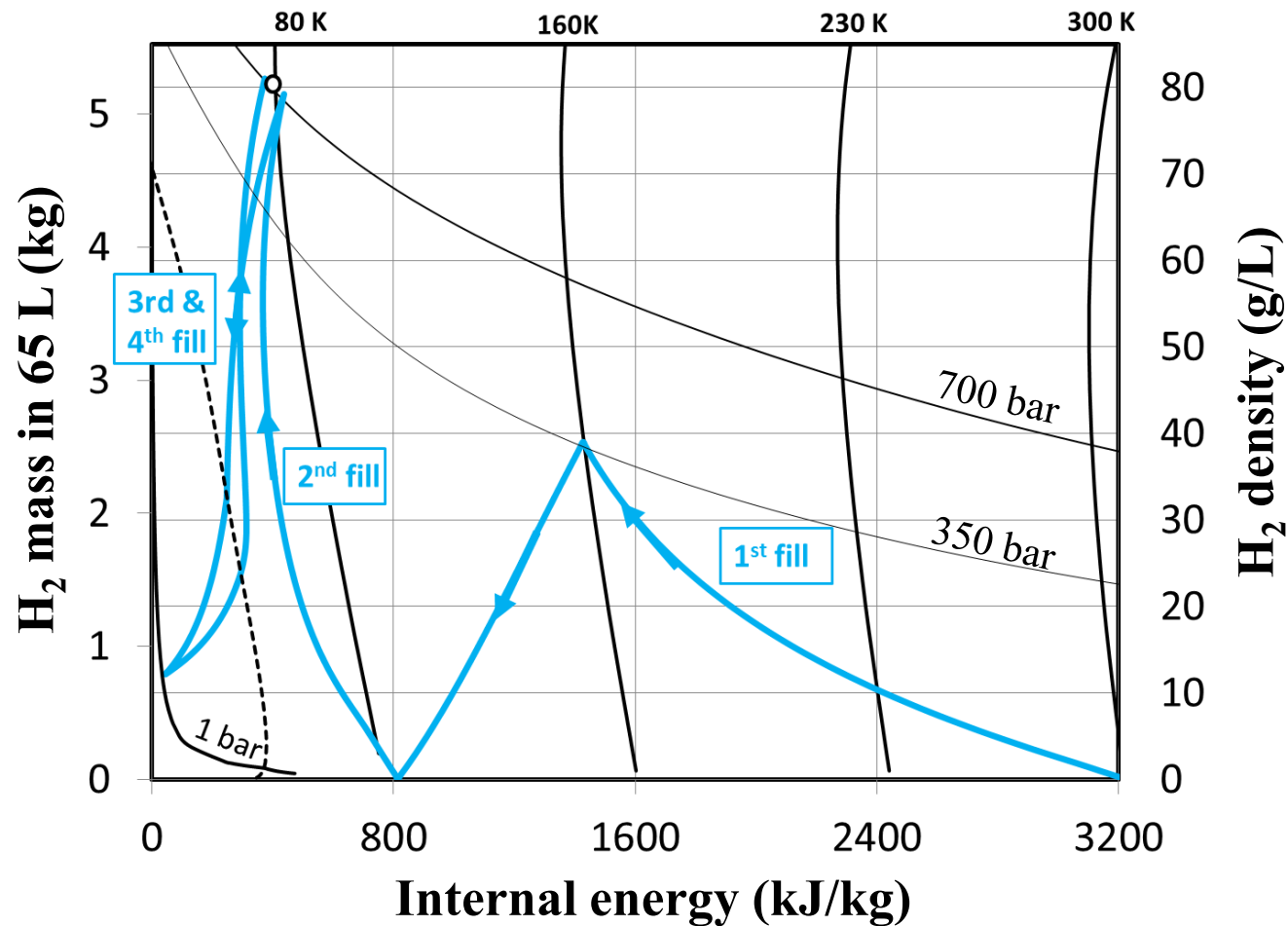


Rapid pressurized LH₂ refuel from any condition

- 100 kg/hr, up to 875 bar
- Refueled H₂ density 63-80 g/L (up to 700 bar)
- Low LH₂ evaporation (1-3%) returned to Dewar
- Test degradation by pumping 24 tonnes LH₂



Future work: Monitor pump degradation by performing test fill sequence every 500 cycles while recording key pump performance parameters



power analyzer



boil-off meter



temperature sensor

Pump performance metrics: duty cycle, peak density, boil-off, outlet H₂ temperature, electricity consumption, and fill time



Proposed Future Work

Future work includes:

- Manufacture and cycle testing of four thin-lined high fiber fraction vessels
- Test pump durability by dispensing 24 tonnes of LH₂
- Thin (1 cm) vacuum insulation of top cryogenic vessel design

Second Go/No Go successful cryogenic 1300 bar strength test of prototype vessel after 1,000 pressure and temperature cycles

Milestones	Description
Q2/FY16	Complete 1,000 accelerated thermomechanical cycles on two 65 L 700 bar, 80+% volume ratio vessels
Q3/FY16 <i>2nd Go/No-Go</i>	Demonstrate 1,300 bar minimum strength for at least one of the two cycled prototype vessels
Q4/FY16	Deliver compact vacuum jacket to exceed 50 gH ₂ /L and 9 wt% H ₂ when integrated with thin metallic liner
Q1/FY17	Complete 1000 cycles on two vessels with 1.5 mm metallic liners. Deliver 24 tonnes H ₂ through LH ₂ pump while measuring electricity use, venting, and fill speed
Q2/FY17	Vacuum jacket prototype thin-lined high fiber fraction vessel and demonstrate 50 g/L, 9% H ₂ weight fraction



Technology transfer activities: Technology jointly developed with BMW and Spencer Composites Corporation

- **BMW CRADA II signed July 2014: Includes \$1M cost share**
- **Two recent patents:**
 - Espinosa-Loza, F, Ross, TO, Switzer, V., Aceves, SM, Killingsworth, NJ, Ledesma-Orozco, E, **Threaded Insert for Compact Cryogenic Capable Pressure Vessels**, United States Patent US 9057483 B2, June 2015.
 - Weisberg AH. **Methods for tape fabrication of continuous filament composite parts and articles of manufacture thereof**. United States Patent US 8545657 B2, November 2013.
- **A provisional patent:**
 - Petitpas G, Aceves SM, Ortho-H2 Refueling for Extended Cryogenic Pressure Vessel Dormancy, United States Patent Application 2015-0330573, June 2015.
- **and two records of invention**



Project Summary

Relevance

- Demonstrate performance limits for cryo-compressed storage and delivery technology in the most adverse conditions by manufacturing small, durable vessels with thin insulation refuelable to high density with LH₂ pump.

Approach

- Combine fundamental experiments and detailed finite element models to produce thin-walled, durable (1,000 cycles) cryogenic vessels.
- Test pump performance, durability with 24 tonnes LH₂.
- Demonstrate compact (<1 cm thick) vacuum insulation with acceptable dormancy (4 W)

Accomplishments

- Design and build vessels to meet desired cycle life
- Model stresses during operation and warm fill (BMW)
- Build most capable Hydrogen Test Facility
- Conduct HAZOP analysis of H₂ Test Facility (Linde)

Future work

- Cycle test new 65 L thin lined vessel prototypes
- Demonstrate strength of cycled vessel (1300 bar)
- Vacuum jacket future 65 L vessel prototype
- Demonstrate pump durability with 24 tonnes LH₂

