Thermomechanical Cycling of Thin Liner High Fiber Fraction Cryogenic Pressure Vessels Rapidly Refueled by LH_2 pump to 700 bar

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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 Technology Validation, Storage, and Delivery

Barriers

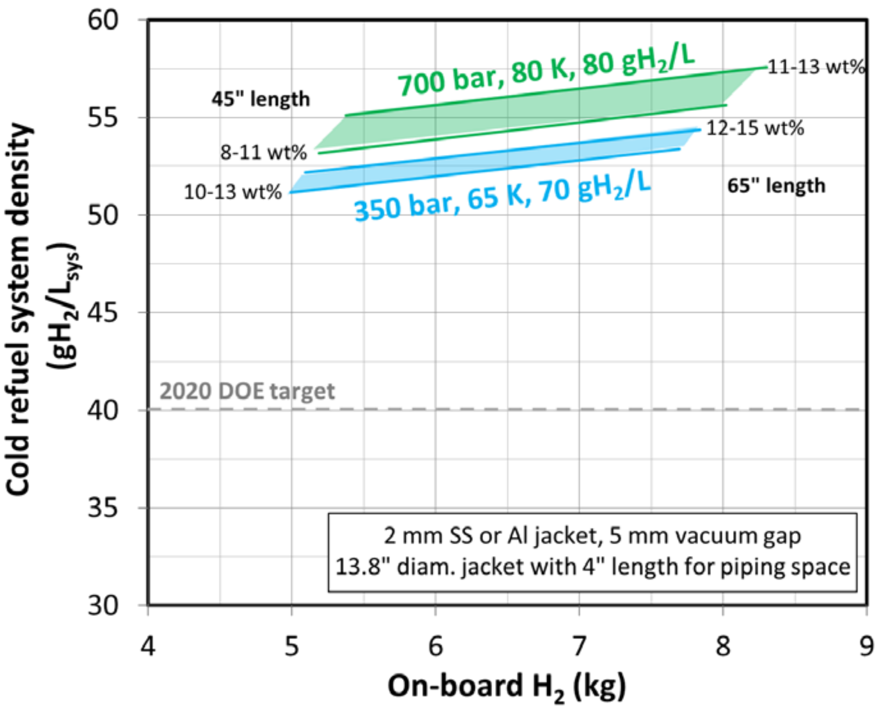
- A. System Weight & Volume
- D. Durability/Operability
- N. Hydrogen Venting

Partners

- Linde: LH_2 pump operation & maintenance, LH_2 delivery
- BMW: 350 bar cryogenic H_2 testing, system geometry, automaker perspectives
- Spencer Composites: design & build of 6 thin liner cryogenic prototype vessels

Relevance : Cryogenic H_2 offers rapidly refueled storage with volume, capacity, & safety advantages that outweigh technical challenges

- High density (cryo) H_2 allows minimum vessel volume & mass per kg H_2, thus *minimum* cost
- Min burst energy @ refueling, high on-road safety factor (5-10), inert secondary containment
- Integrated with large scale LH_2 pathway, low station footprint (100+ kg/hour, < 1.5 kWh_e/kg)



7 minute 10 kgH_2 fill to 70 g/L (350 bar, 65 K)

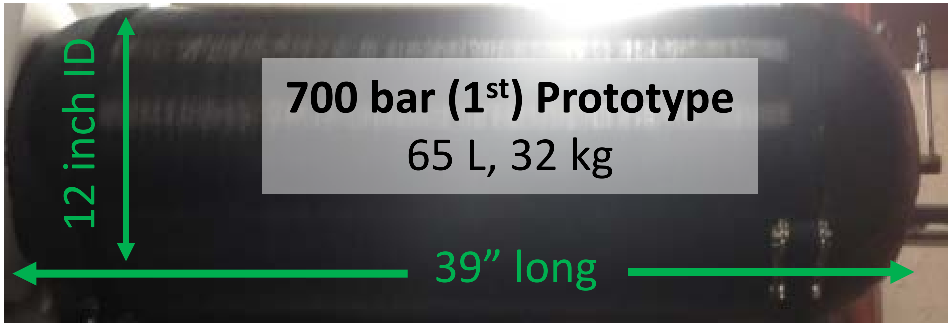
__Challenges for the technology:__

- *Compact* vacuum jacket necessary for system density
- Need both minimum heat transfer (parking) *AND* strong suspension (driving)
- Temperature *variations* alter material properties, density, dormancy, H_2 burst energy

Goal: demonstrate a 5 kg H_2 system at 700 bar with 9+ wt% & 50 g/L

Volumetric efficiency improves system tradeoffs for cryo-compressed systems (pressure, dormancy, capacity & cost). Objective : explore thermomechanical limits of specifically designed 12" cryo-vessels

9 mm Al liner
Inner volume = 163 L
Outer volume = 233 L
163 L / 233 L = *70 % volumetric efficiency*



1.8 mm non-Al liner
Inner volume = 65 L
Outer volume = 80.36 L
65 L / 80.36 L = *80.9 % volumetric efficiency*

Ultra Thin liner (1.3-1.5 mm): necessary for small diameters pressure vessels
Non-Al liner: liner, piping, and weld durability under cryogenic H_2 cycling
Maximum fiber fraction: minimum wall volume & thermal inertia

Approach: develop and test 700 bar prototype pressure vessels with a minimum 80% volumetric efficiency

Approach : Test cryogenic H_2 durability of four (65 L) prototype vessels before building a 5 kg 700 bar CcH_2 system demonstrating 50 gH_2/L

Phase 1 (proof-of-concept)

- ✓ Install instrumentation to measure cryo-pump power, outlet temperature & boil-off
- ✓ Safety plan for cryogenic H_2 cycling facility rated for 5kg H_2 prototype vessels
- ✓ 1600 bar cryogenic (LN_2) strength test of initial prototype design (2.28 safety factor)

Phase 2 (durability)

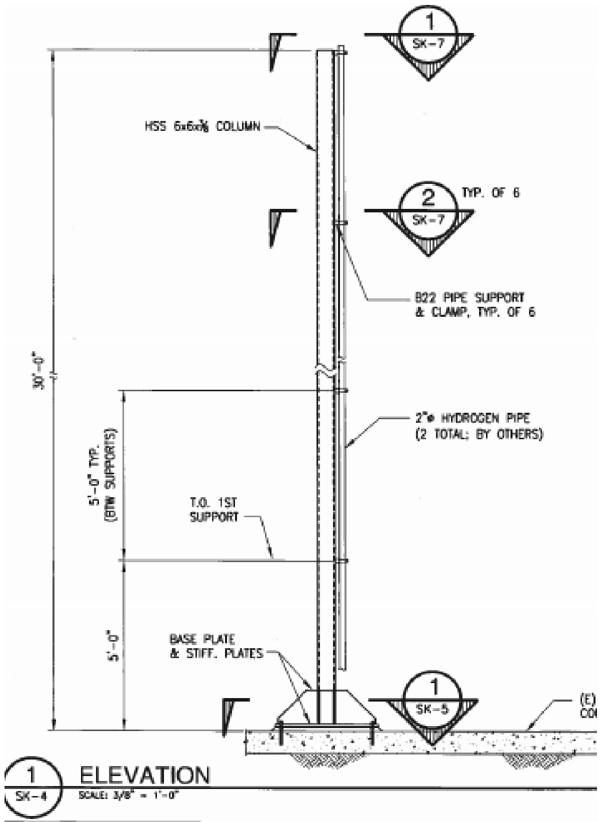
- ✓ Install containment for 1300 bar 160 Kelvin H_2 burst and 700 bar cycling to 300 Kelvin
- 1500 refuelings & cryogenic H_2 strength test (1.85 safety factor EOL) of two vessels
- Initial 700 bar characterization of LH_2 pump (peak density, kWh/kg, boil-off)

Phase 3 (demonstration)

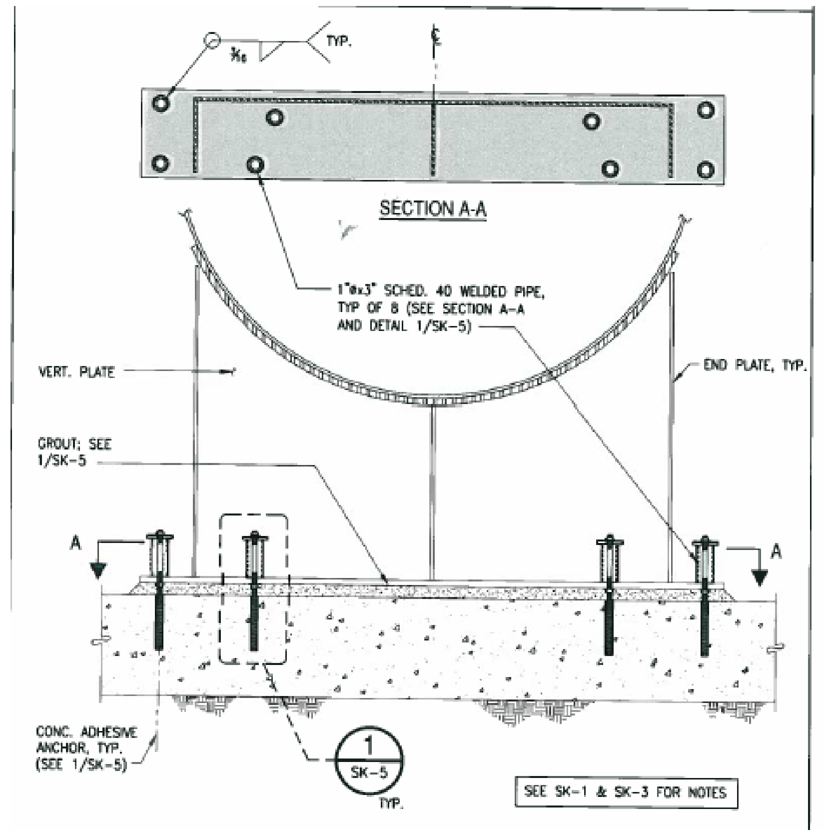
- Aggressively cycle then strength test two higher performance vessels
- Select and install final vessel design in lightweight compact vacuum jacket
- Performance demonstration (volume, peak H_2 density, dormancy, vacuum stability)
- Compare for any LH_2 pump degradation after 6,000 refuelings to 700 bar

Phase 1 go/no-go successfully completed
Phase 2 go/no-go on hold : difficulties with vessels manufacturing

Accomplishments: Seismic restraint design performed for 30 ft vent stack and 11,000 lb. containment vessel



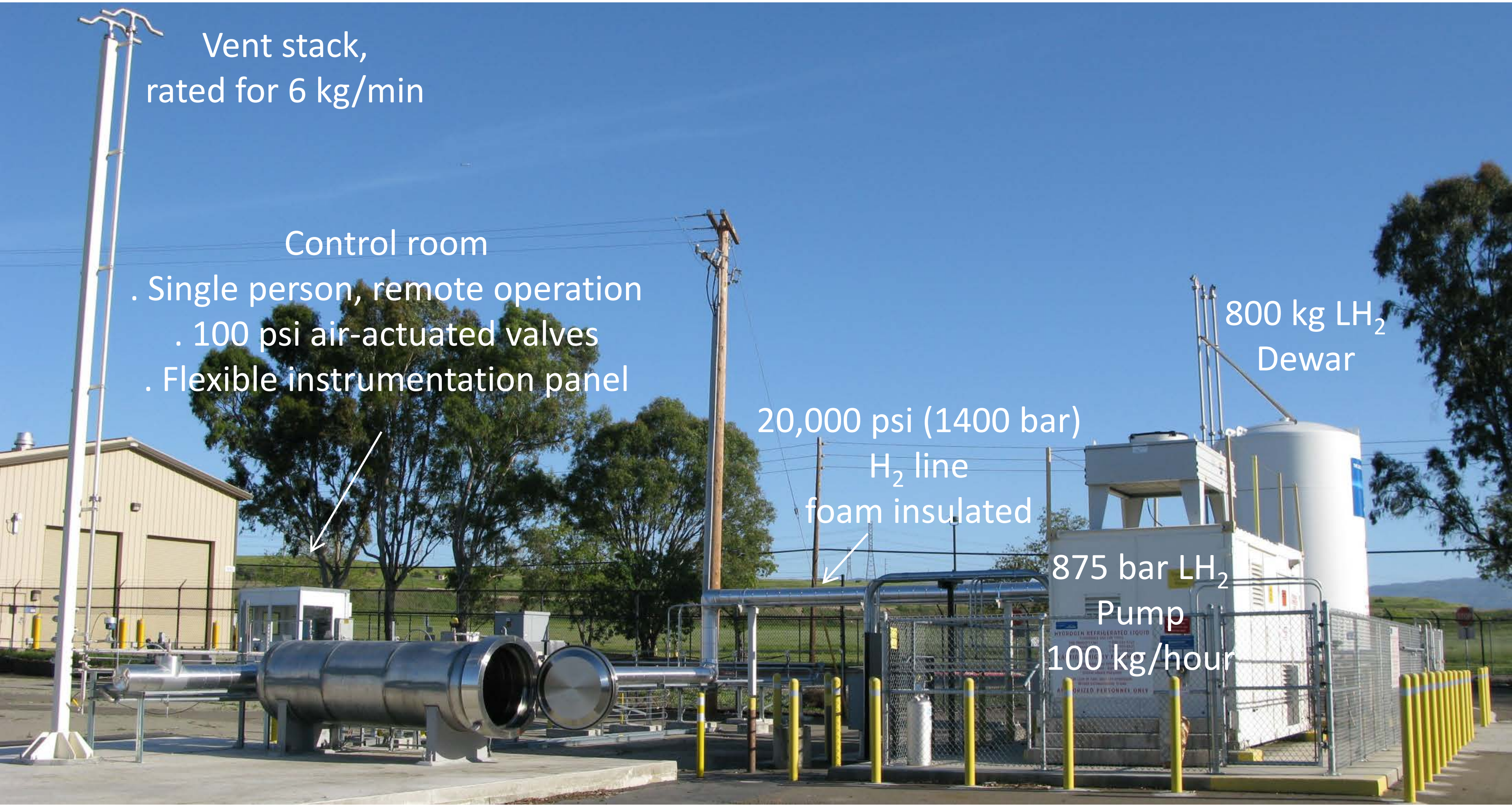
Stand-alone 30 ft support for two 2" stacks
3'x3' base plate, 8 rods
In-house (LLNL) design



Support for 11,000 lb. containment vessel
8 rods per support, 16 total

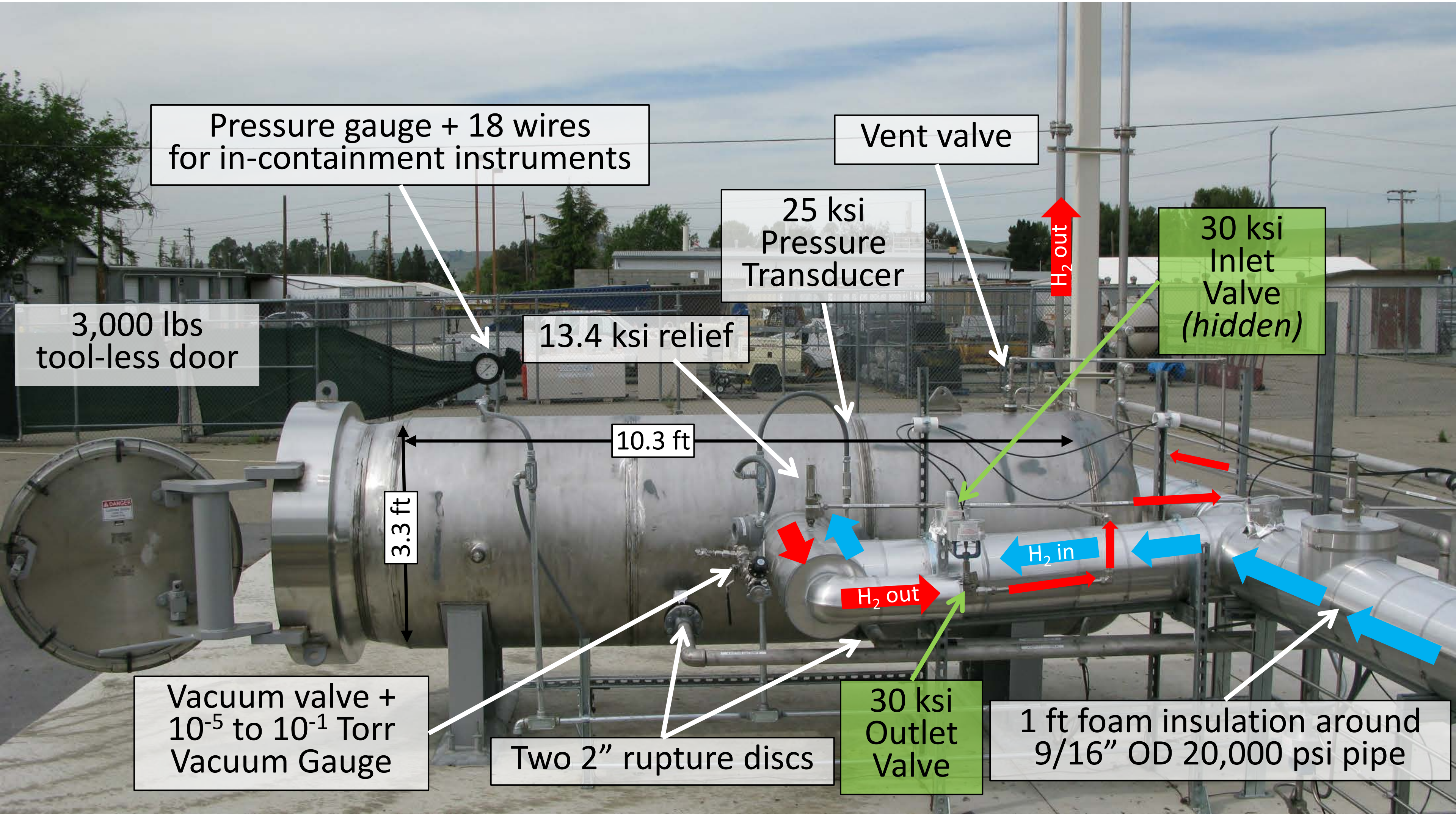
California Building Code requires Seismic Category D and Risk Category III for hydrogen. Threaded rods go 5" below ground level.

Accomplishments: Test facility construction for cryogenic H_2 cycling within 3 m^3, 65 bar containment using 875 bar LH_2 pump



Vent stack installed Sept 2015, Containment delivered Nov 2015
Facility grounded then commissioned in February 2016

Accomplishments: Test facility construction for safe cryogenic H_2 cycling within 3 m^3, 65 bar rated containment vessel



11,000 lb 3 m^3 inert stainless steel containment can withstand 2.4 kg H_2 @ 360 K, 875 bar and 7.4 kg H_2 @ 160 K, 700 bar

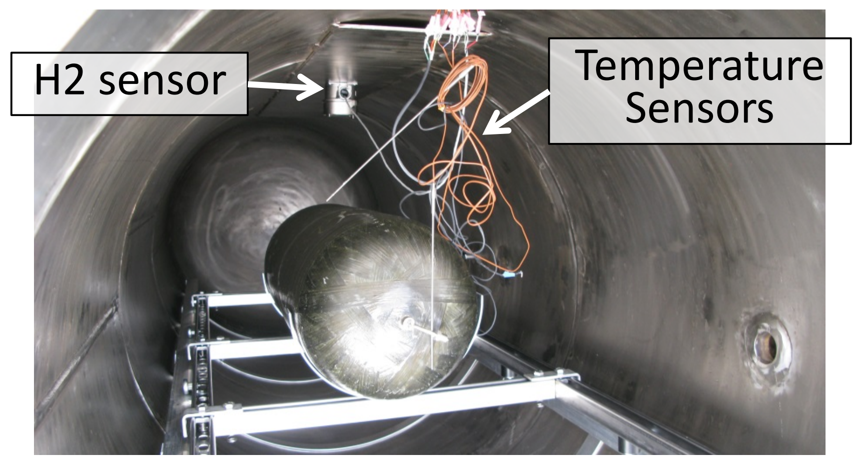
Accomplishments: Test facility construction for cryogenic H_2 cycling within 3 m^3, 65 bar containment using 875 bar LH_2 pump

"Cold-shocking" (bare fittings)

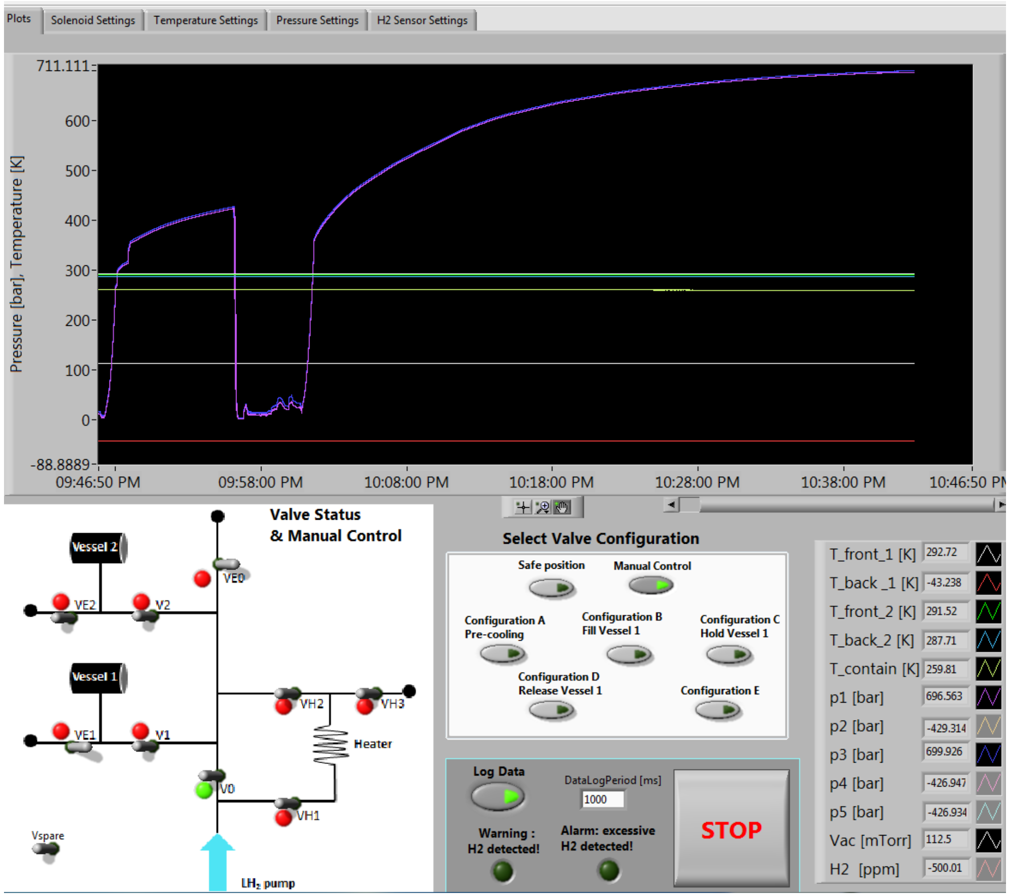
Prototype vessel + rail

1 ft foam insulation

Prototype vessel inside containment



Accomplishments: LH_2 testing facility was commissioned in Feb 2016, enabling preliminary check on fittings and vent stack



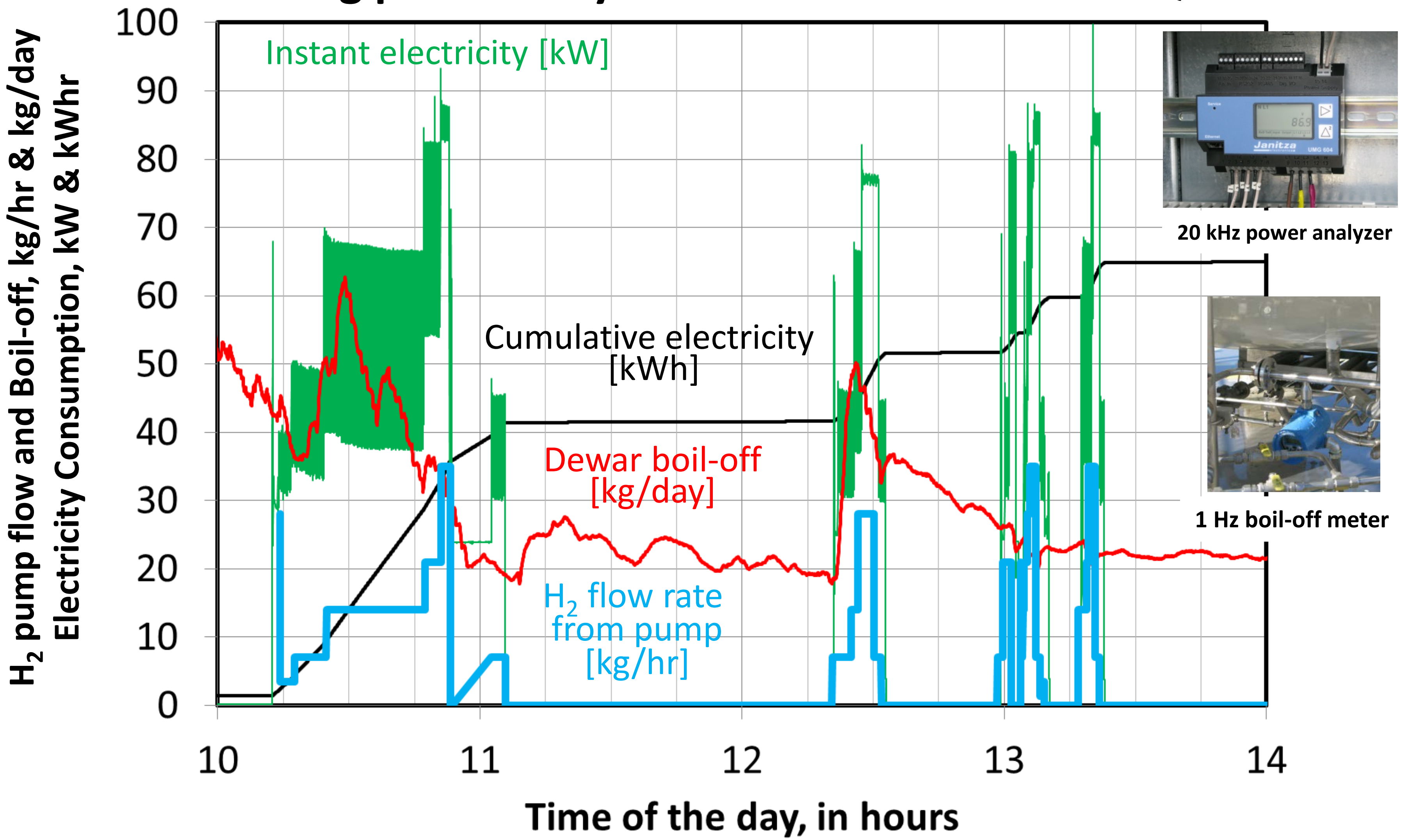
DAQ Screenshot

Piping filled with cryogenic H_2 to 350 bar, then warmed up to >700 bar

35 kg/hr , ~5 bar cryogenic H_2 release

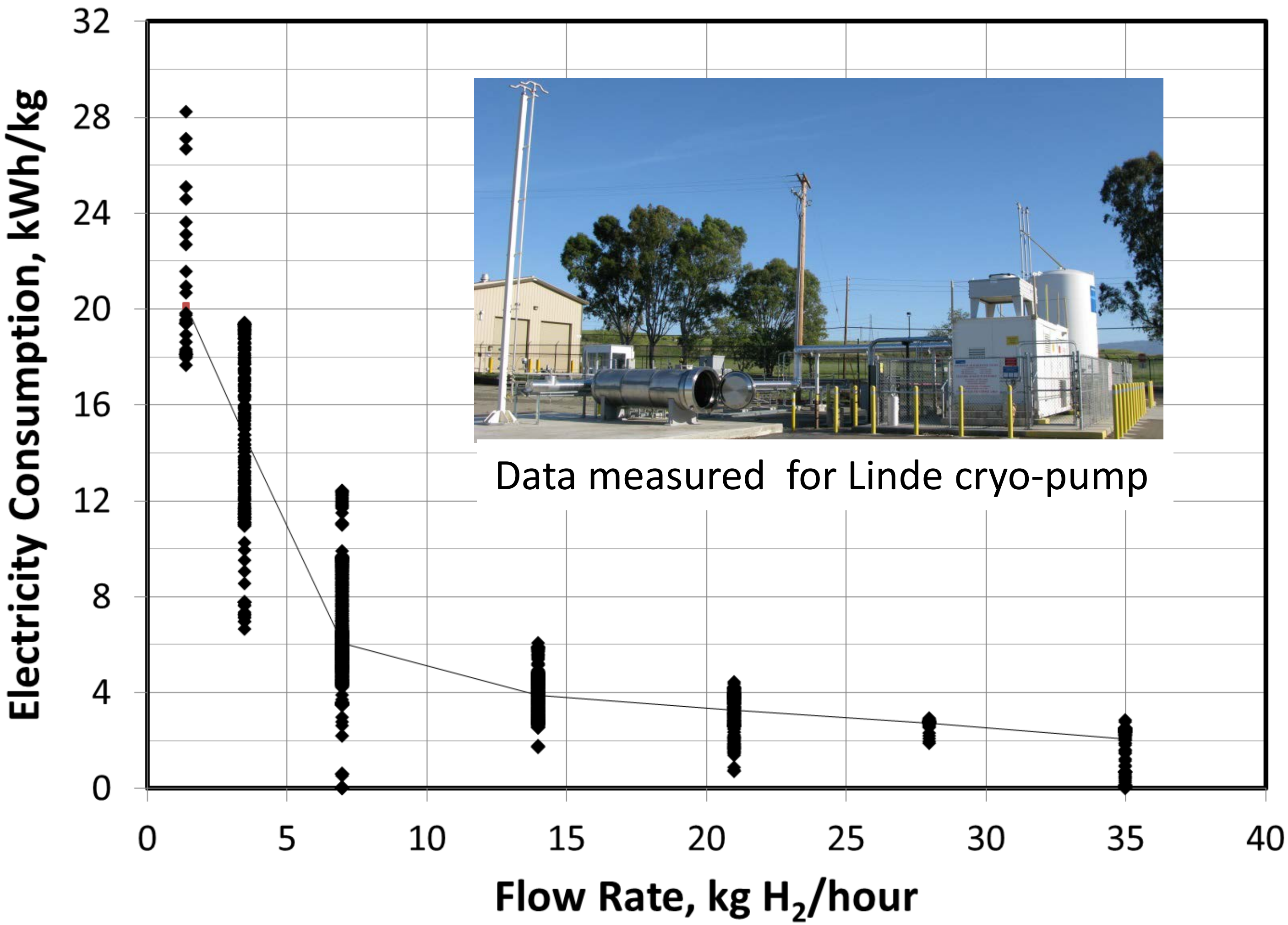
Piping system was "cold shocked" and leak-checked at > 700 bar

Accomplishments: LH_2 testing facility was commissioned in Feb 2016, enabling preliminary check on controls and DAQ



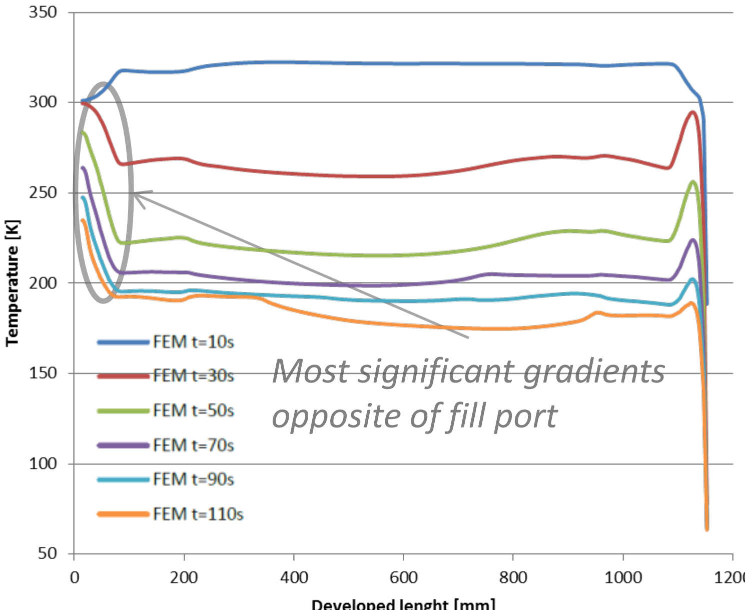
Boil-off, electricity consumption, pump flow (and pressure and outlet temperature- not shown) measured every second.

Accomplishments: LH_2 testing facility was commissioned in Feb 2016 , enabling preliminary baseline on pump performance

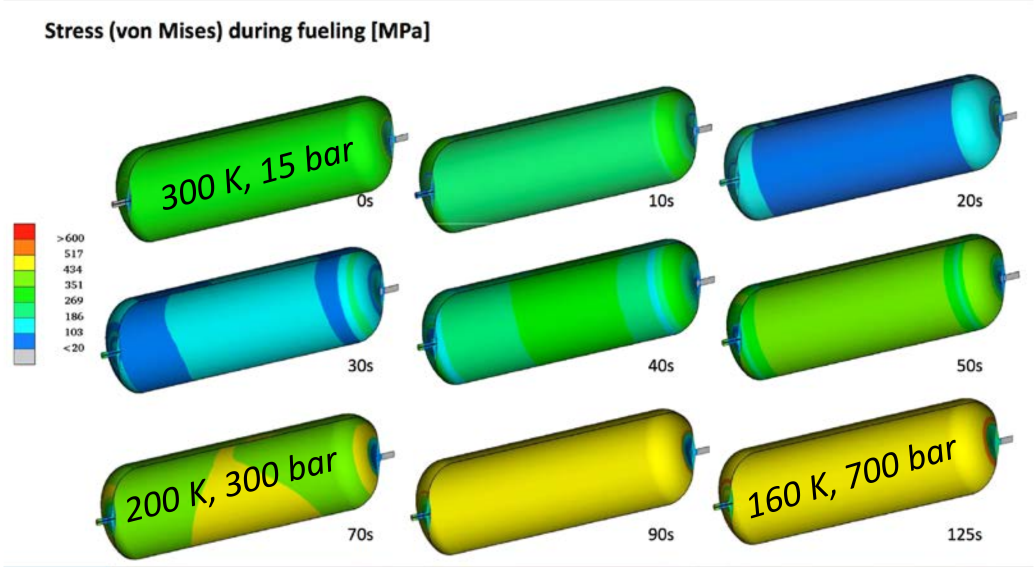


Preliminary results show low electricity consumption (< 2 kWh/kg H_2) expected under typical refuel conditions (~100 kg H_2 /hour)

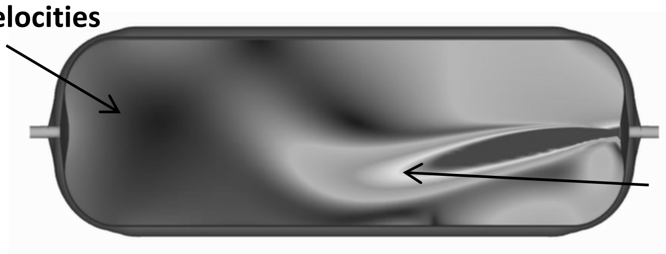
Accomplishments : Fluid + Structural computational modelling of LH_2 refuel of a warm thin-lined pressure vessel, by BMW



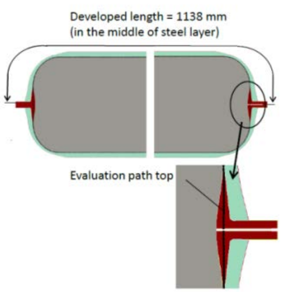
Liner temperature along length



Liner stress vs. refuel time (pattern of uniform transients)



LH_2 flow contours during refill

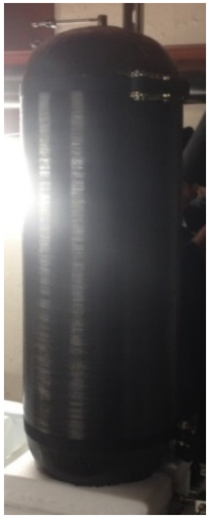


Most challenging case (warm, empty 1.3 mm SS liner, 700 bar LH_2 fast fill) shows:

(1) peak thermal gradient <u>opposite</u> of fill port

(2) peak liner tension at circumferential boss welds

Accomplishments: Manufactured and cycle tested (ambient H_2O) 6 thin/non-Al lined 80+% pressure vessels, at Spencer Composites



(#0) initial prototype (32 kg)
1.7 mm SS 316 liner/epoxy
Modified neck, 1560 bar LN2 burst

(#1) Aggressive design (28 kg)
1.3 mm SS liner/cryogenic resin
buckled during autofrettage
(H2O burst at 8,000 psi)

(#2) Conservative design
1.5 mm liner/epoxy
buckled during autofrettage
(H2O burst at 11,000 psi)

(#4 Vessel dome)
1.5 mm liner/epoxy
Analyzed by Optical, X-ray, Dye Penetration
(T-weld ruled out, but root cause not found)

(#4) Conservative design
1.5 mm liner/epoxy
pinhole leak after 247 cycles @ 700 bar
(8,000 psi H2O leak NOT at T-weld)

Water cycling revealed unexpected failure modes, mostly attributed to manufacturing ("roundness") and weld quality flaws

Accomplishments: Manufactured and cycle tested 6 thin/non-Al lined 80+% 700 bar vessels with continuously improving cycle life

Date	#	Liner	Resin	Failure during water testing
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)

Overcame buckling & weld quality (#4 dome inspected)
Best room temperature H_2O cycle life: 250 & 500 cycles at 700 bar

Responses to Reviewers' comments: AMR 2015 feedbacks highlight future opportunities for efficiency & address technical questions

- This project may be too broad in scope in addressing handling, storing, and pumping as well as cycling influences from a newly designed tank. This project, though very relevant, could actually have been split into two projects. This larger scope appears to force LLNL to take a controlling stance and to segregate the industry partners, all of whom are focusing on their own influence but not learning from one another. *Crosscut funding and economies of scale drove broad scope. Linde/BMW have longstanding relationships using this technology. LLNL ensures high BMW interest and communications with Spencer Composites.*

- The effort is ambitious. It relies on the facility test system to perform challenging testing that involves numerous cycles and parallel tests in a fashion not yet demonstrated elsewhere. *Schedule is most ambitious program element, due to long-lead hardware and cycling*

- Considerable resources and labor are required to fabricate and certify both the filling/cycling facility and the prototype and larger vessels. The important issues of the dormancy and thermal stability of the vessels may not be getting sufficient attention. *Making sure we have the right pressure vessel is really important for future developments of cryo-compressed . Dormancy and thermal stability can be improved then, and are addressed by higher pressure.*

- The project is focused on too high a pressure and should consider additional work in the area of insulation robustness. *Higher pressures were chosen to bookend the potential design space as it is much easier to extrapolate to lower pressures. Project does contain insulation task in Phase 3, but initial focus is thermomechanical cycling / material compatibility at low temp.*

Collaborations with Industry Leaders

- **Linde:** Very cooperative, sharing detailed information throughout pump development, construction, and installation. Interpreting and sharing data from multiple pumps. LH_2 handler's perspective on testing facility design. Will provide 50 LH_2 tanker deliveries over project duration.
- **BMW:** Automotive LH_2 experience. Extensive 350 bar system design and subscale cycling. Safety validation of commercial vessels. Guidance on storage geometry, use cases, cycling design. Monthly phone meetings discussing thin liner potential, vacuum stability, LH_2 pump operation and performance comparisons.
- **Spencer Composites (Sacramento, CA):** Long expertise in custom composite vessel development. Very close collaboration on component testing, first 700 bar thin liner vessel design & build. Will build many custom prototypes during the project (6 thus far, at least 2 more to be built)

Remaining Challenges and Barriers for FY16 & FY17 milestones

- ***Prototype pressure vessels manufacturing***
  - **Challenge**: 65 L 80% volumetric efficient 700 bar have shown limited cycle life during hydraulic testing (<500 cycles), although never tested cold nor with H_2
  - **Solutions** : We expect cryogenic temperatures will increase elastic range, ultimate stress and fiber modulus; hence cycle life. Given resources spent thus far, best way to demonstrate those hypotheses is to proceed with cryogenic H_2 cycling
- ***Milestones delay***
  - **Challenge**: Quarterly milestones for FY16/FY17 are strongly related and mainly rely on cryogenic H_2 cycling with prototype vessels, which has not started yet
  - **Solutions** : Due to unforeseen difficulties, project structure will be re-valuated provided first leg of cycling with 2 vessels is successful (Go/No-Go decision point)

Critical challenges should be addressed during upcoming months (April-June 2016 timeframe), allowing to best refine project scope

Proposed Future Work

Future work includes:

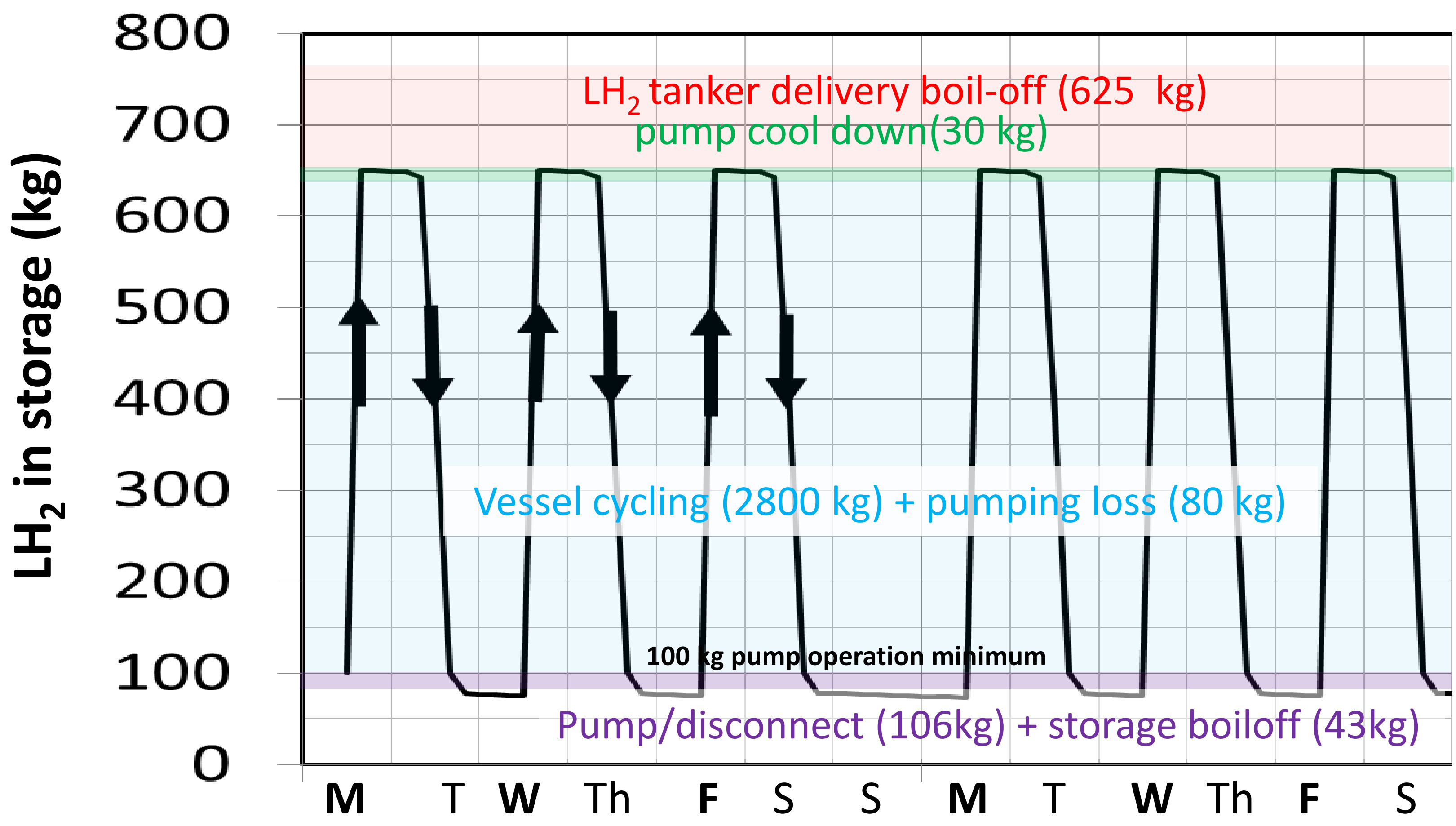
- Manufacturing of 80% vol. efficient 700 bar prototype vessel
- Cryogenic H_2 cycling of the prototype vessel
- 40 kW_e heat exchanger installation (expected shipping : May 2016)

Milestones	Description
Q2/FY16	Complete 1,000 accelerated thermomechanical cycles on two 65 L 700 bar, 80+% volume ratio vessels
Q3/FY16 2nd Go/No-Go	Demonstrate 1,300 bar minimum strength (1.85 end of life safety factor) 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 **(may be renegotiated)**
Q1/FY17	Complete 1000 cycles on two vessels with 1.5 mm metallic liners. Deliver >20 tonnes H_2 through LH_2 pump while measuring electricity use, venting, and fill speed **(may be renegotiated)**
Q2/FY17	Vacuum jacket prototype thin-lined high fiber fraction vessel and demonstrate 50 g/L, 9% H_2 weight fraction **(may be renegotiated)**

Second Go/No-Go : Successful cryogenic 1300 bar (SF=1.85) strength test of *at least one* prototype vessel after 1,000 thermomechanical cycles

Future Work : Cryogenic H_2 cycling of the prototype vessel

Baseline case: \$16/kg LH_2 cost , 188 cycles/day, 3 minutes per 2.8 kg 15-700 bar cycle



1,000 cycles (15-700 bar) of 65 L prototype uses 3700 kg LH_2 in 2 weeks with MWF Tanker Delivery and 188 cycles/day

Technology transfer activities: technology jointly developed with BMW and Spencer composites Corporation

- **BMW CRADA 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**

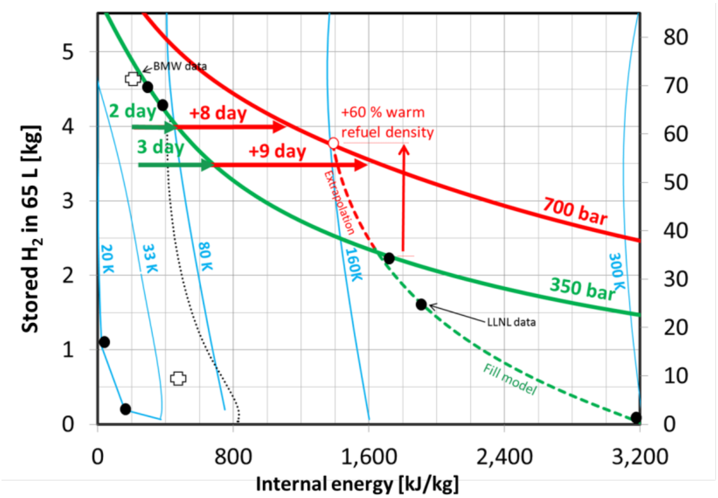
Challenges for cryo-compressed H_2 storage

Cryogenic durability of Type III composite pressure vessels, especially for the liner, is unknown

- Project is addressing this by building and cycle testing specifically designed Type III vessels.
- Cryogenic durability is aided by improved material properties at low temperatures:
  Metal: Increased yield and ultimate stress. Fiber: increased stiffness.

Driving range inconsistency due to cryogenic refueling might not be acceptable for the driver

- Driving range remains constant once driving habits are established and maintained.
- Driving range is self-regulated:
  - Frequent use maintains the vessel cold and enables high density refueling
  - Infrequent use warms up vessel and reduces fill density, avoiding fuel venting
- Higher pressure helps reduce driving range variations



The composite of the vessel outgasses over time, reducing the performance of the insulation

- Preliminary results show that cryogenic temperatures reduce outgassing ("cryo-pumping")
- It is still critical to demonstrate a long-term solution to vacuum stability
- We have proposed a promising approach and look forward to demonstrating its feasibility

Summary: LLNL will demonstrate cryogenic durability of 12” thin liner vessels over 1000 refuelings, achieving 50 gH_2/L_{sys} & 9 wt% H_2

Relevance

LH_2 pump can rapidly and consistently refuel cryogenic H_2 onboard storage to 700 bar, with potential to exceed *weight* & *volume* DOE targets with substantial dormancy improvement for modest cost, with ideal scalability.

Approach

Determine cryogenic durability of 4 full scale 65 L thin liner 700 bar composite prototypes with maximum volumetric efficiency at 12” diameter. Demonstrate system volume, weight, dormancy and vacuum stability at 5 kg H_2 capacity.

FY16 Progress

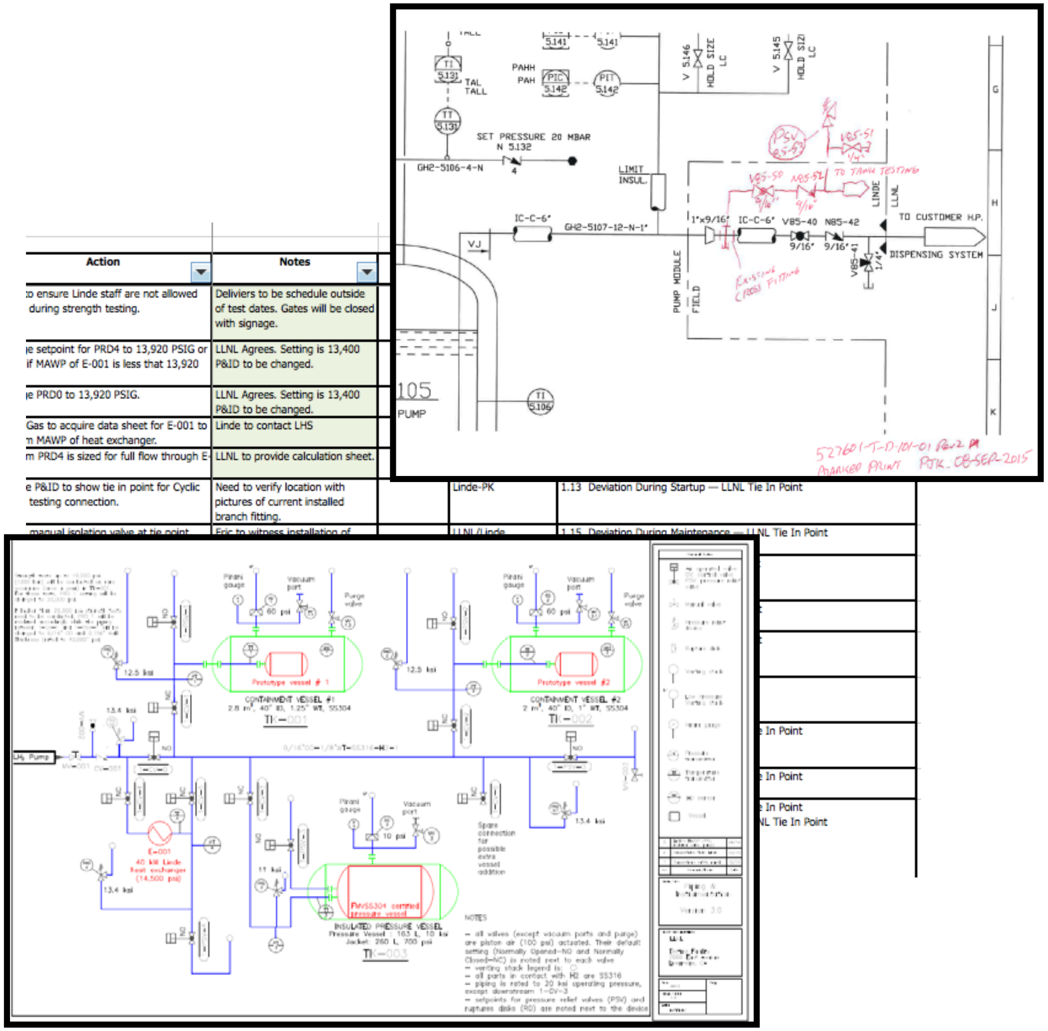
Completed construction & successfully commissioned cryogenic H_2 test facility, for full scale, rapid pressure vessel cycling.
Modeled fluid + structural for warm/empty refill of prototype vessel.
Manufactured 6 prototype vessels with 80% volumetric efficiency.

Future work

Cycle at least 1 vessel 1,000 times with cryogenic H_2 then demonstrate minimum 1.85 EOL safety factor (Go/No-Go decision).
Measure pump degradation over life of project.

Technical back-up slides

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



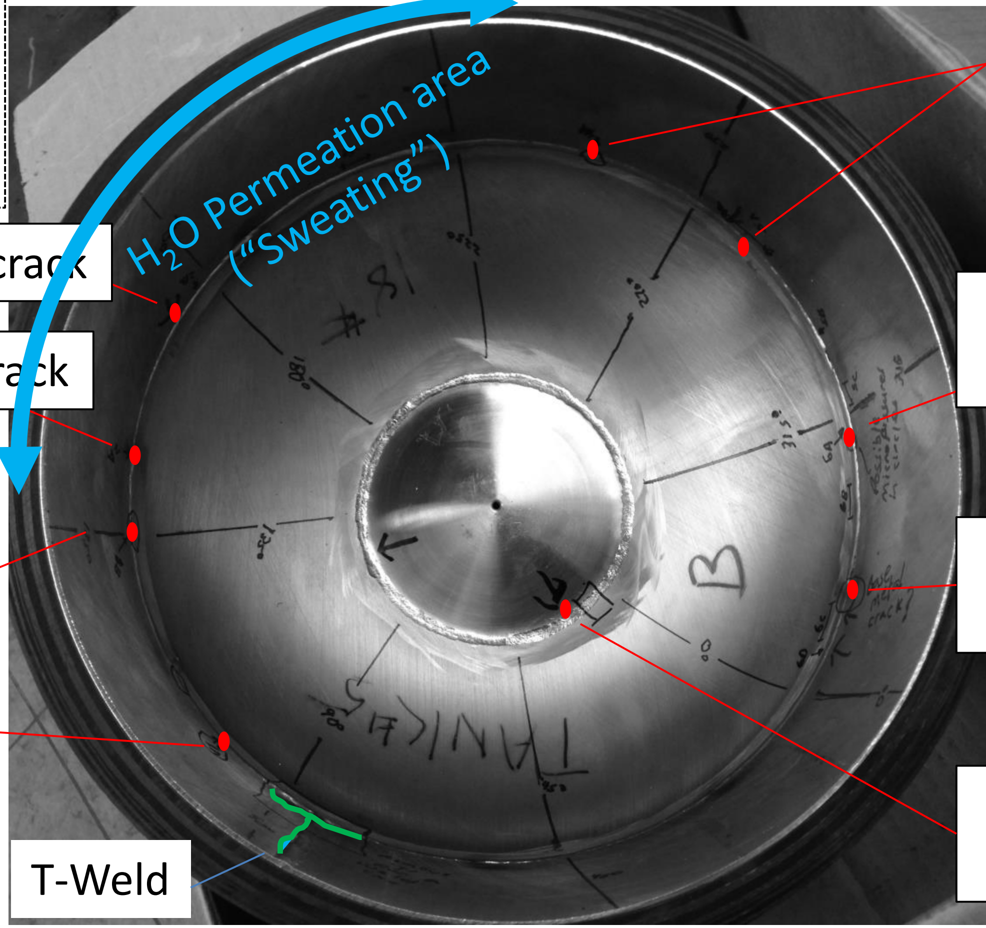
Items in the review :

- Vent stack (cloud size, heat flux)
- Venting noise levels
- Electrical classification
- Material compatibility
- Integration with LH_2 pump
- Heat exchanger connection
- Thermal stresses on H_2 supply
- Pressure relief valves sizing
- Operational Procedures
- Setback distances

HAZOP review provided external industrial audit and identified system design flaws such as missing isolation and purge valves

Leak in latest vessel (#4) after 247 cycles was investigated via X-ray and dye penetration, then by third parties at LLNL

Notes from:
John Elmer (LLNL), Distinguished Member of Technical Staff (recipient of the McKay-Helm Award from the American Welding Society)
Gordon Gibbs (LLNL), Certified Welding Inspector



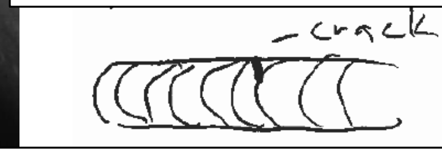
Very small transverse crack

Possible center line crack

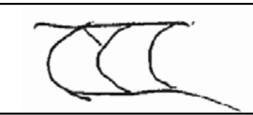
Small transfer cracks

Small transverse line

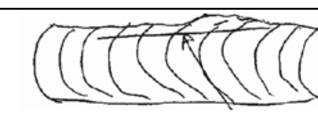
Small transverse crack inside of weld



45 degree crack following grain growth



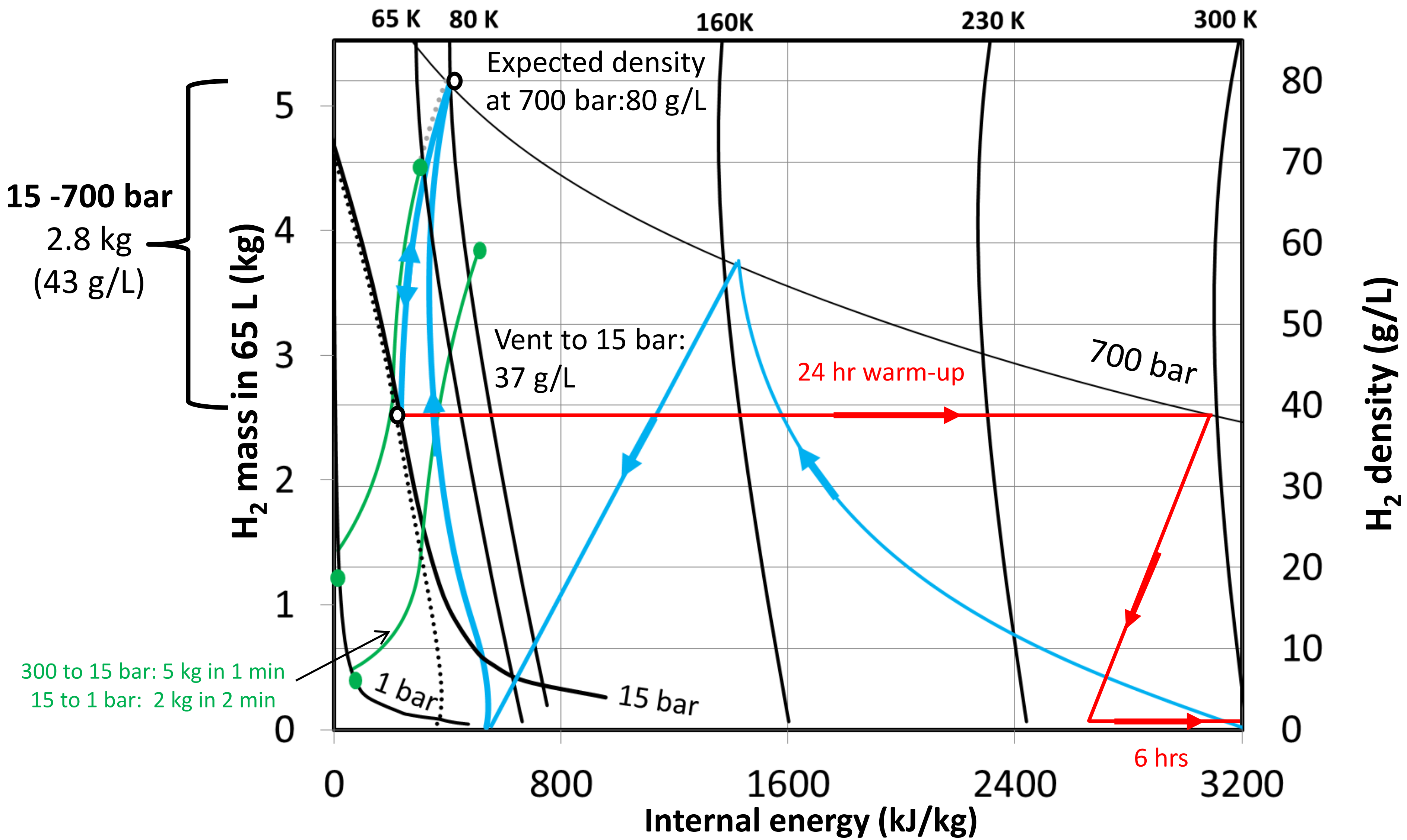
Large linear crack at edge of weld



Possible flaw from dye penetration

Liner was X-rayed before winding and after testing. Pinhole H_2O leak was not located. Welds in dome were visually inspected per ASME procedure and only insignificant anomalies found. **Options**: try to find leak by pressurization of dome or characterize by destructive cross section

Future Work : Cryogenic H_2 cycling will cover the full pressure & temperature range, emphasizing maximum thermomechanical stress



Cycle plan: 3 minute cycles (1480 cold, 20 warm) to 700 bar