DOE Hydrogen Program

Compact (L)H_2 Storage with Extended Dormancy in Cryogenic Pressure Vessels

Gene Berry, Salvador Aceves
Francisco Espinosa, Tim Ross,
Vernon Switzer, Ray Smith,
Andrew Weisberg

Lawrence Livermore National Laboratory

May 22, 2009

Project ID # ST_34_Berry

This presentation does not contain any proprietary or confidential information

Overview

Timeline

- Start date: **October 2004**
- End date: **September 2011**
- Percent complete: **70%**

Budget

- Total project funding
  - DOE: **$4.5M**
- Funding for FY08:
  - **$1.2M**
- Funding for FY09:
  - **$2.25M**

Barriers

- **A. Volume and weight**
- **O. Hydrogen boil-off**

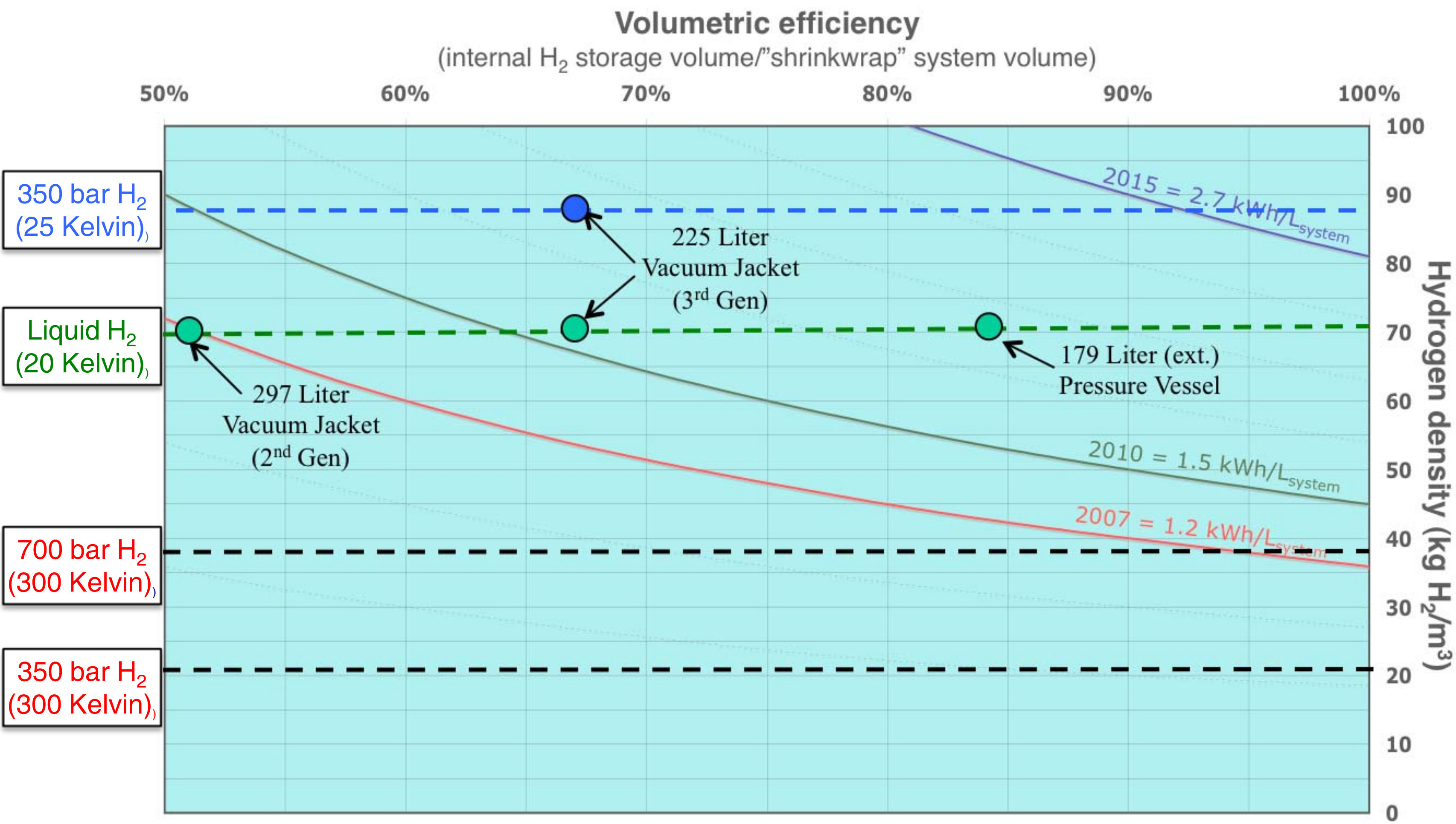
Targets

- **2010 DOE volume target**
- **2010 DOE weight target**

Partners

- **CRADA** with BMW
- **CRADA** with Structural Composites Industries (SCI)

Relevance: Cryogenic pressure vessels offer technical potential to exceed 2010 H_2 storage goals, and approach 2015



Approach: Build systems exceeding 2010 volume/weight targets in collaboration with industrial partners understand fundamental potential of *both* system & H_2 behavior

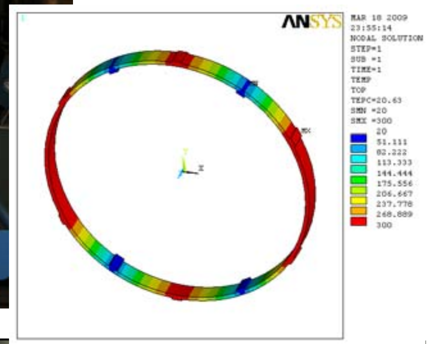
- *Fabricate third generation cryotank storing >45 kg H_2/m^3_{system}*
- *Achieve >1 week of dormancy*
- *Understand dormancy impacts of para-ortho conversion*
- *Investigate composite vessel impacts on vacuum quality*
- *Demonstrate adequate cycle life, (cryogenic shock, high pressure)*
- *Cryogenic vessel development and burst testing*
- *Explore superliquid H_2* (ρ>70 kgH_2/m^3)

Collaborations:
We have entered into cooperative research & development (CRADA) agreements with an automaker and pressure vessel manufacturer

- ***CRADA with BMW*** **collaboration has been intensifying over 3 years. CRADA finalized June 2008 to investigate vacuum stability, conduct cryogenic pressure cycling, and study conversion to *ortho*-H_2. BMW provides great automotive focus to our experimental and demonstration efforts.**

- ***CRADA with Structural Composites Industries (SCI):*** **Jan. 2009 CRADA formalized a longstanding relationship in high pressure and H_2 work of over two decades. Using LLNL's thermal/mechanical analysis capability and H_2 experience as well as SCI's in-depth composite cylinder design & manufacturing expertise to develop highly efficient and lower cost pressure vessels designed specifically for cryogenic H_2 storage.**

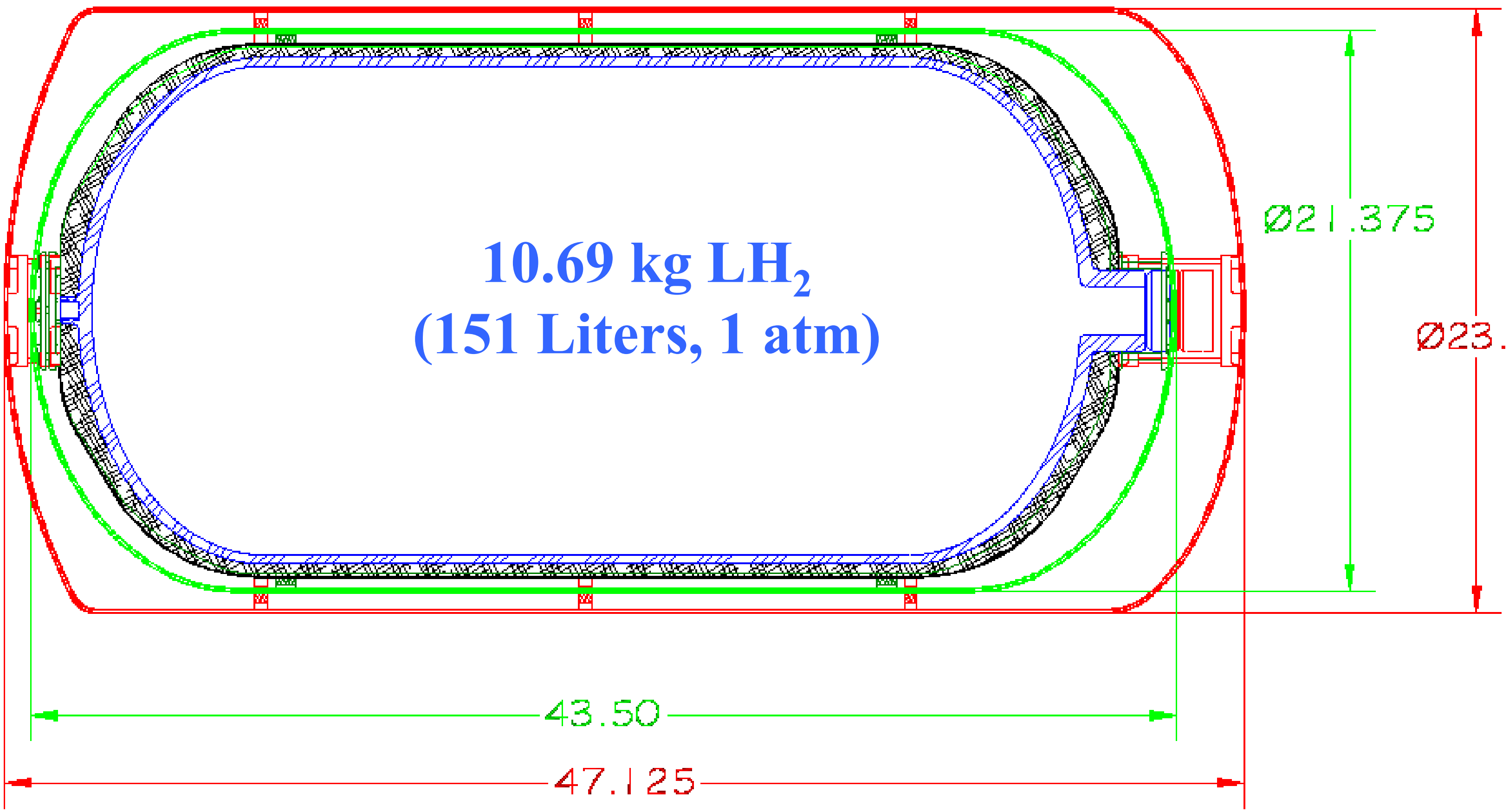
We have refined our 3rd generation system to meet/exceed 2010 volume and weight targets



- Lighter, smaller vessel (4000 psi)
- Shorter, stronger boss (18,000+psi)
- Longer conduction paths (H_2 lines)
- Fewer support rings (3 to 2)
- Vacuum thickness cut by 2/3
- Less MLI layers in complex areas
- 3kW internal heat exchanger (BMW)
- LH_2 fill valve outside vacuum jacket

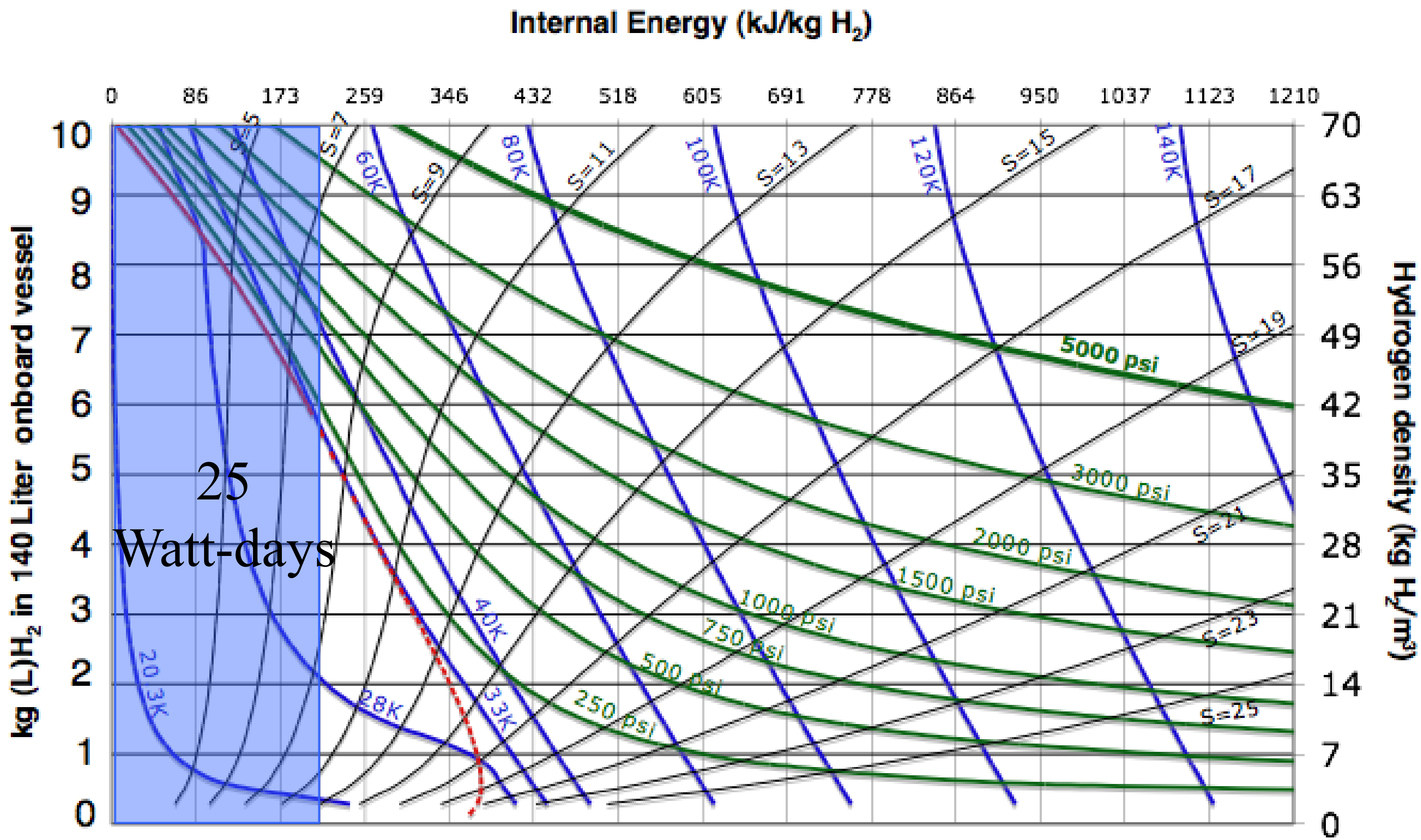
- Proof tested to 6600 psi
- Fabrication/integration complete
- System cryoshocked & leak tested
- Onboard dormancy test scheduled

3rd generation cryotank & vacuum jacket saves 25 kg & 70 liters
Storing 7.4 wt% H_2 at 45.2 kg H_2/m^3



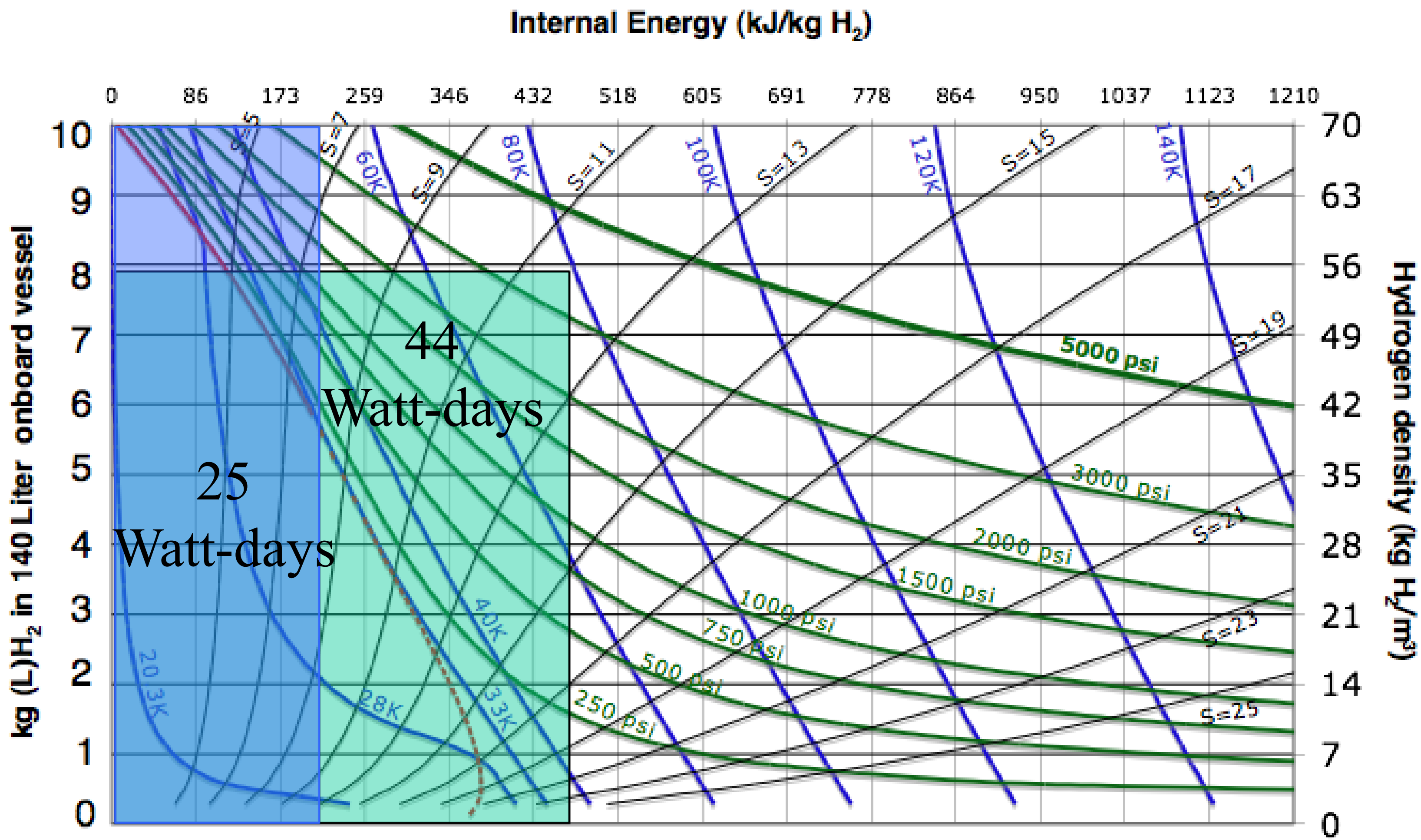
	Weight (kg)	wt%H_2	Volume (L)	kgH_2/m^3
4000 psi vessel+boss	60.9	14.9	179	59.7
Steel vacuum jacket	57.1	8.3	225.4	47.4
Ancillary components	16	**7.4**	11	**45.2**

3.5 day calculated dormancy of 10.7 kgLH_2 (full) in 3[rd] gen vessel (~7 watts, 4000 psi, H_2 heat capacity only)



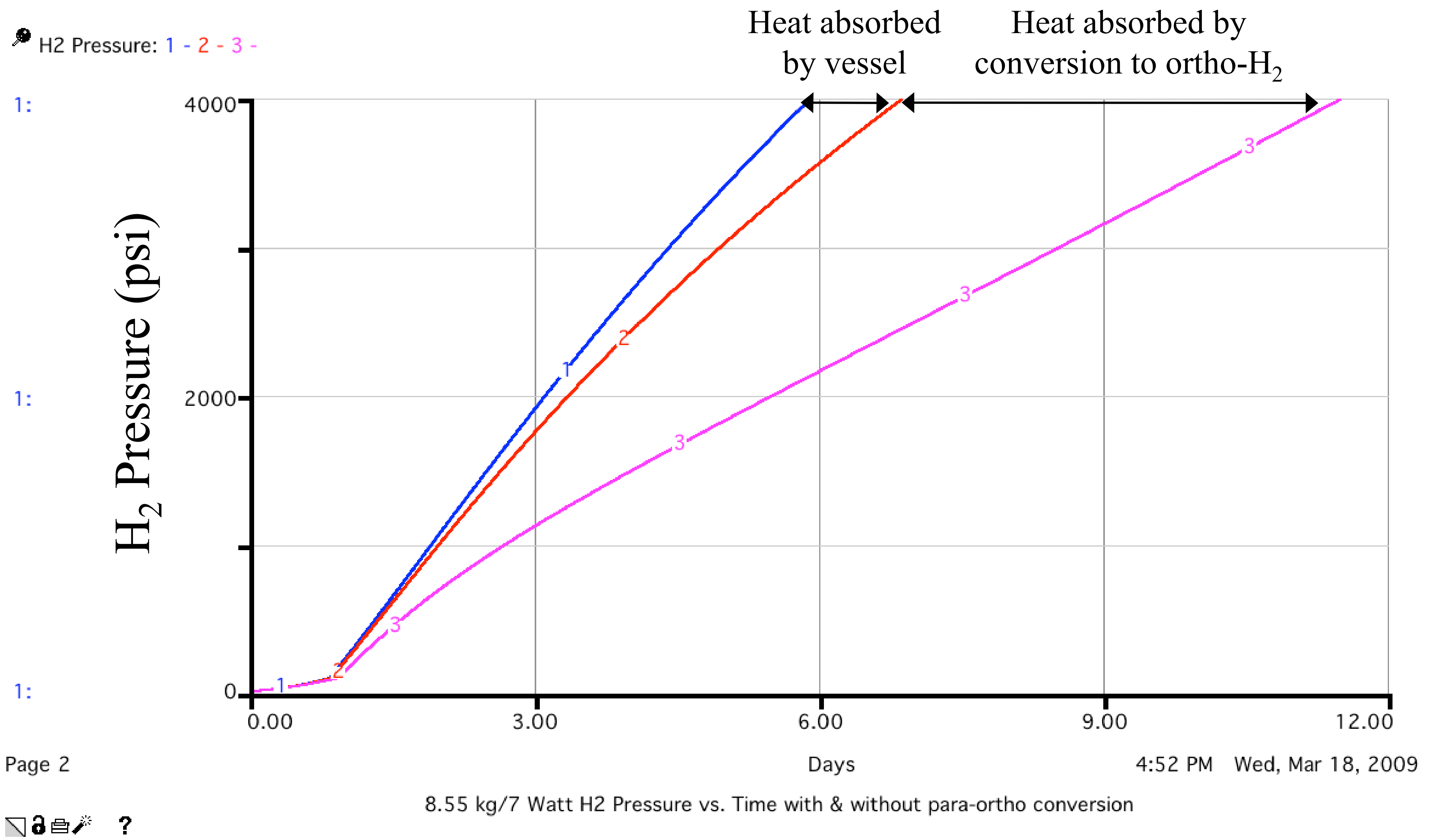
Hydrogen annual merit review, LLNL, May 22, 2009, p. 8

6.5 day calculated dormancy if 80% full w/LH_2 (7 Watts, 4000 psi, H_2 heat capacity only)

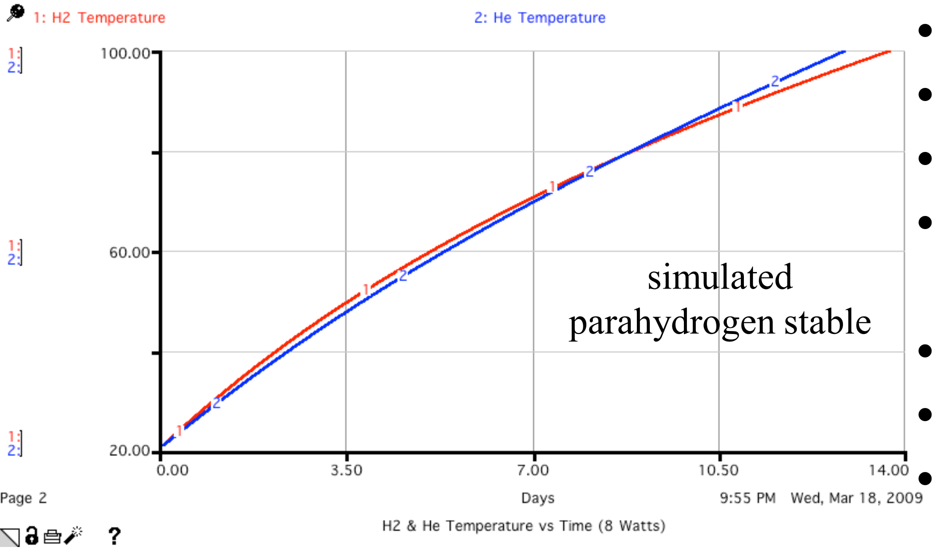


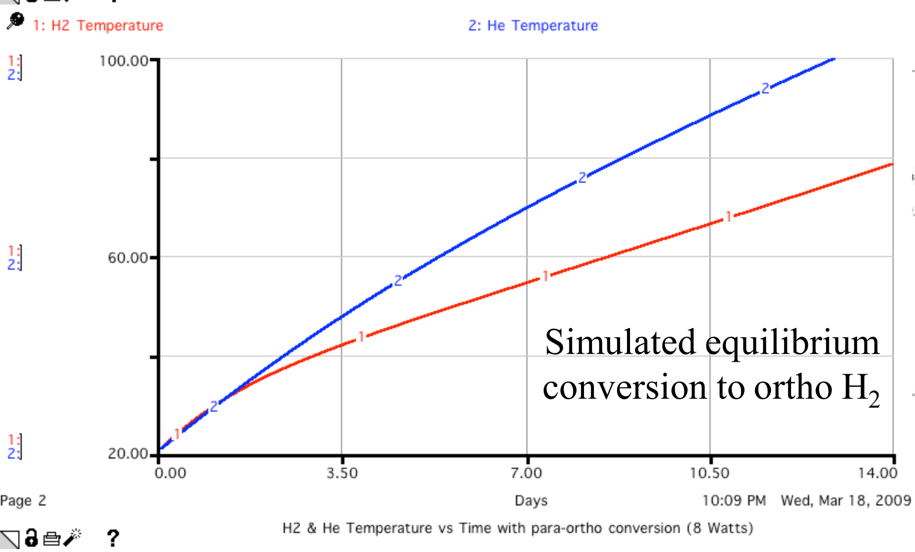
Hydrogen annual merit review, LLNL, May 22, 2009, p. 9

Vessel warming combined with (theoretical) conversion to *ortho*-H_2 could extend dormancy of 8.55 kg LH_2 (80% full) to 11+ days

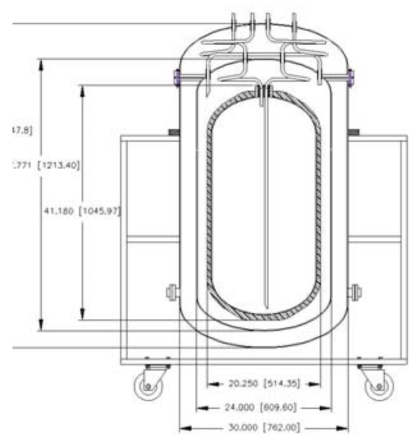


We will assess *para-H_2* to *ortho-H_2* conversion by experiments warming H_2 outside two-phase LH_2 region complemented by a surrogate test with He if warranted



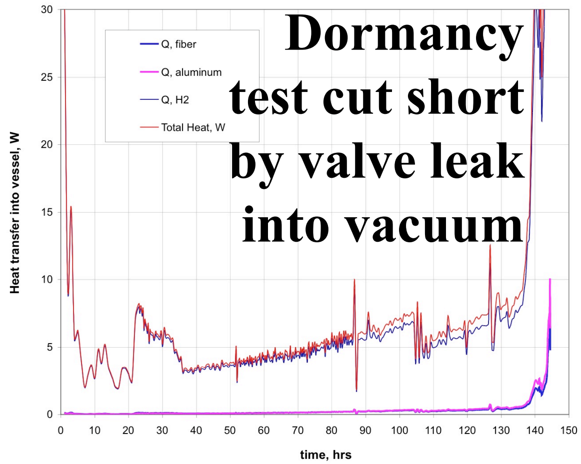


- Measure Weight, Pressure, & Temperature
- Integrated (20-100K) test and/or fixed T
- Results interpretable w/o vessel corrections
- Aggregate *para-ortho* conversion impact directly measured by He surrogate test
- Full scale (163 L) test & expt. range (T,P, ρ)
- 10 ksi vessel w/ coolant & vacuum jacket
- Hardware capability to confirm/reverse *para-ortho* conversion at automotive scale



- Collaborating with BMW on experimental strategy, methodology
- Exp't simulations use real properties of all $L(H_2)$ states, phases

Outgassing experiments on as received 1 liter composite vessel: H_2O majority component, hydrocarbons not improved by baking



Oven in pressure cell

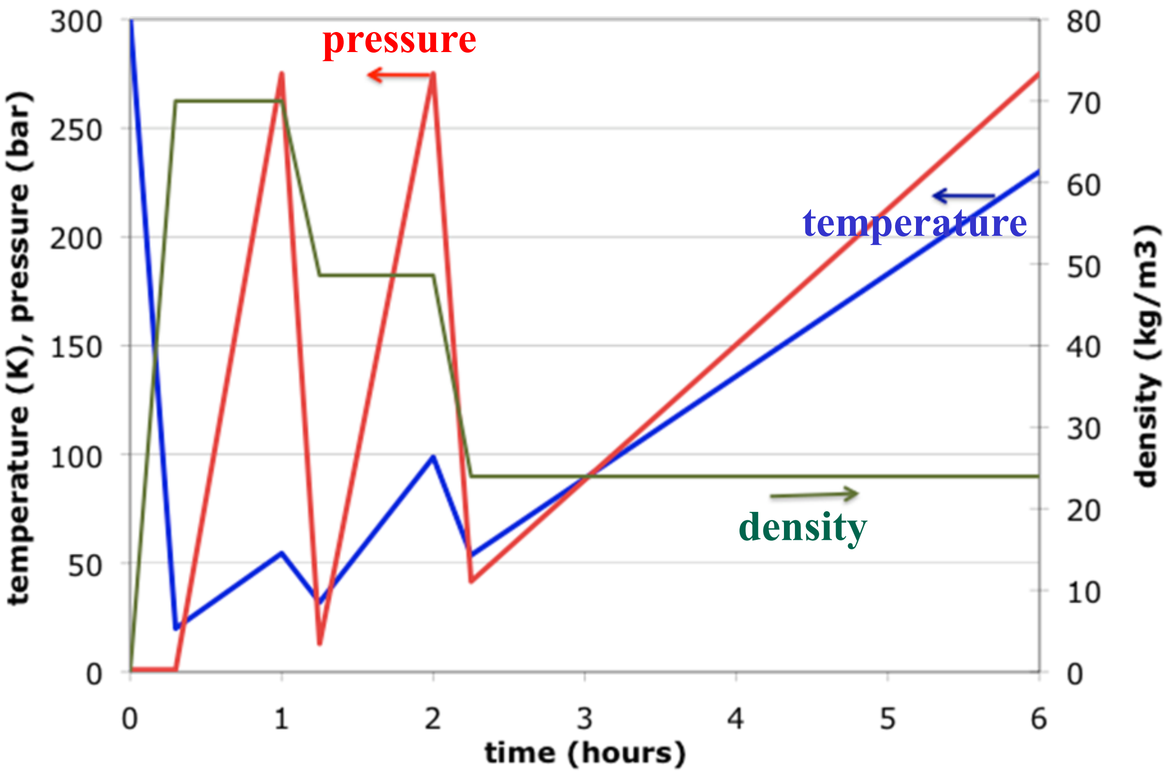
1 liter vessel under vacuum in oven

Compound (and boilng point)	Concentration in parts per billion by vol.					
	Ambient		60ºC		82ºC	
	First test No cycling	2nd test 10 cycles	First test No cycling	2nd test 10 cycles	First test No cycling	2nd test 10 cycles
Water (100ºC)	80,000	4,000	350,000	4,500	300,000	5,500
Acetaldehyde (20.2ºC)		23	230	22,000	1500	11,000
Acetone, (56.5ºC)	85	74	1100	23,000	8300	19,000
Ethanol, (78.4ºC)	87	29	800	97	4500	3000
Isopropyl alcohol (83.6ºC)	23	17	110		690	
Trichloroethylene (87.2ºC)	6.2	9.2	4.1			
1-propanol (97.1ºC)			360	120	2400	
Toluene (110.6ºC)			2.7		14	
Acetic acid butyl ester (126ºC)	47	260	2900	2900	8200	9500
Ethyl benzene (136ºC)	4.7	6.5	120	52	700	210
Xylenes, total (140ºC)	20	30	430	240	2500	1000
Styrene (145ºC)	5.9	8.7	110	70	630	290
2-heptanone (151ºC)	39	530	4800	2900	12,000	25,000
1, 3, 5 trimethylbenzene (164ºC)	1.7	1.1	20	8.5	91	120
1, 2, 4 trimethylbenzene (169ºC)	1.9	1.6	39	11	180	130
Total hydrocarbons	**321**	**990**	**11,026**	**51,490**	**41,705**	**69,250**
Total	**80,321**	**4990**	**361,026**	**55,890**	**341,705**	**74,750**

Outgassing experiments have been planned in collaboration with BMW to separate pressure cycling (Ar) from thermal effects and investigate vessel processing and surface treatments

- ***Pre-bake vessels to 100°C:*** **Determine if H_2O can be essentially eliminated.**
- ***Cycle vessels slowly or with cooled gas:*** **Keeping vessels at ambient temperature (or below) better represents expected onboard conditions. Measurements after 10 & 100 pressure cycles**
- ***Outgassing from vacuum cured vessels with/without UV coating:*** **Investigate processing effects on outgassing, and potential cycling effects on coatings**

A 4000 psi vessel identical to the 3rd generation storage system will be cryogenically cycle tested

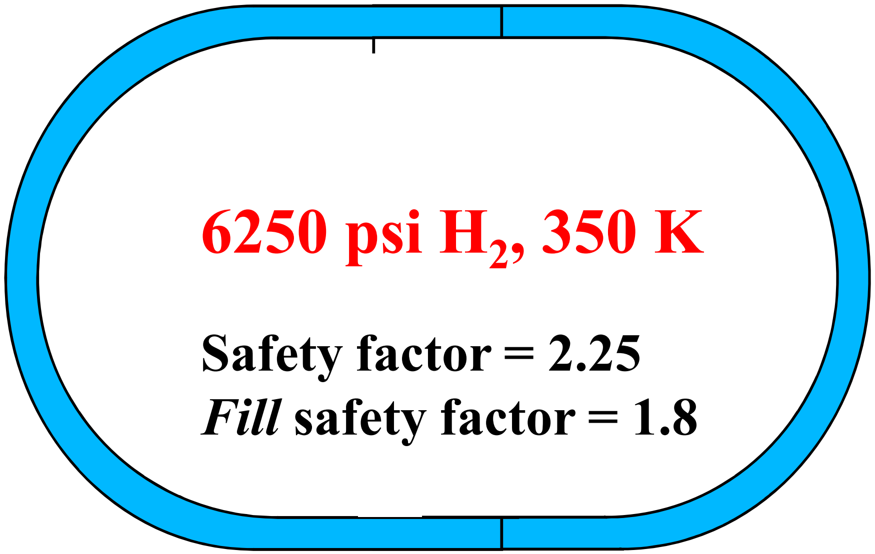


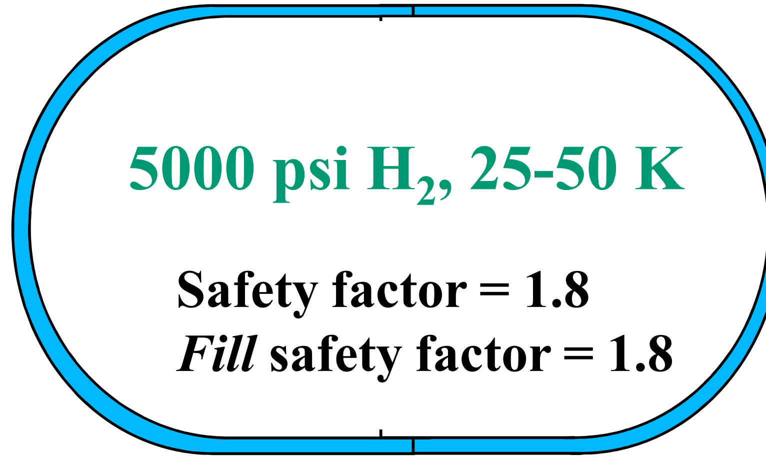
- High & Low Pressure at Cryogenic T (20-100 Kelvin)
- Vacuum jacketed vessel warmed internally (2-5 kW)
- Ultrasound characterization after hundreds of cycles

We will acquire a high pressure cryogenic H_2 fueling capability

- ***We currently fill at low pressure*** **from a conventional LH_2 storage vessel**
- ***A high pressure LH_2 pump*** **offers rapid single phase refueling without boiloff**
- ***Site Permission and Utilities granted*** **Will also serve for high pressure cryogenic H_2 testing (e.g. *para-ortho*)**
- ***We plan to explore densities beyond LH_2*** **to meet DOE's ultimate storage goals. Pressurized LH_2 is up to ~25% more compact and needs to be studied, tested, and ultimately demonstrated onboard**

Pressure vessel designs can be improved by accounting for vessel usage





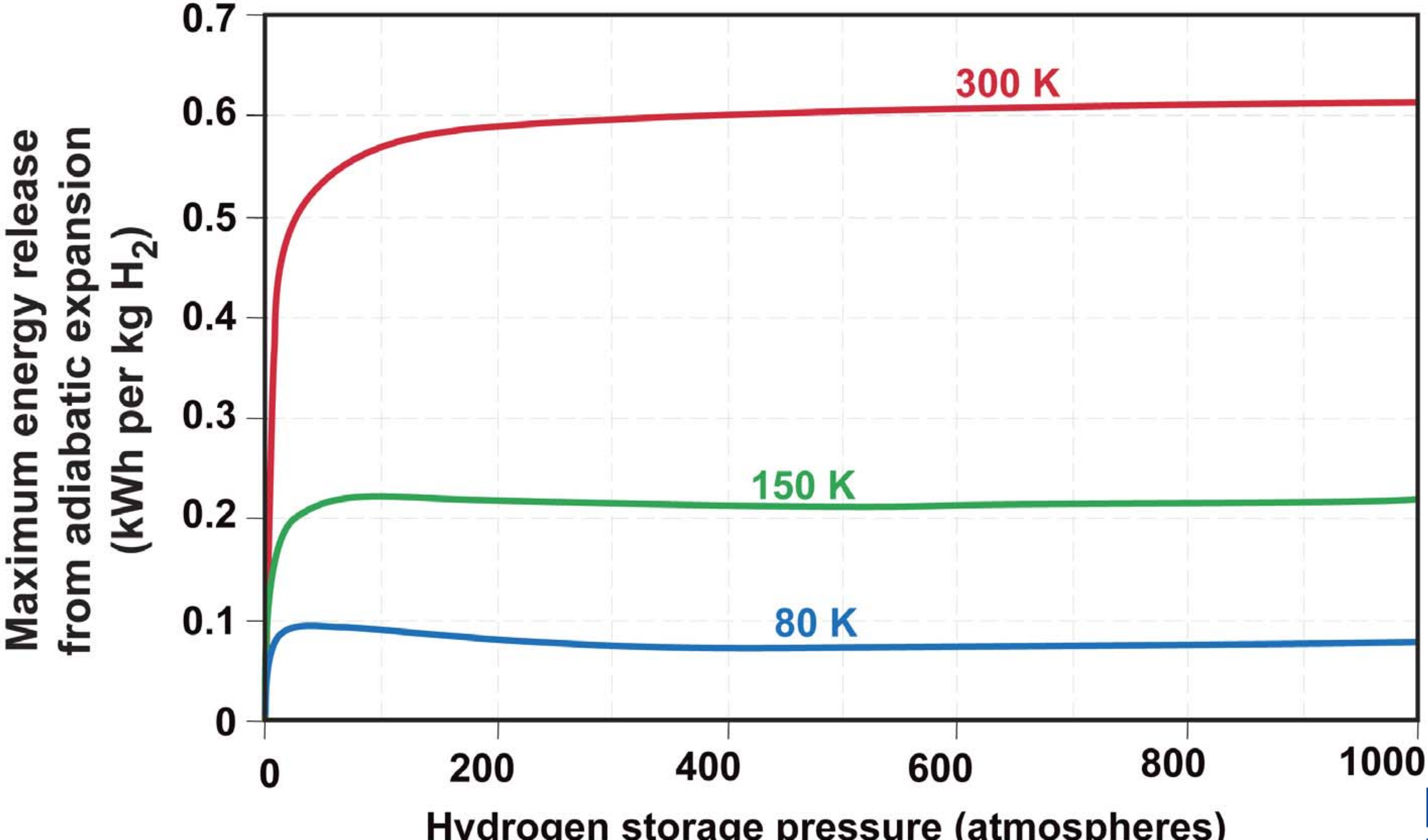
Current automotive H_2 vessel

- Filled with H_2 at up to 80°C
- Service pressure: 5000 psi
- Fill pressure: 6250 psi
- Burst pressure: 11,250 psi

Future automotive cryo-H_2 vessel

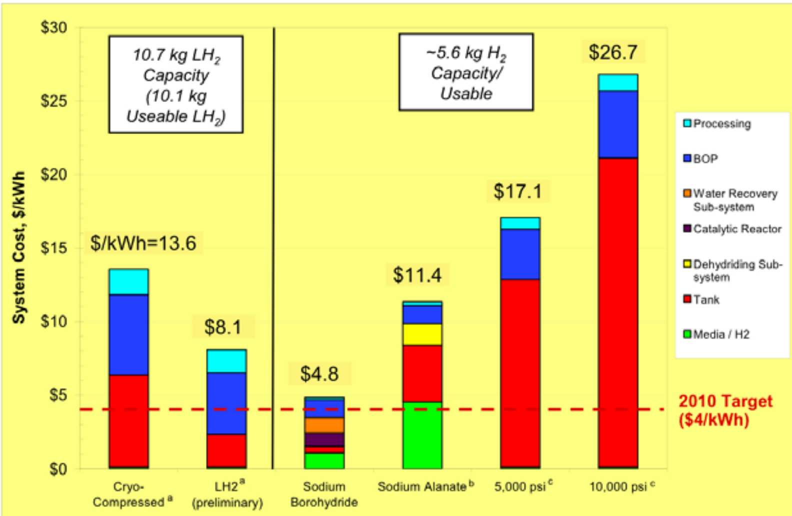
- Filled only with cold H_2
- Service pressure: 5000 psi
- Fill pressure: 5000 psi
- Burst pressure: 9,000 psi

Cryogenics offers dramatic safety opportunities: cooling H_2 *removes* far more burst energy than reducing pressure



Hydrogen annual merit review, LLNL, May 22, 2009, p. 17

Cryogenic pressure vessel systems will be less expensive than ambient compressed H_2 storage for fundamental reasons



Source: TIAX

- SCI cryotank (350 bar) cost estimates (per kgH_2 stored):
- 30% less vs. ambient 350 bar
- 60% less than 700 bar

- ***Compact LH$_2$ (71 vs. 23-39* kgH$_2$*/m^3)*** **cuts carbon fiber (per kg H_2 stored)**
- ***Pressurized LH$_2$*** **even more compact ('top off' potential up to 88 kgH$_2$/m^3)**
- ***Cryogenic H$_2$*** **in protective vacuum jacket may enable glass fibers to provide more value than carbon**
- ***Very low burst energy, no fast fill overpressure, secondary containment*** **of vacuum jacket could justify lower burst pressure ratio ($P_{burst}/P_{dormancy}$), improving pressure vessel mass, volume, and structural efficiency**

Future work: after demonstrating superior weight and volume of cryogenic pressure vessels and adequate cycle life, study a spectrum of H_2 states and flexible pressure vessel systems

- ***Pressurized*** LH_2 **offers fertile ground for achieving ultimate DOE storage goals but requires new refueling strategies.**
- ***Normal*** LH_2 **if our *para-ortho* transition experiments measure slow kinetics then we plan to investigate "normal"** LH_2 **(25% *para*) in cryotanks, anticipating liquefaction capital cost & energy savings.**
- ***Multiple Volume Vessels*** **offer flexible blend of capacity, weight, cost, shape, and dormancy over a single state** H_2 **storage vessel, but multiple states of onboard** H_2 **adds complexity.**

Summary

- ***Cryogenic pressure vessels can exceed 2010 DOE storage targets*** **for weight and volume, with promising dormancy & cost relative to conventional LH_2 tanks and ambient pressure vessels**

- ***In collaboration with industrial partners, we are addressing interactions between pressure, temperature, and materials.*** **Outgassing, cryogenic cycling, and cryogenic burst tests**

- ***We are investigating fundamental operational aspects at full scale:*** **internal heat exchange, dormancy and dormancy recovery, *para-ortho* conversion, higher density (pressurized) refueling**

- ***Safety advantages of cryogenic pressure vessels are yet to be assessed.*** **Very low burst energy, fill vs. dormancy safety factor, protective vacuum jacket, material strength at cryogenic temps**