Inexpensive Delivery of Cold Hydrogen in Glass Fiber Composite Pressure Vessels

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June 9, 2010

Project ID # PD020

This presentation does not contain any proprietary or confidential information

Overview

Timeline

- Start date: **October 2004**
- End date: **October 2012**
- Percent complete: **70%**

Budget

- Total project funding
  - DOE: **$1.5 M**
  - Spencer: **$125 k/yr**
- Funding received in FY09:
  - **$0 k**
- Funding for FY10:
  - **$300 k**

Barriers

F. Gaseous hydrogen storage and tube trailer delivery cost
G. Storage tank materials and costs

Targets

Exceed DOE 2012 delivery targets:

- **Delivery capacity: 700 kg - > over 1000 kg**
- **Tube trailer operating pressure: 7000 psi**
- **Tube trailer capital cost: < $500 / kg-H2d**

Partners

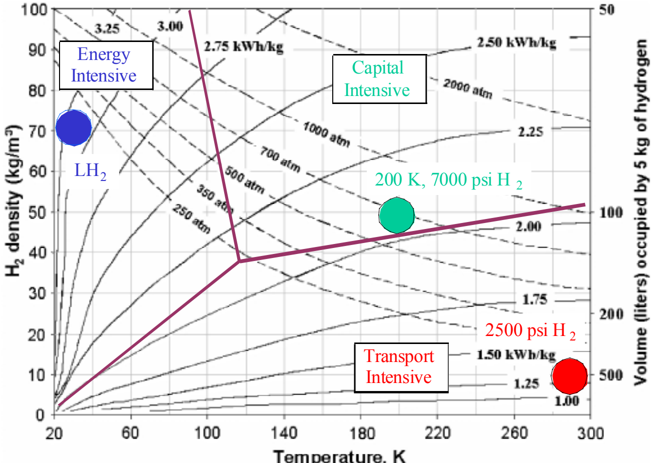
Ongoing joint projects with composite/vessel manufacturers

- **Spencer Composites**
- **Structural Composites (SCI)**
- **Quantum**
- **Boeing**

Relevance: Glass fiber vessels reduce hydrogen delivery cost through synergy between low temperature (140 K) hydrogen densification and glass fiber strengthening

- **Colder temperatures (~140 K) increase density ~70% with small increases in theoretical storage energy requirements, can be achieved at gas-terminal scale with LNG refrigerators**
- **Low temperatures are synergistic with glass fiber composites**
  - **higher glass fiber strength (by > 80%, published for A-Glass) at 140 Kelvin (compared to 300 K)**
  - **higher gH_2 density increases delivered-H_2 trailer capacity**
- **glass fiber (~$6/kg for Glass vs. ~$23/kg for carbon fiber) minimizes high composite materials cost**
- **Increased pressure (7,000 psi) minimizes delivered H_2 costs, same design can deliver up to 12,000 psi or build cascade**
- **Dispensing of cold hydrogen reduces *vehicle* vessel cost ~25% by avoiding over-pressurization during fast fill**

Approach: Conduct experiments and analysis to demonstrate high performance inexpensive glass fiber at low temperature



October 2006: **Discovered favorable P-T conditions for H_2 delivery**

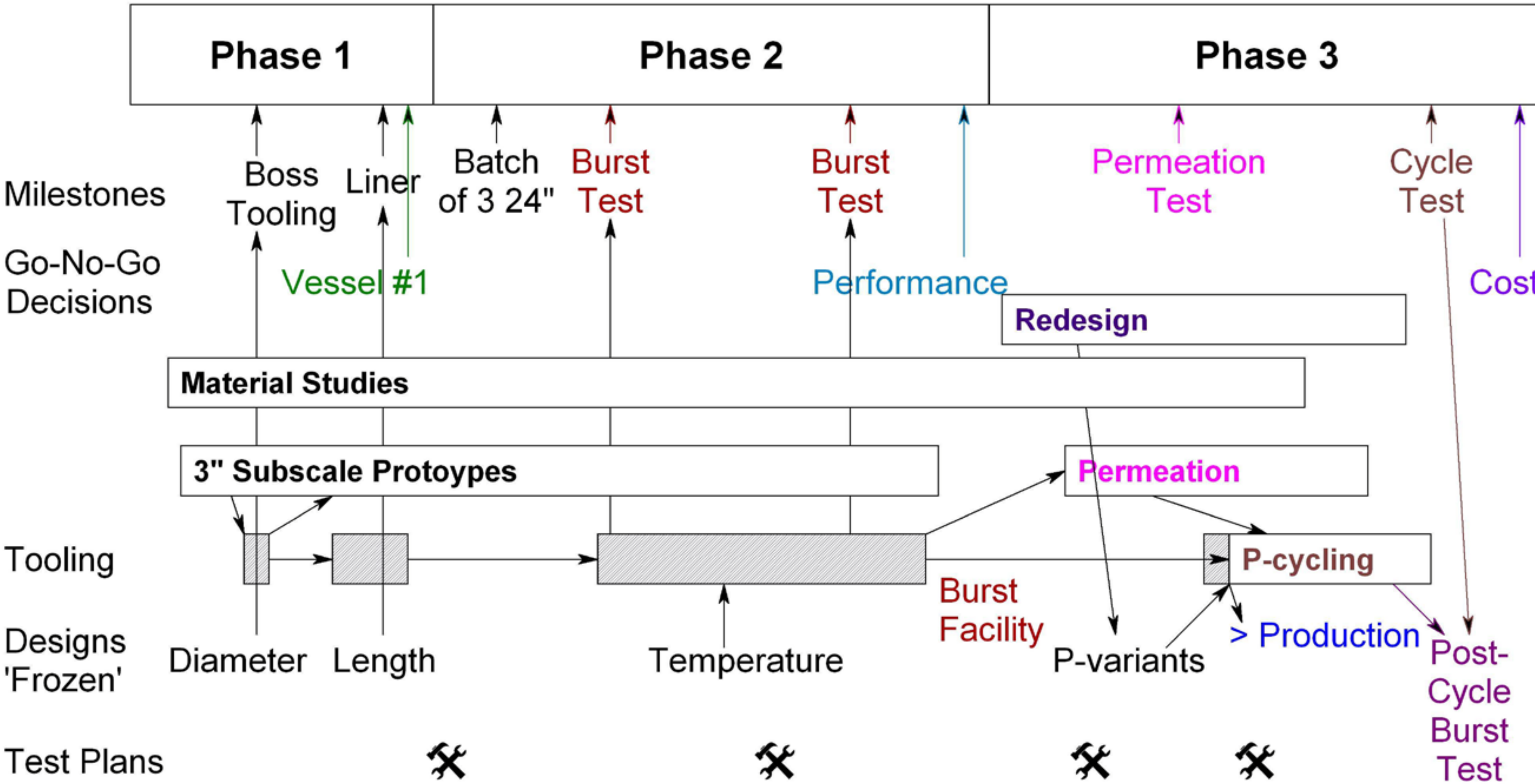
January 2008: **Proved > 40% strengthening due to cold operation**

April 2010: **Built and tested first batch of 3 full scale (24″) vessels**

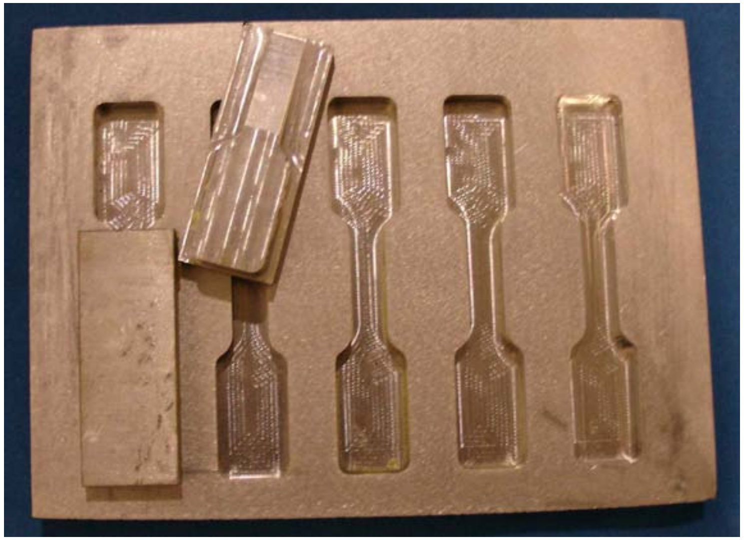
March 2009: **Built and tested many 3″ pressure vessels, using ROMP plastic qualified 77 to ~335 K, designed 24″ boss**

Approach: 3 Phases (stretched out to 4 years) address technical risks

- **Fundamental innovation in plastics for liners and composites**
  ROMP **plastics are tough, stiff, strong, thermosetting -> big ΔT**
  Ring Opening Metathesis Polymerization **(Chemistry Nobel Prize)**
- **Program plan addresses technical risk for all key unknowns :**
  compliance, toughness, strength, permeation, novel phenomena



Accomplishments: we built & tested multiple small-scale specimens

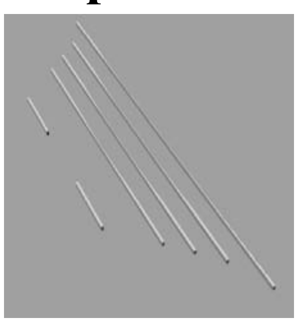


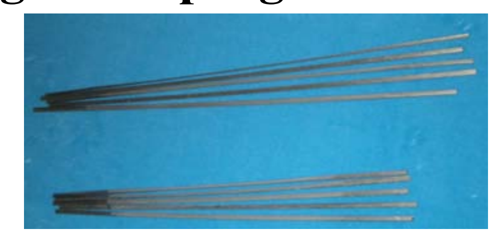
Molded ROMPs, including lap seam

coupon strength test programs

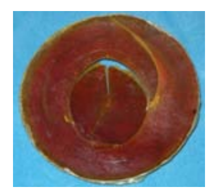
3″ liners and vessels test program

"dog bones"



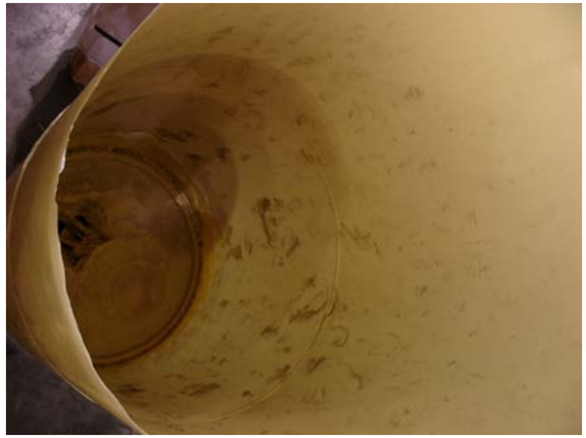


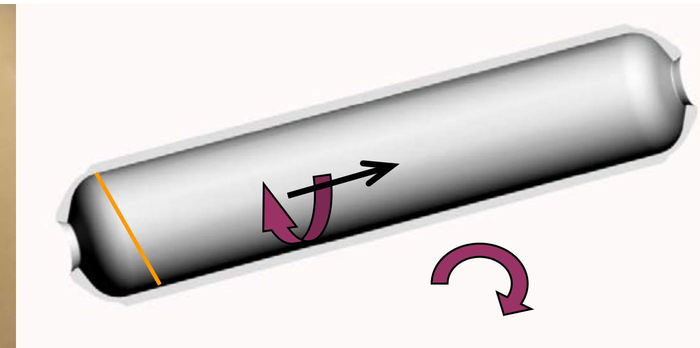
machined composites



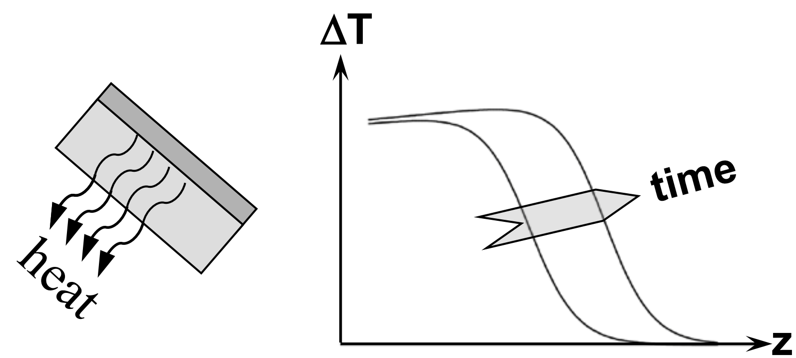
toughness plaques

Scale-Up Liner Process Failure Mode: overcome with multi-pour introduction of ambient-T ROMP liquid into liner mold tooling





closed mold was poured with a single shot of ambient-T ROMP, then spun on 2 axes



catalysis waves propagate through ROMP, retarded by thermal inertia

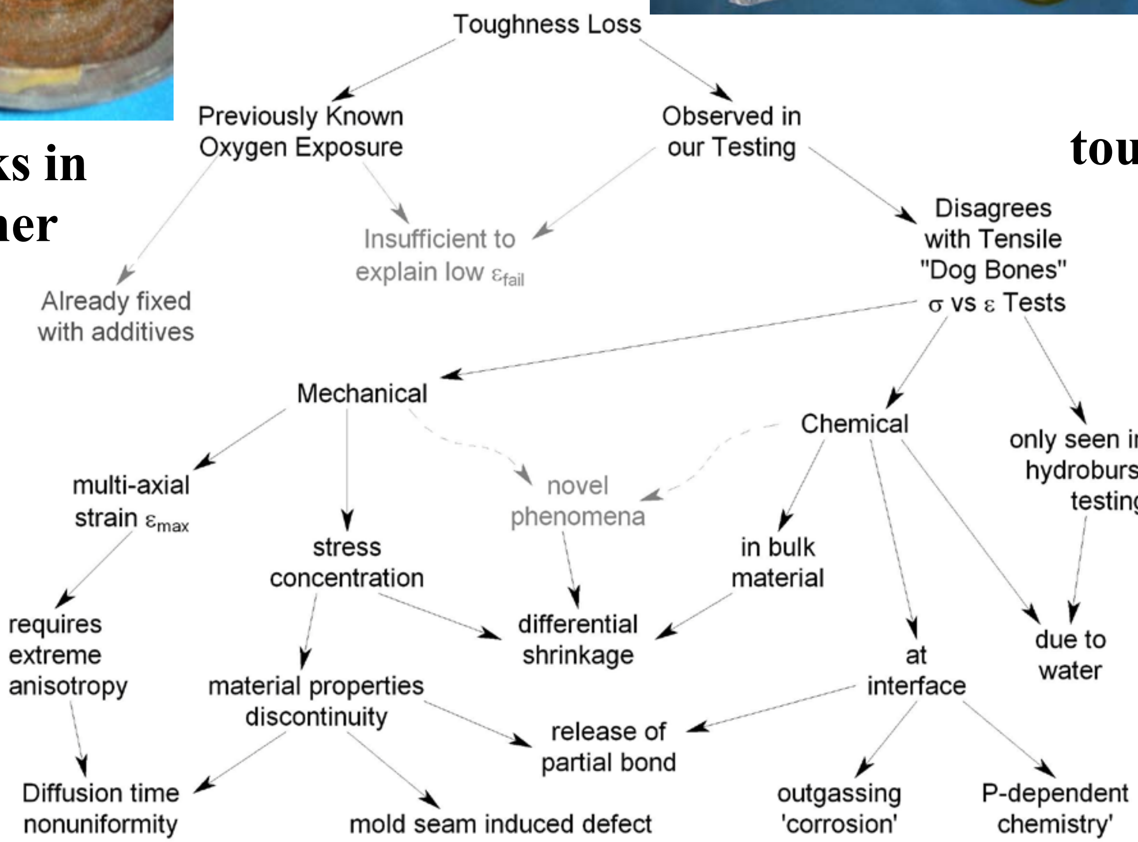
Unpleasant Surprise: 20 minute "pot life" worked smoothly for molding 48″ liners – yet emerged from the mold in 2 pieces at 114″

The Anomalous Toughness Failure Mode: tensile tests show sufficient stiffness and toughness, yet parts fail at low strain !

cracks in 3″ liner

many toughness test plaques were cast and smashed

toughness test drop tower



We have demonstrated innovative plastic-lined glass cryogenic vessels

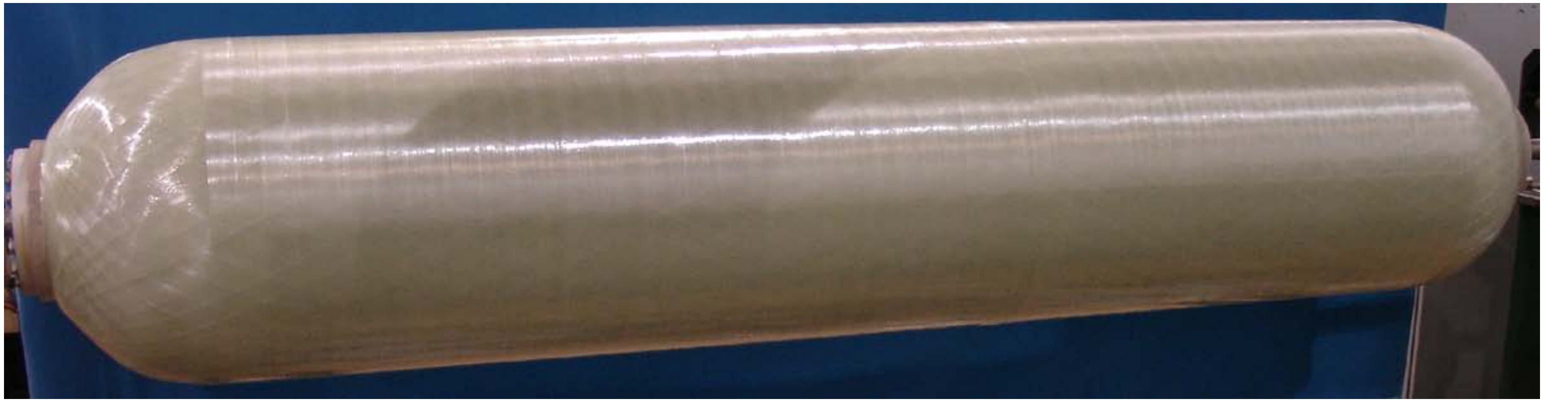
first full scale liner inspected, (x'lucent + borescope) -> no flaws

first hydro-burst test article

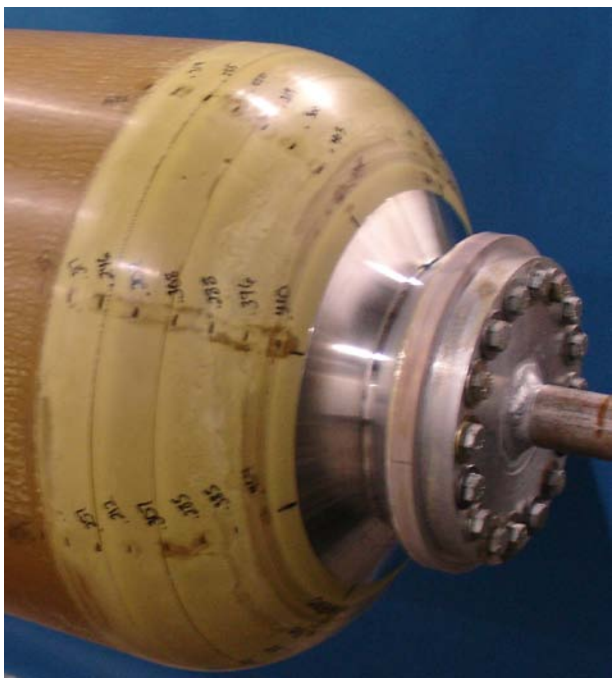
winding the first full scale 8,000 psi, S-Glass

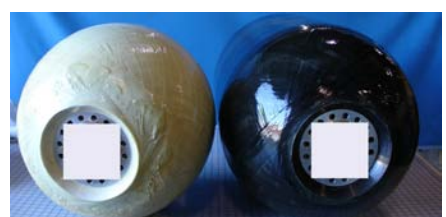
permeation test rig being built as next iteration of shipping case

We have built the first batch of full scale vessels and have commenced destructive/hazardous testing

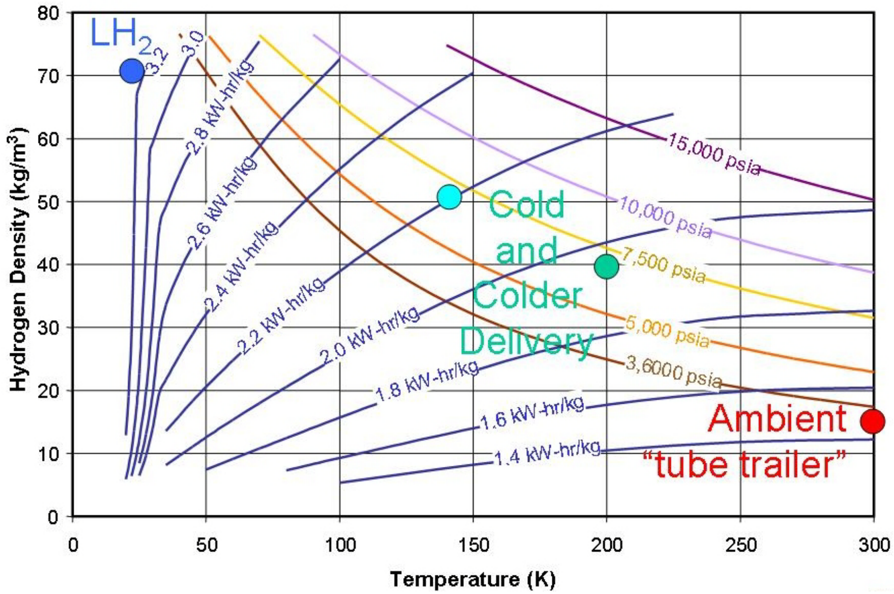


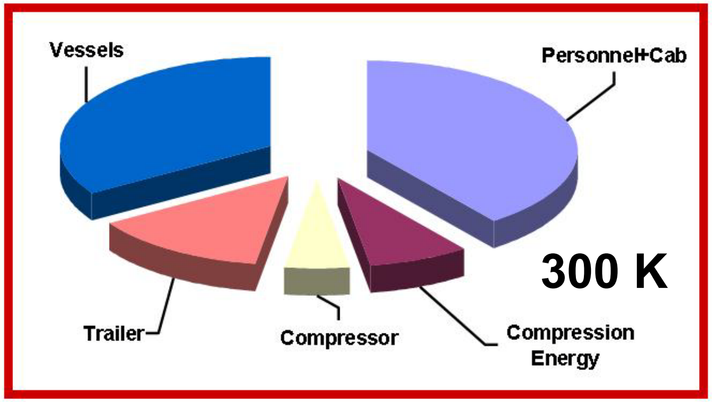
First 114″ S-Glass Pressure Vessel





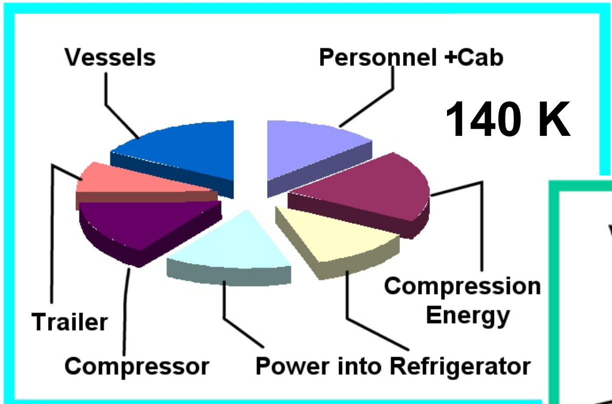
The Refrigeration Problem: a realistic comparison between delivery options calls for an understanding of cooling costs



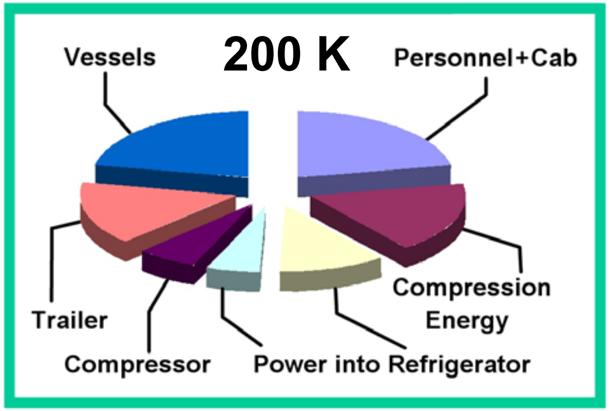


Ambient delivery needs no gas-terminal scale refrigeration

Refrigeration power and capital costs are estimated with a conservative 30% efficiency atop the Carnot refrigerator efficiency times the required exergy to achieve the delivered state



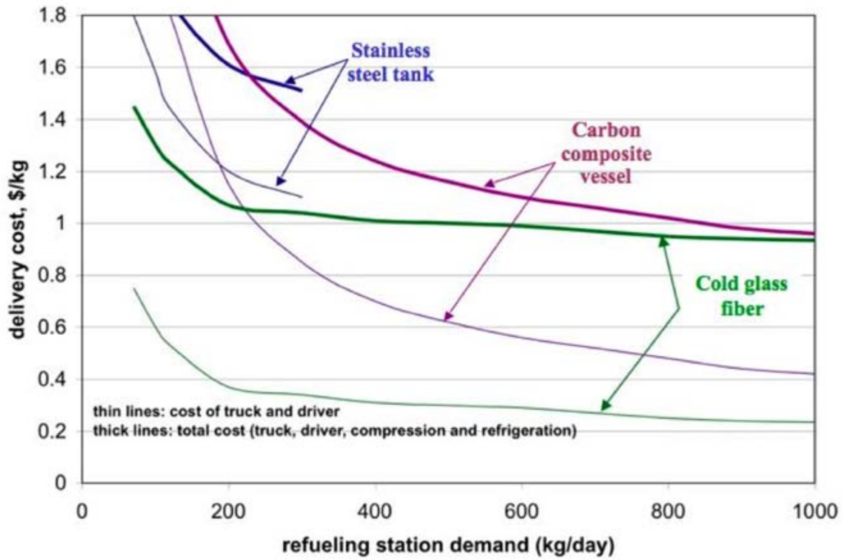
Cold and colder 200 K and 140 K options are shown scaled by $/kg-d

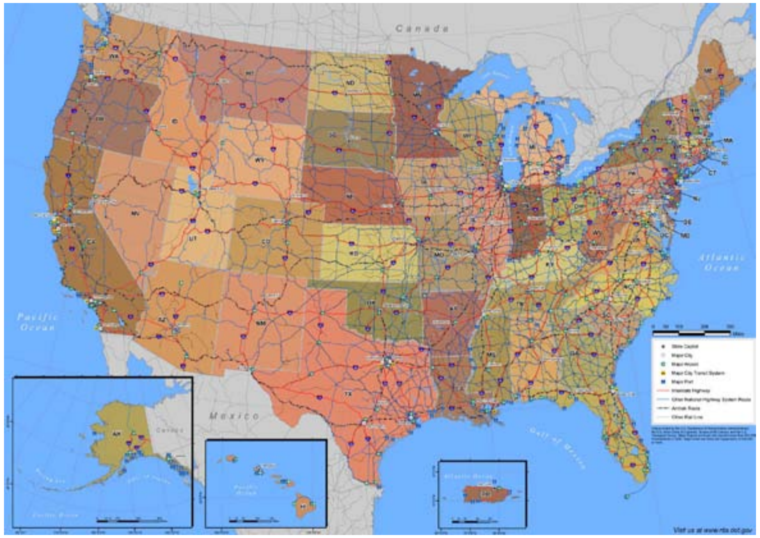


Detailed modeling predicts cost advantage for 140-200 K H_2 delivery

Delivery Container	Steel 'Tube' Trailer	'Proven' Graphite	300K Glass Fiber	200K Glass Fiber	200K (Max. Capacity)	140K Glass Fiber	140K (Max. Capacity)
Structural Material [only steel is not a composite]	Welded [H2A 2005]	Graphite / Epoxy	Glass / Epoxy	Glass / Epoxy	Glass / Epoxy	Glass / Epoxy	Glass / Epoxy
Mass (kg $H_{2\text{-delivered}}$)	340	1,000	1,000	1,000	1,803	1,000	2,348
MEOP (psi) [SF = 2.25]	2,640	6,000	6,000	6,000	6,000	6,000	6,000
T (filled, K)	300	300	300	200	200	140	140
Delivery Cost ($/kg-$H_{2\text{-d}}$)	1.54	1.13	0.95	0.91	0.84	1.01	0.82
Personnel+Cab ($/kg-$H_{2\text{-d}}$)	0.61	0.20	0.20	0.20	0.15	0.20	0.11
Compr. Energy ($/kg-$H_{2\text{-d}}$)	0.12	0.16	0.16	0.16	0.16	0.16	0.16
Compressor ($/kg-$H_{2\text{-d}}$)	0.08	0.10	0.10	0.10	0.10	0.10	0.10
Cooling Energy ($/kg-$H_{2\text{-d}}$)	-	-	-	0.05	0.05	0.12	0.12
Refrigerator ($/kg-$H_{2\text{-d}}$)	-	-	-	0.06	0.06	0.12	0.12
Trailer ($/kg-$H_{2\text{-d}}$)	0.21	0.15	0.15	0.14	0.11	0.14	0.07
Vessels ($/kg-$H_{2\text{-d}}$)	0.52	0.52	0.34	0.20	0.21	0.17	0.14
Vessels Cost ($)	165,000	470,000	305,000	186,000	352,000	155,000	306,000
H_2 Density (kg/m^3)	13.73	26.54	26.54	36.64	36.64	47.68	47.68
Total Volumetric Eff. (%)	56%	45%	45%	44%	47%	36%	54%
Vessel Volumetric Eff. (%)	70%	84%	80%	84%	85%	85%	86%
Fiber Strength (ksi)	-	700	500	750	750	900	900
Vessel Wall Strength (ksi)	60	385	275	412	412	485	485
Vessel Mass (w/o-liner, kg)	40,000	10,291	15,882	7,267	12.426	5,327	11,533

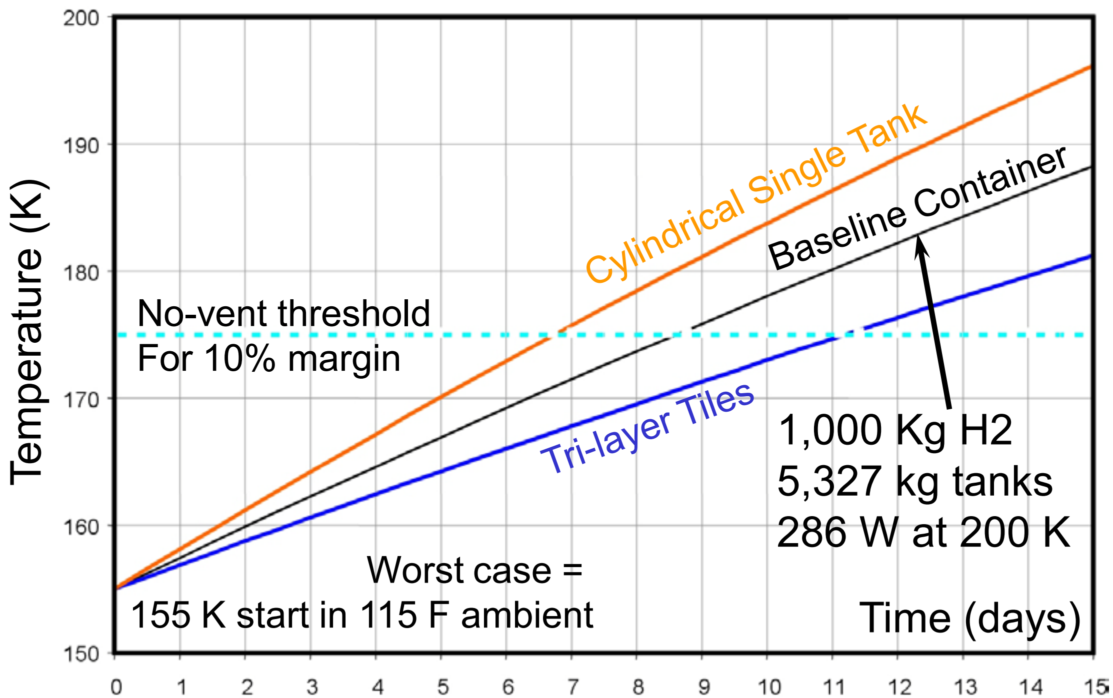
Longer-Reach Transitional Infrastructure: H2A-based modeling, EoS energies predict refrigeration minimizes delivered \$/kg-H_2



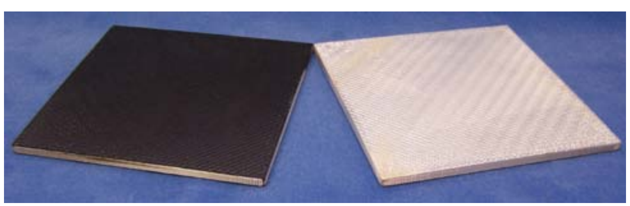


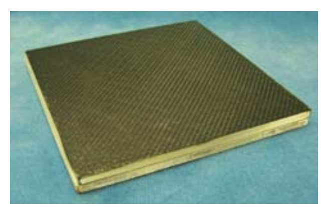
- **Gulf and West Coasts have an existing large gH2 supply which can reach the rest of the US for ~\$0.30/kg-H_2 delivered using the vessel+container technology we are developing**
- **The refrigeration cost is already paid *before* filling our containers could continually chill onboard the long haul platform - *but***
- **Thermal endurance is sufficient to add a 1 day, 1000 mile rail trip**
- **LH_2 and Cold-H_2 delivery can mix advantageously, serving all users**

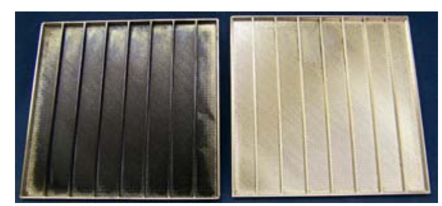
The Insulation Sub-Problem: no risk due to weakening as a result of warming unless stranded for *weeks*



H_2 losses can be avoided due to the large size of our container, its high pressure capability, and a strength margin that must be exceeded before forced venting (via a thermal relief system) is required

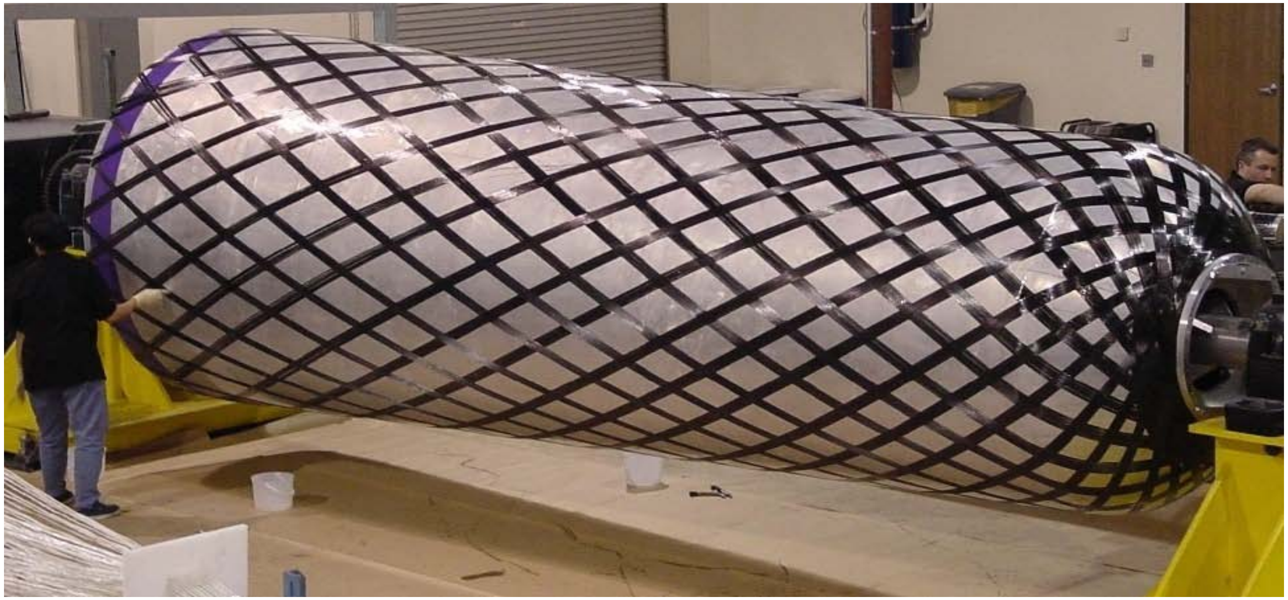




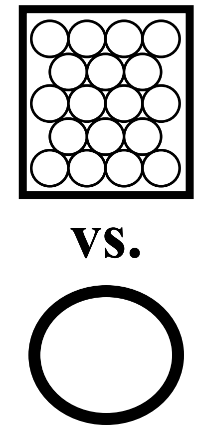


Prototype insulation tile development: low- and high-emissivity faces, outside an internal anti-bending structure, clamp gap width in a planar vacuum (metal foil, welded, no-recharging) inner layer

Collaborations: LLNL is teamed with a rocket innovator eager and able to develop novel, very large composite parts



18 in a box



1 cylinder

Spencer Composites contributes all of this project's cost share

- **Spencer's began developing ultra-low-cost ROMP in 2003**
  - **DARPA sought 48″ diameter in 2003, remains unproven in large vessels**
  - **compatibility with H_2 since tested, strength retained at cryogenic temp's**
- **Aerospace and Maritime applications, also energy terminals**
- **May make sense for less mass- and volume-constrained Rail**

Future work:

- **Full scale pressure vessel test program eliminates key risks**
  proof of concept tests = hydrostatic burst, P+T cycling, and long duration (weeks) hydrogen permeation (P vs. time)
  site selection and preparation for explosive-potential tests
  build and destroy more pressure vessels
- **Materials Research and Development efforts**
  toughness vs. Temperature testing and improvement
  permeation tests on subscale vessels and mitigation layers
  stress rupture life vs. temperature testing
- **Design and modeling efforts**
  insulating tiles, acceleration loaded vessel suspension, length and diameter expansion isolation from container
- **Regulatory initiatives: negotiate with regulators on cold safety**
- **Funding Initiatives: Joint DOE/DoT container field demo**
- **Industrial Partnerships: gas vendors, trailer integrators**

Summary: We are demonstrating glass fiber vessels that minimize delivery cost through cold strengthening

- **First batch of full-scale glass fiber vessels demonstrated manufacturability of all trailer processes and components**
- **Successfully burst tested subscale 3″ vessels at 300 and ~170K seal design does not scale up, but composite performance within 2% of design at ambient burst pressure of 20,000 psi and > 15% over design in liquid acetone when seal leaked**
- **Found and fixed novel manufacturing problems**
- **Investigated materials properties and made beneficial changes**
- **Designed thermal management system for delivery trailer**
- **Optimized delivery model for \$/kg-H_2-delivered vs. P and T**
- **Identified development pathway for single large vessel delivery**