Inexpensive Delivery of Cold Hydrogen in Glass Fiber Composite Pressure Vessels

Andrew Weisberg, Salvador Aceves, Blake Myers, Tim Ross

Lawrence Livermore National Laboratory

May 10, 2011

PD020

Project Overview

Timeline

- Start date: **October 2004**
- End date: **October 2013**
- Percent complete: **65%**

Budget

- Total project funding
  - DOE: **$1.5 M**
  - Spencer: **$125 k/yr**
- Funding received in FY10:
  - **$300 k**
- Funding for FY11:
  - **$312.5 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/kgH2**

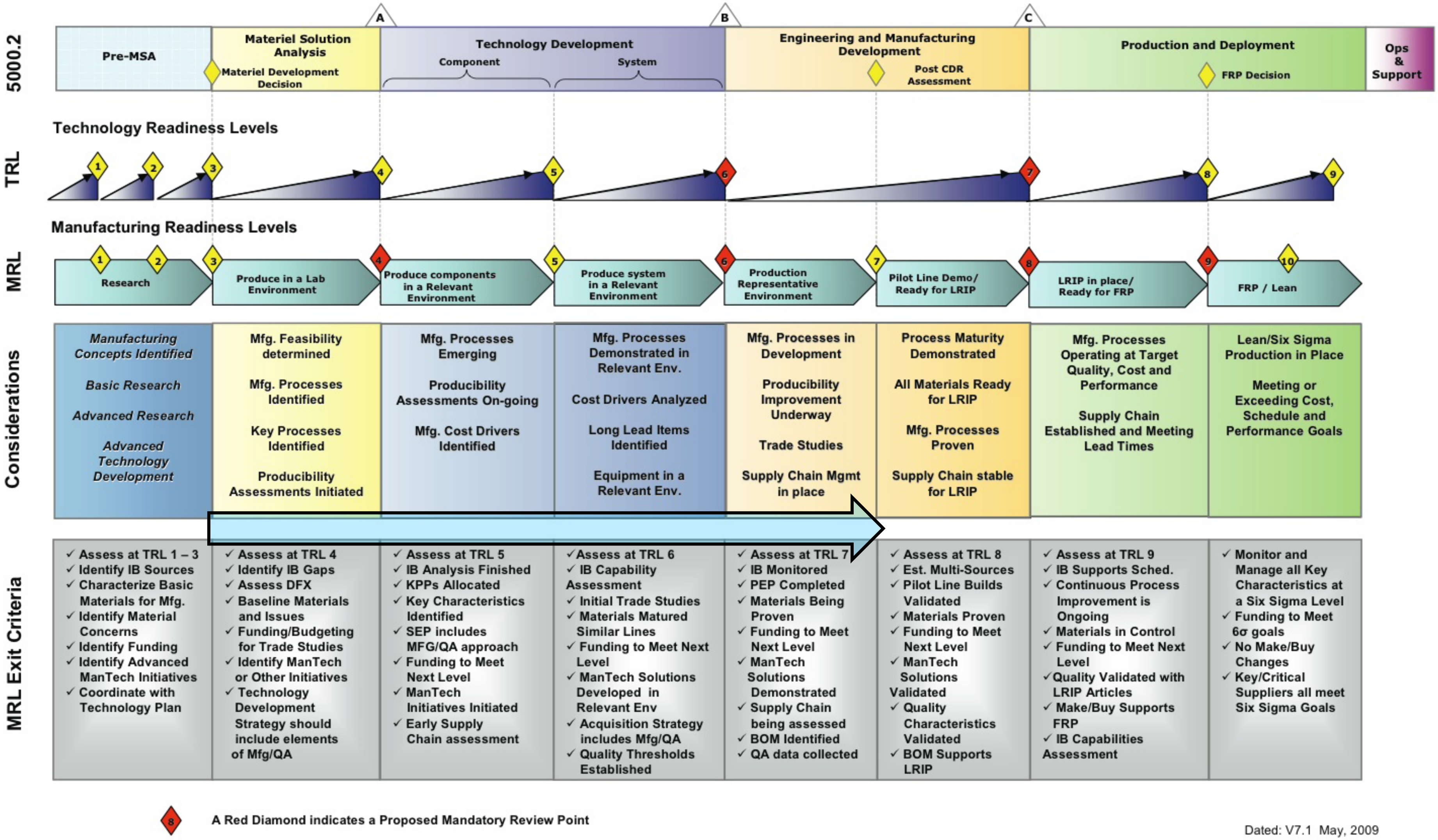
Partners

Ongoing joint projects with US Agencies: NASA, NIST, FAA, and DOT (NHTSA); various composite/vessel manufacturers

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

Manufacturing Readiness Levels (MRLs, used by DoD):

This cold glass trailer project began at MRL 3 and will achieve MRL 7 at the end of Phase 3. Initial estimates of MRL 4 onset achieving MRL 8 don't alter project being DOE's only mid-MRL Hydrogen Infrastructure effort.

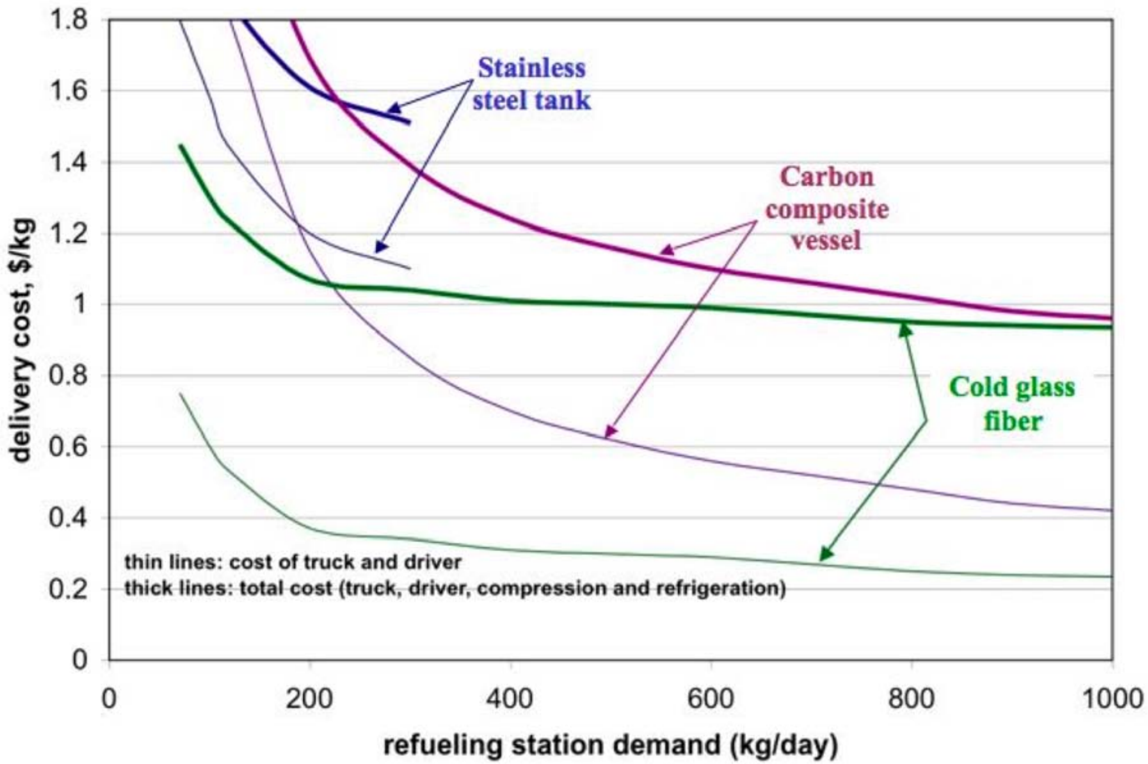


Relevance: Glass fiber vessels reduce hydrogen delivery cost through synergy between low temperature (140 K) hydrogen densification and glass fiber strengthening

- **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 K (compared to 300 K)**
  - **higher gH_2 density increases delivered-H_2 trailer capacity**
  - **low T's would eliminate Type IV's capital savings ~30% without plastics innovations or cyanate esters (hazmat)**
- **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**

Cost Projections: (Results of Modeling in 2005, 2010)

Cost of Delivery is minimized by delivering as much hydrogen as possible:

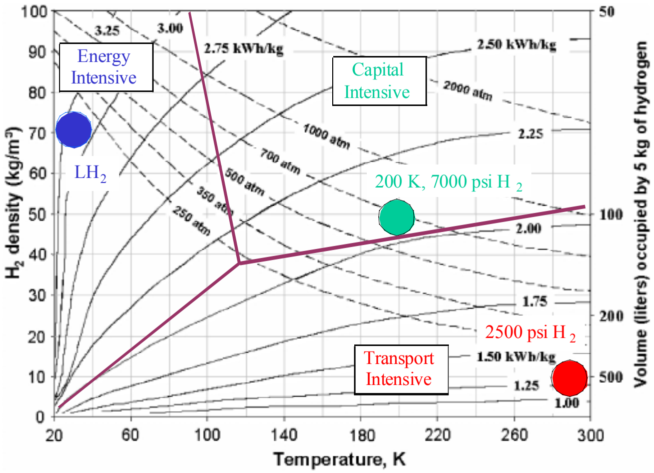


Note: plateau in curves for higher station demand due to relative insignificance of cab, mileage (100 mile round trip), and labor costs

Table of more detailed ("bottom up") cost comparisons prepared in 2010: (appears at legible scale as Slide 14)

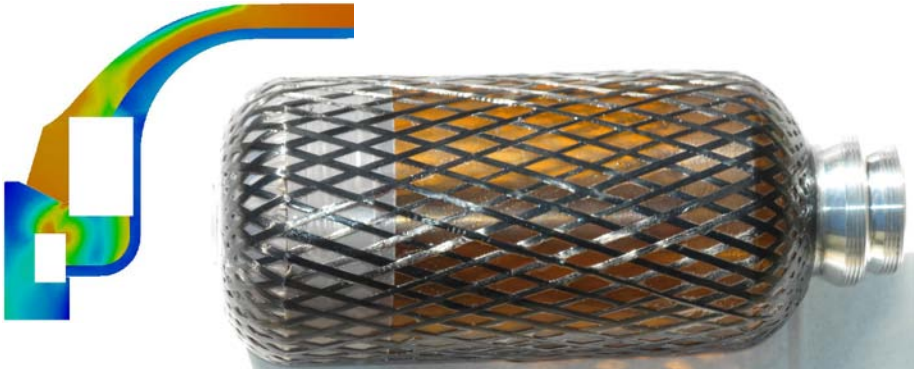
		ven' phite	300K Glass Fiber	200K Glass Fiber	200K (Max. Capacity)	140K Glass Fiber	140K (Max. Capacity)
		hite / oxy	Glass / Epoxy	Glass / Epoxy	Glass / Epoxy	Glass / Epoxy	Glass / Epoxy
		000	1,000	1,000	1,803	1,000	2,348
		000	6,000	6,000	6,000	6,000	6,000
		00	300	200	200	140	140
		13	0.95	0.91	0.84	1.01	0.82
		20	0.20	0.20	0.15	0.20	0.11
		16	0.16	0.16	0.16	0.16	0.16
		10	0.10	0.10	0.10	0.10	0.10
Cooling Energy (\$/kg-H_{2-d})	-	-	-	0.05	0.05	0.12	0.12
Refrigerator (\$/kg-H_{2-d})	-	-	-	0.06	0.06	0.12	0.12
Trailer (\$/kg-H_{2-d})	0.21	0.15	0.15	0.14	0.11	0.14	0.07
Vessels (\$/kg-H_{2-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

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

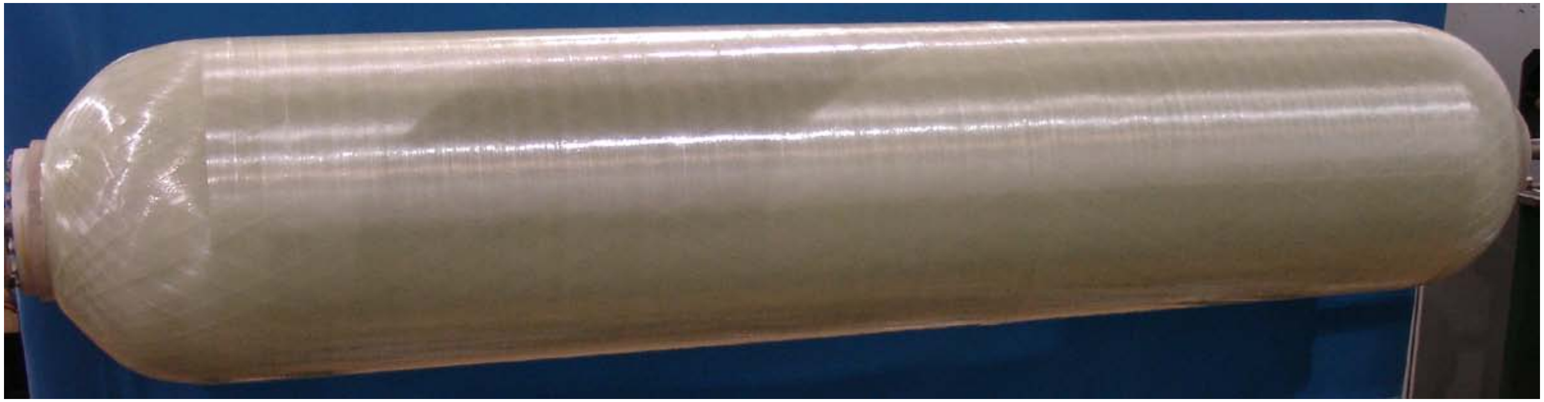
January 2008: Proved > 40% strengthening due to cold operation



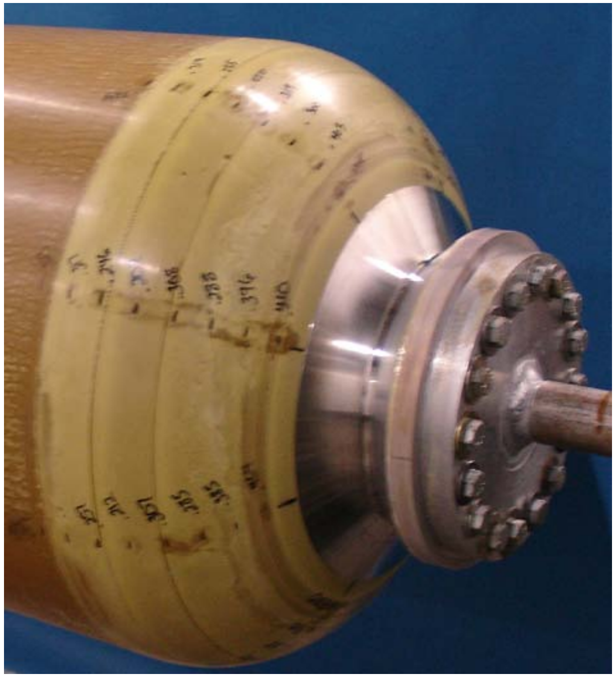
March 2009: Built and tested many 3" pressure vessels, using ROMP plastic qualified 77 to ~335 K, designed 24" boss

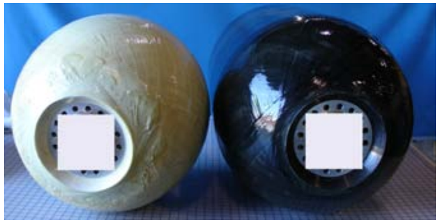
April 2010: Built and tested first batch of 3 full scale (24") vessels

Photographs of the first generation of full scale vessels which all failed prematurely in destructive/hazardous testing



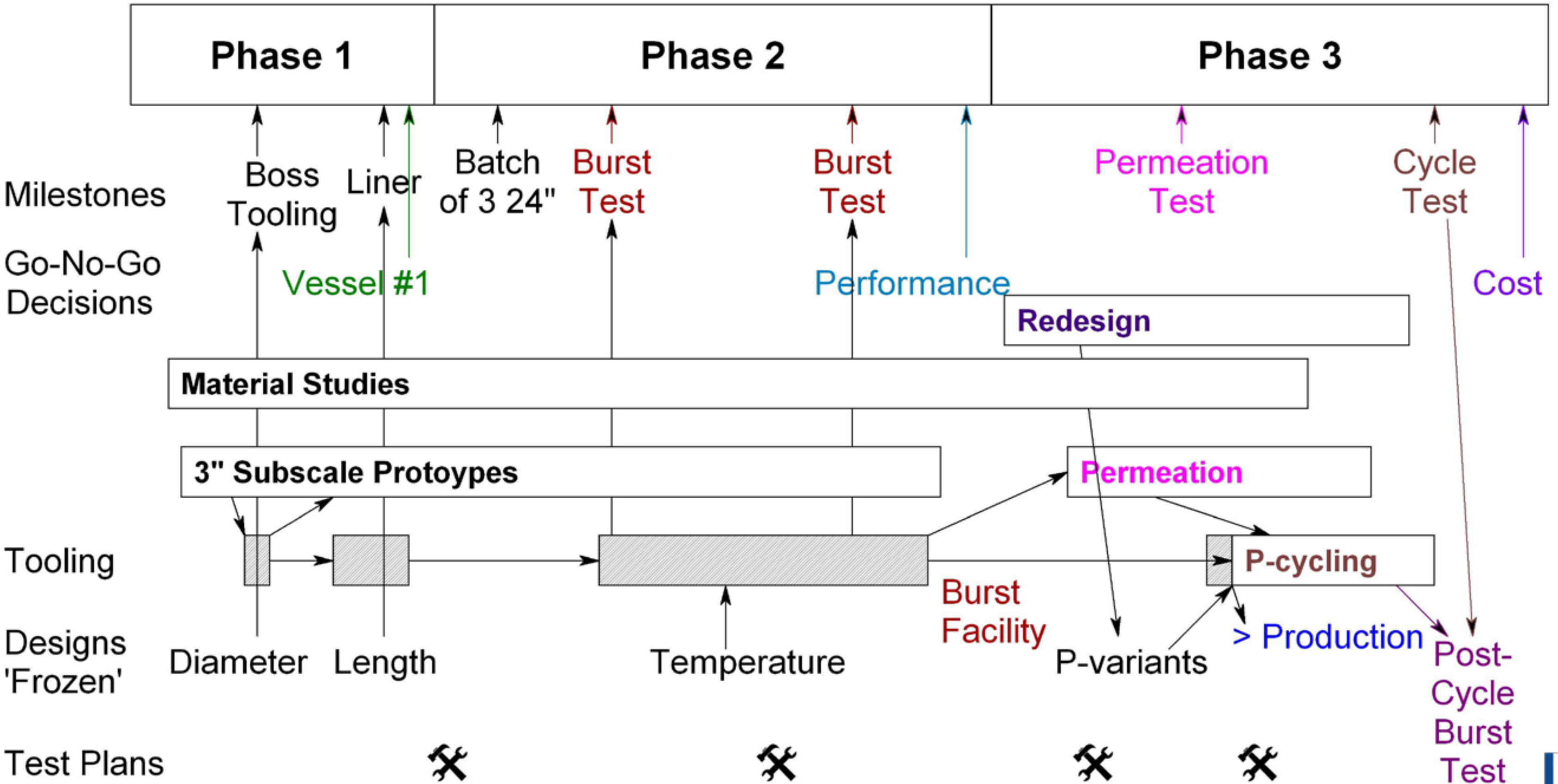
First 144” S-Glass Pressure Vessel





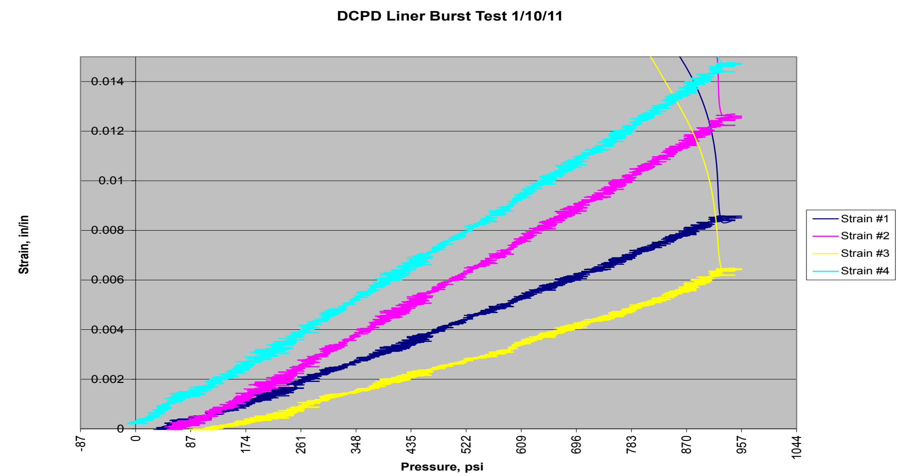
Approach: 3 Phases (stretched out to 5 years) address technical risks

- **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



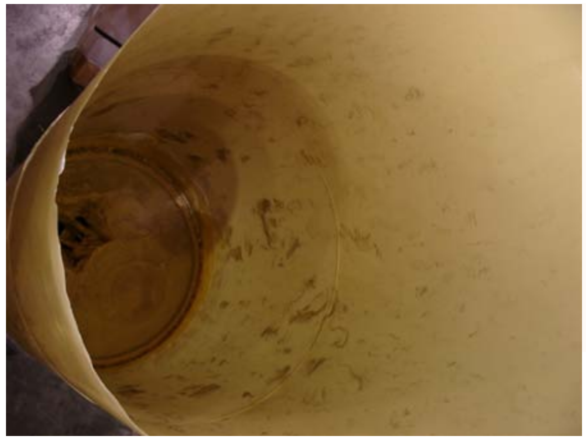
Accomplishments (January 2011): New tooling yields first successful burst test of full scale (23” diameter) S Glass fiber pressure vessel

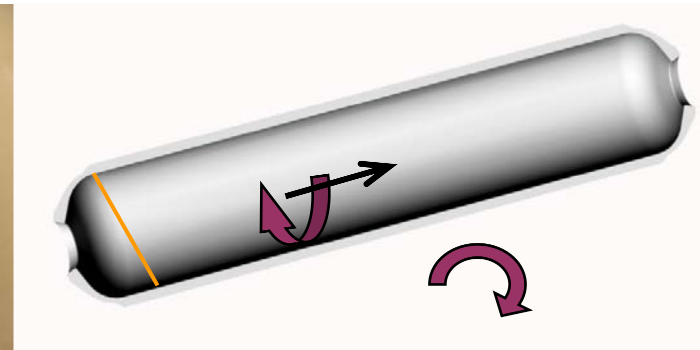
Failure Mode not observed previously in hydroburst testing of composite pressure vessels proves liners and seals operate at strains > trailer design levels



Failure Mode shown with loose failed hoop fiber layer cut away

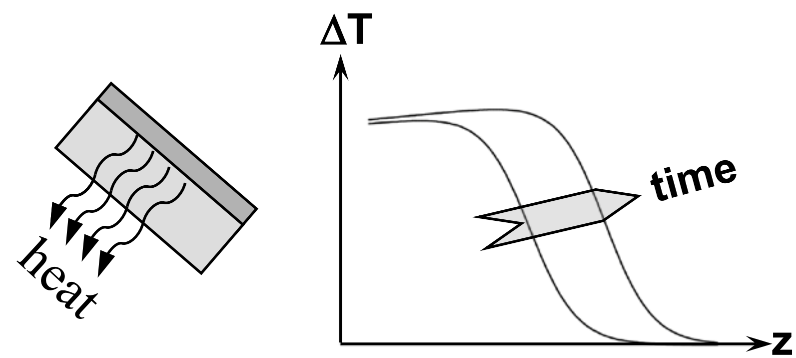
Scale-Up Liner Process Failure Mode: overcome with multi-pour introduction of ambient-T ROMP liquid into liner mold tooling





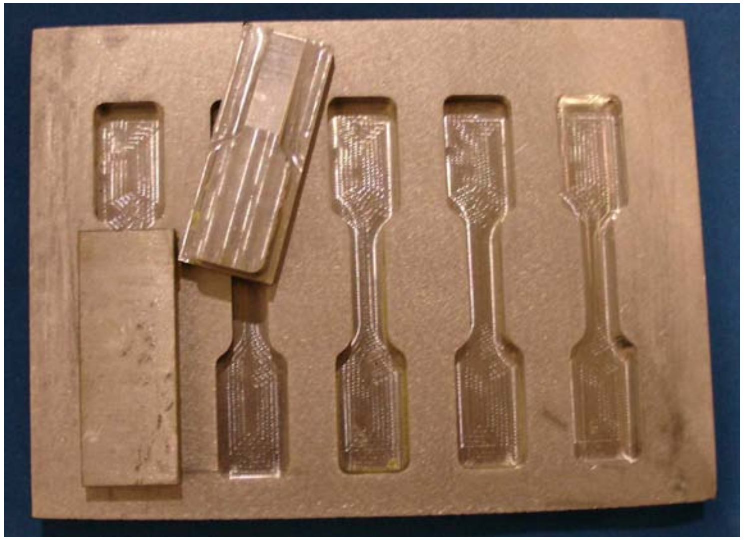
closed mold was poured with a single shot of ambient-T ROMP, then spun on 2 axes

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



catalysis waves propagate through ROMP, retarded by thermal inertia

~150 small-scale specimens built & tested so far for Materials R+D

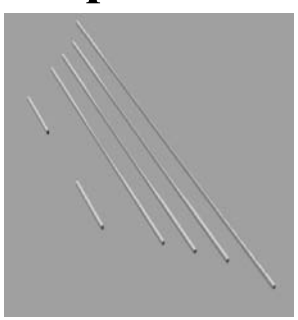


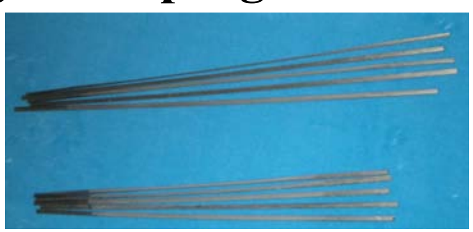
Molded ROMPs, including lap seam

coupon strength test programs

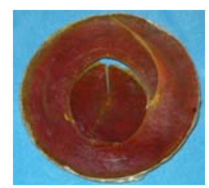
3” liners and vessels test program

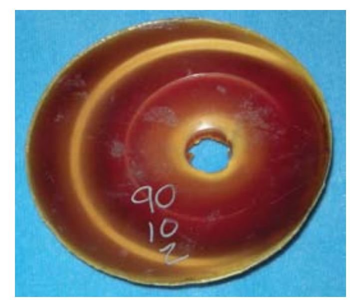
“dog bones”





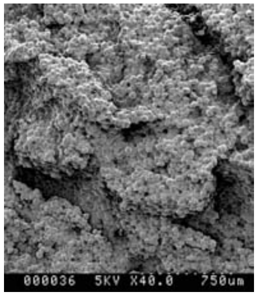
machined composites





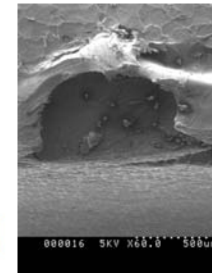
toughness placques

Considerably More Understanding Gained on Why Vessel Liners Failed at Low Strain



cracks with extreme detail

Ultimate Strain Disagrees with Tensile "Dog Bones"



bubbles on crack surfaces

Mechanical

Chemical

multi-axial strain ε_{max}

stress concentration

novel phenomena

in bulk material

requires extreme anisotropy

differential shrinkage

at interface

material properties discontinuity

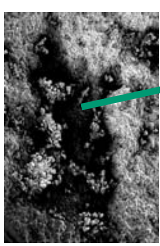
release of partial bond

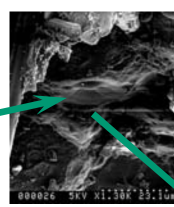
Diffusion time nonuniformity

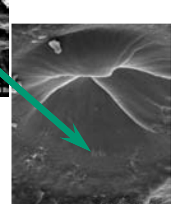
mold seam induced defect

outgassing 'corrosion'

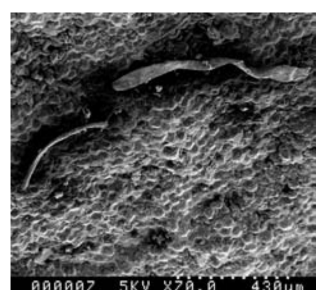
P-dependent chemistry'



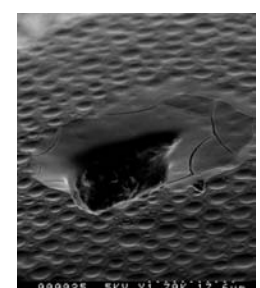




crater with fangs “tells all”



Process-induced defects of many kinds

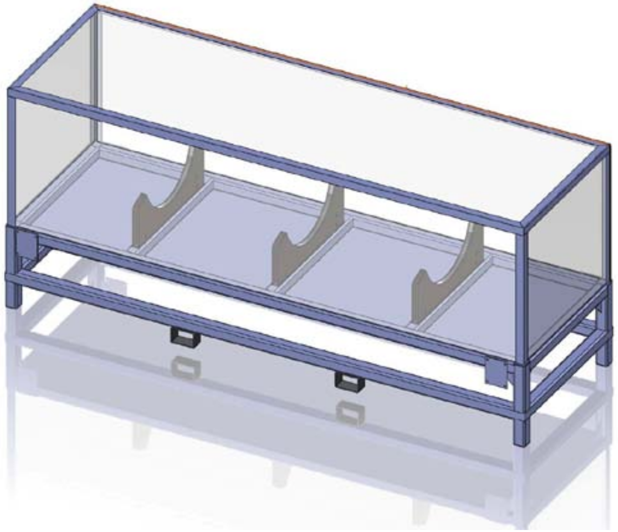


Developing innovative plastic-lined glass cryogenic vessels

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

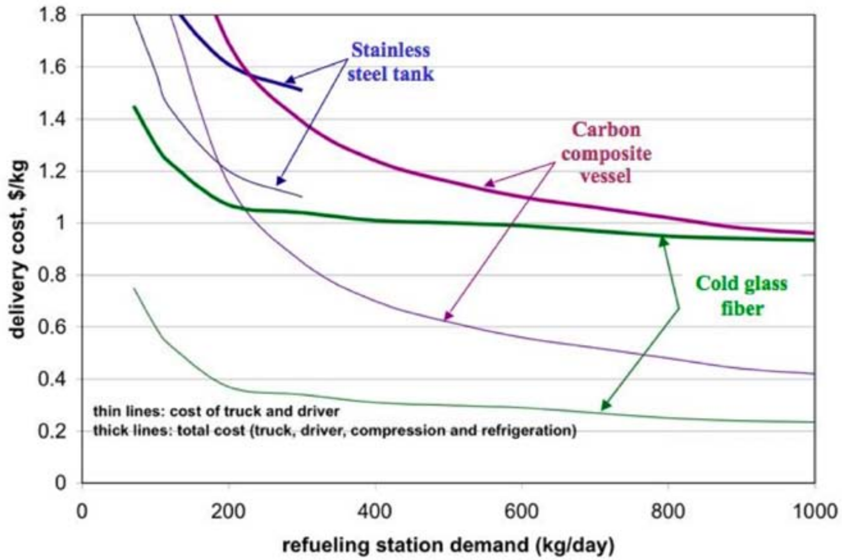


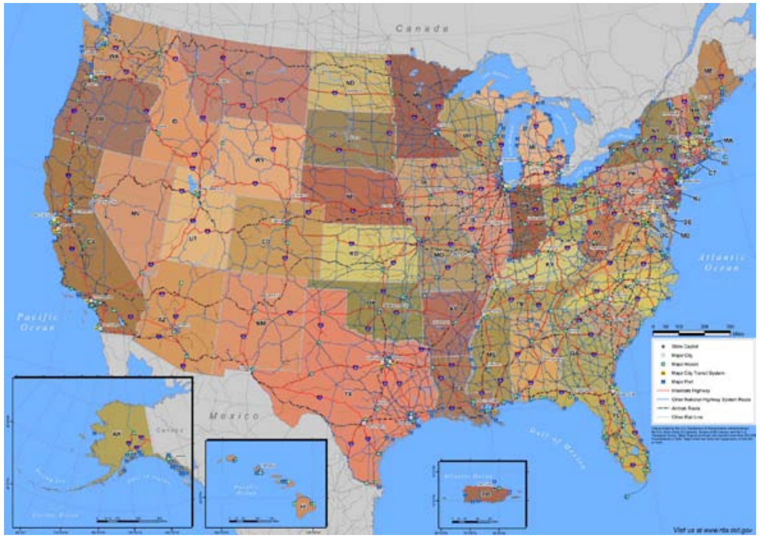
permeation test rig in design phase

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

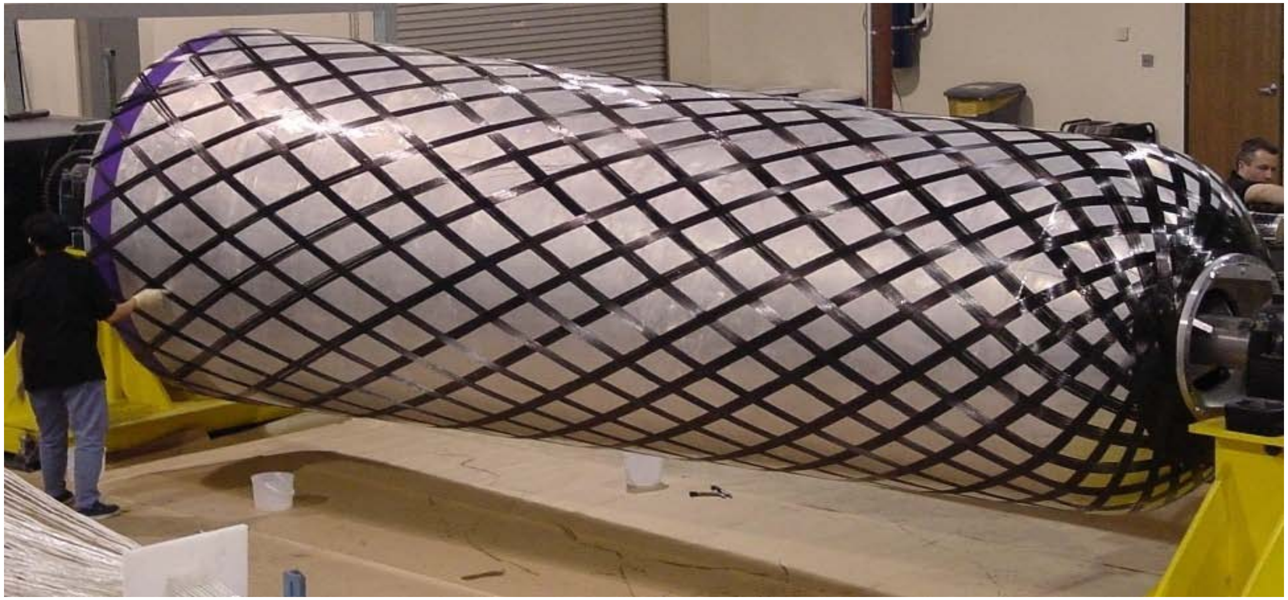
Longer-Reach Transitional Infrastructure: H2A-based modeling, EoS energies predict refrigeration minimizes delivered \$/kg-H_2



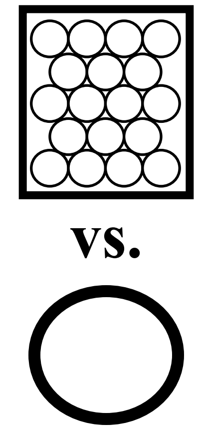


- Gulf and West Coasts have an existing large gH2 supply which can reach the rest of the US for ~\$0.30/kg-H_2 delivered using the vessel+container technology we are developing
- The refrigeration cost is already paid *before* filling our containers could continually chill onboard the long haul platform - *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

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



18 in a box



vs.

1 cylinder

- **DoD/MDA restarted developing ultra-low-cost ROMP in 2005**
  - **DARPA sought 48” diameter in 2003, remains unproven in large vessels**
  - **compatibility with H_2 since tested, strength retained below at least 77K**
- **Aerospace and Maritime applications, also energy terminals**
- **May make sense for less mass- and volume-constrained Rail**
  - **Truck mounting for ISO-container-sized vessel already developed**
  - **Mounting inside insulated ISO container still makes sense for 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

- **Second batch of full-scale glass fiber vessels demonstrated manufacturability of all trailer processes and components**
- **Successfully (water) burst tested full scale 24" vessel at 300K seal design sufficient for design burst pressure of 20,000 psi remains to be tested at 300K and in liquid nitrogen**
- **Found more novel manufacturing problems, fixed at 24" scale proceeding to scale up to single-cylinder ISO-scale vessels *without DOE funding*, likely to require until 2012 to prove**
- **Investigating materials properties -> more beneficial changes expecting ROMP plastics commercial availability in 2011**
- **Designed thermal management system for delivery trailer**
- **Optimized delivery model for \$/kg-H_2-delivered vs. P and T**
- **Development pathway for large vessel delivery underway**

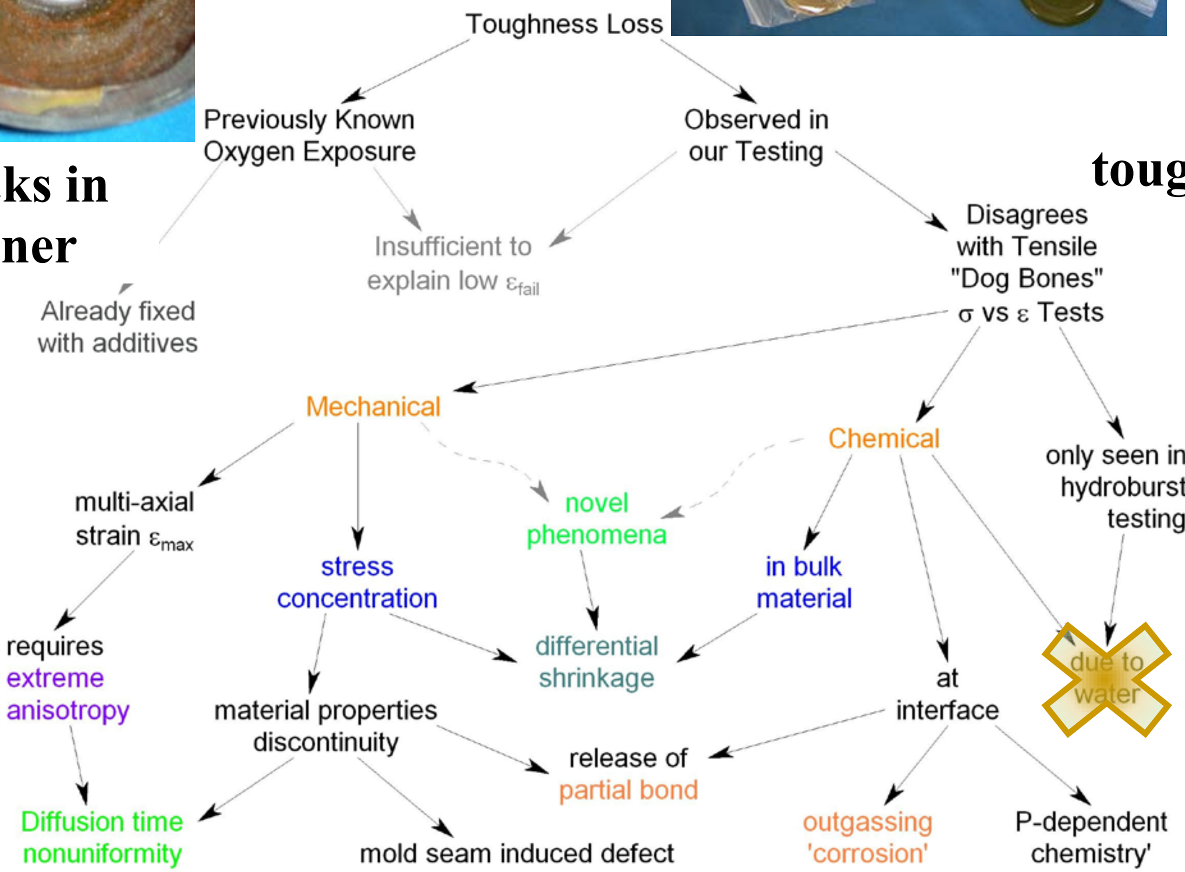
Technical Backup slides

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

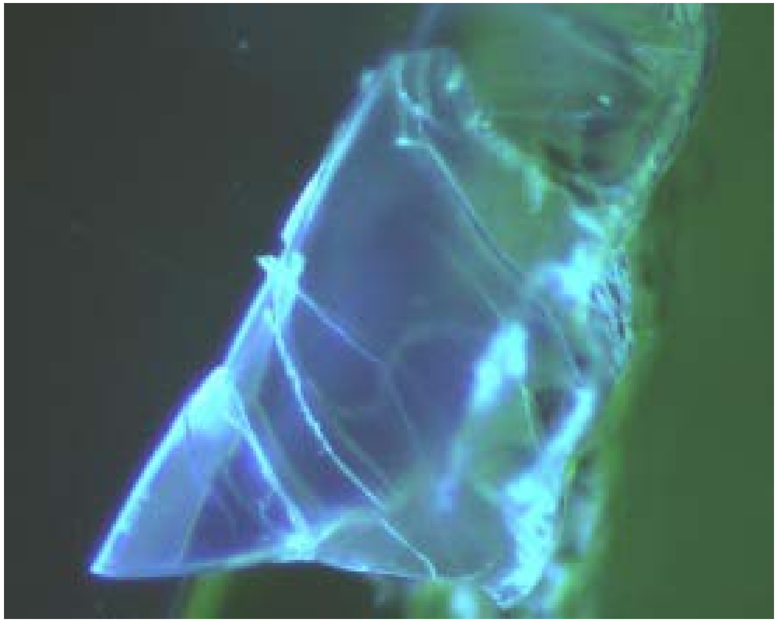
cracks in 3” liner

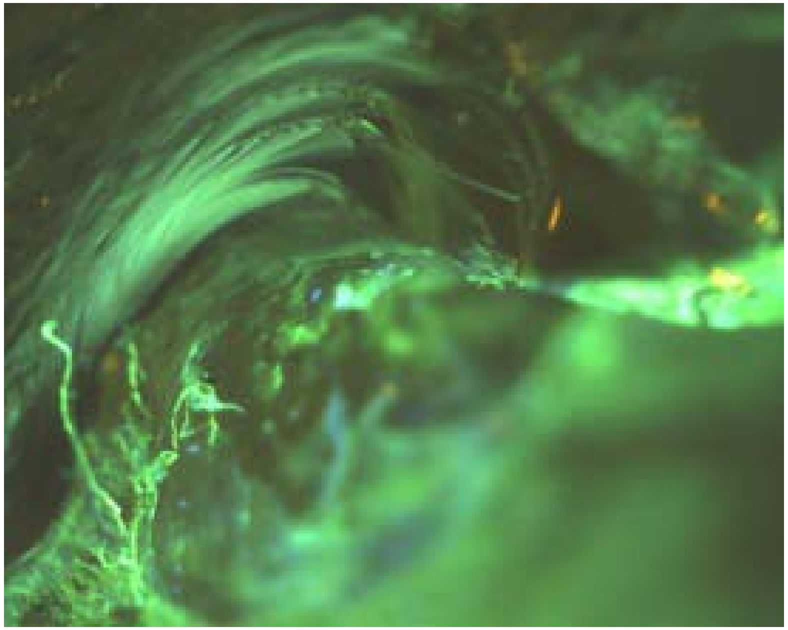
many toughness test plaques were cast and smashed

toughness test drop tower



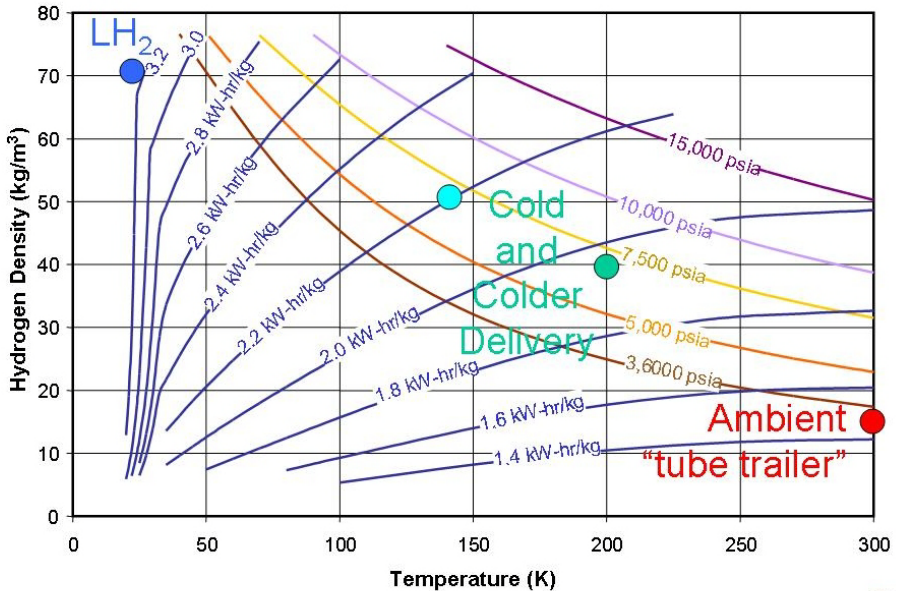
New Phenomena Microphotographs: UV dye-penetrant glow decorates failure surfaces, overlap indicates crack forking

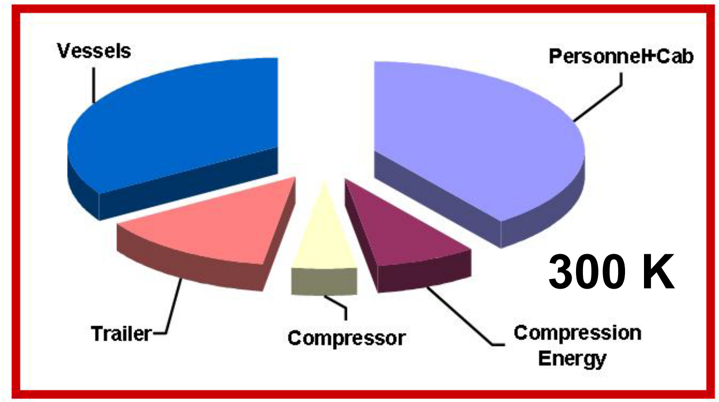




These specimens were cut from the manufactured wall of the recent successful burst test vessel, after it burst, from the specimen shown at the March 2011 DTT meeting. The region corresponding to diffuse nano-cracks was centered roughly in the middle of 0.3” x 0.3” x 1” bars, which were pulled (left) and twisted (right) to failure. Nearly 100% elongation was seen at tensile failure, but only a few percent at torsion failure!

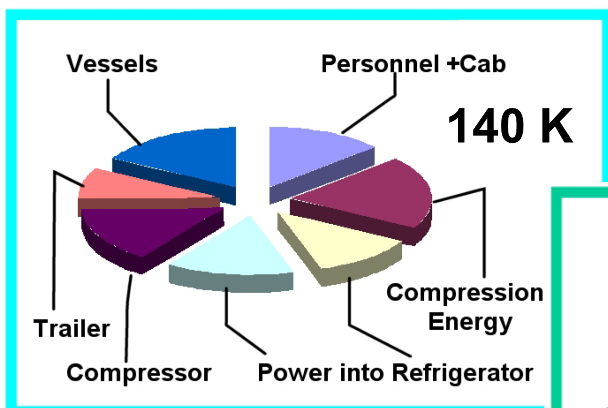
The Refrigeration Problem: a realistic comparison between delivery options calls for an understanding of cooling costs

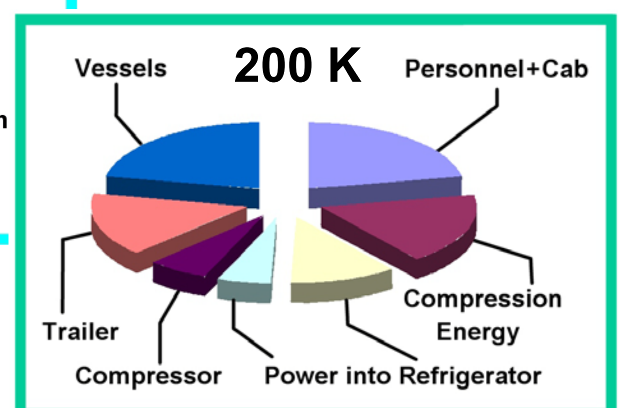




Ambient delivery needs no gas-terminal scale refrigeration

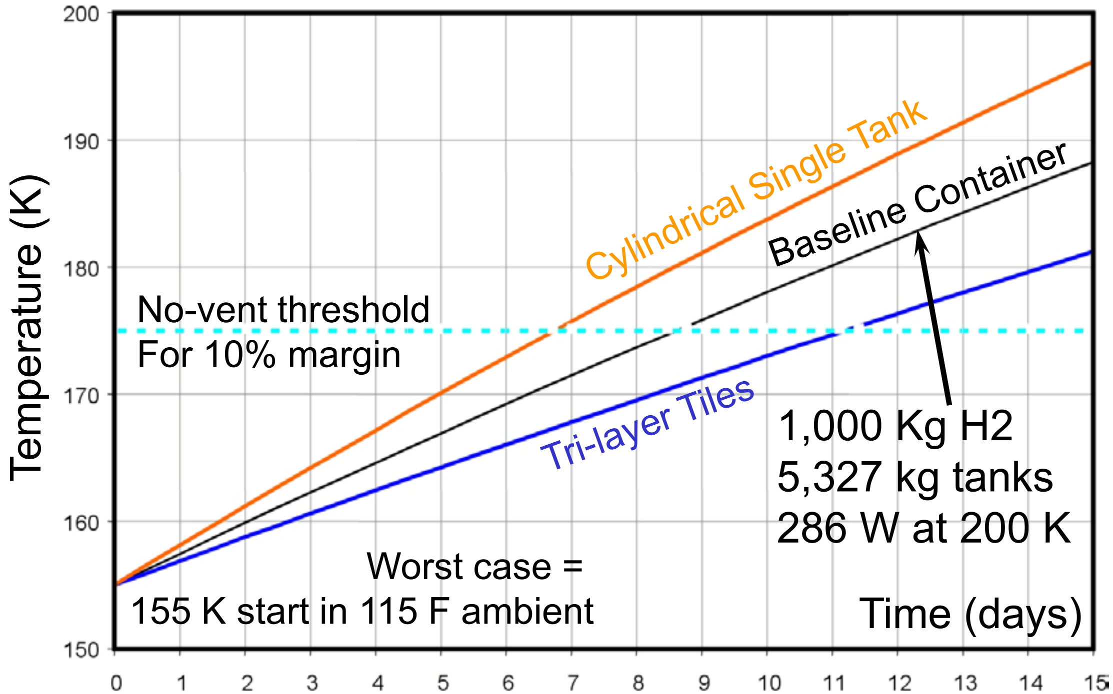
Cold and colder 200 K and 140 K options are shown scaled by $/kg-d



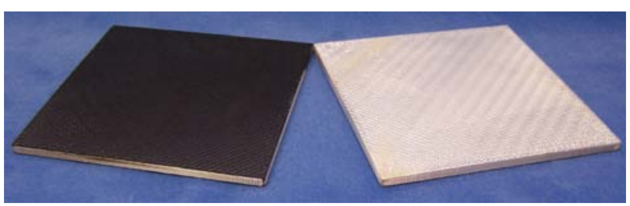


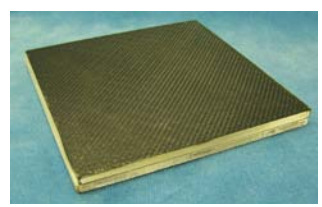
Refrigeration power and capital costs are estimated with a conservative 30% efficiency atop the Carnot refrigerator efficiency times the required exergy to achieve the delivered state

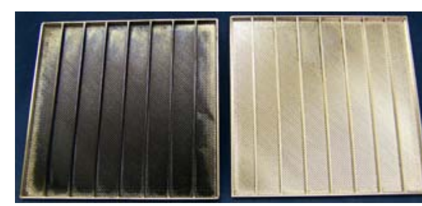
The Insulation Sub-Problem: no risk due to weakening as a result of warming unless stranded for *weeks*



H_2 losses can be avoided due to the large container size, 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