Inexpensive Delivery of Cold Hydrogen in Glass Fiber Composite Pressure Vessels

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PD020

Project Overview

Timeline

- Start date: **October 2004**
- End date: **October 2012**
- Percent complete: **85%**

Budget

- Total project funding
  - DOE: **$1.45 M**
  - Spencer: **$125 k/yr**
- Funding received in FY11:
  - **$240 k**
- Funding for FY12:
  - **$200 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 (SCC)**
- **Structural Composites (SCI)**
- **Lincoln Composites**

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

- Colder temperatures (~100-140 K) increase density ~70% with small increases in energy required for chilling, with affordable capital already available at gas-terminal scale (N_2 liquifiers)

  gH_2 density X trailer volume => delivered-H_2 trailer capacity

- Low temperatures are synergistic with glass fiber composites

  higher glass fiber strength (at 140 K compared to 300 K)

  ultimate stress gains > 80% published for A-Glass (1972)

  LLNL observed gains > 40% (2008), recent S-Glass data

  but low T's would eliminate the (~30%) capital savings from plastic-lined vessels or need to use cyanate esters (hazmat)

  ∴ LLNL and SCC innovated liner plastics for low-T CPVs

- Glass fiber (~$6/kg for E2-Glass vs. ~$23/kg for carbon fiber) minimizes high materials cost for high strength composites
- Optimized pressure (~7,000 psi) minimizes delivered H_2 costs, same design can deliver up to 12,000 psi or build cascade
- Significant savings downstream in filling stations and vehicles

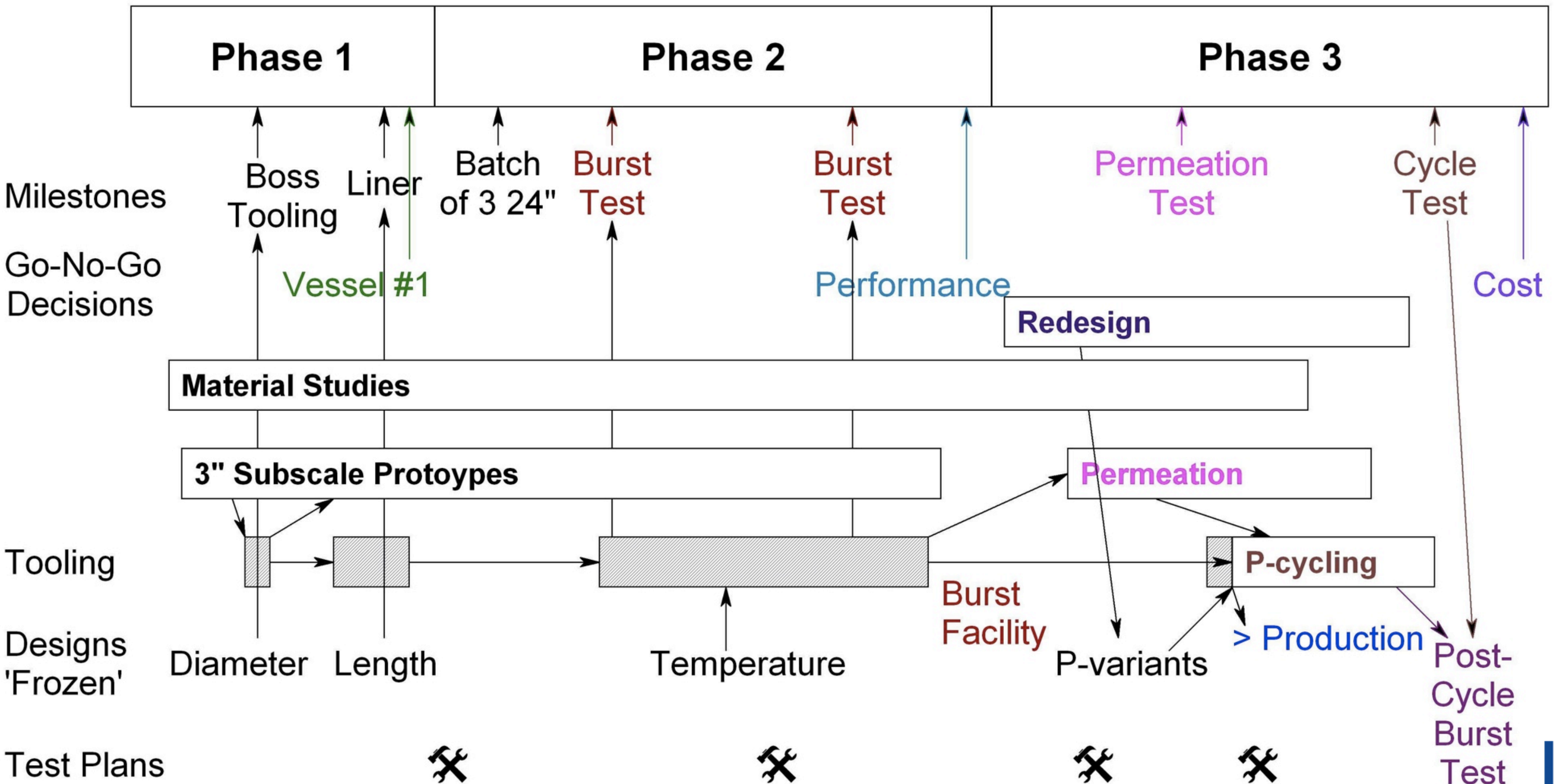
Relevance: Updated model predicts cost advantage for 140-200 K H_2 delivery

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

LLNL+SCC

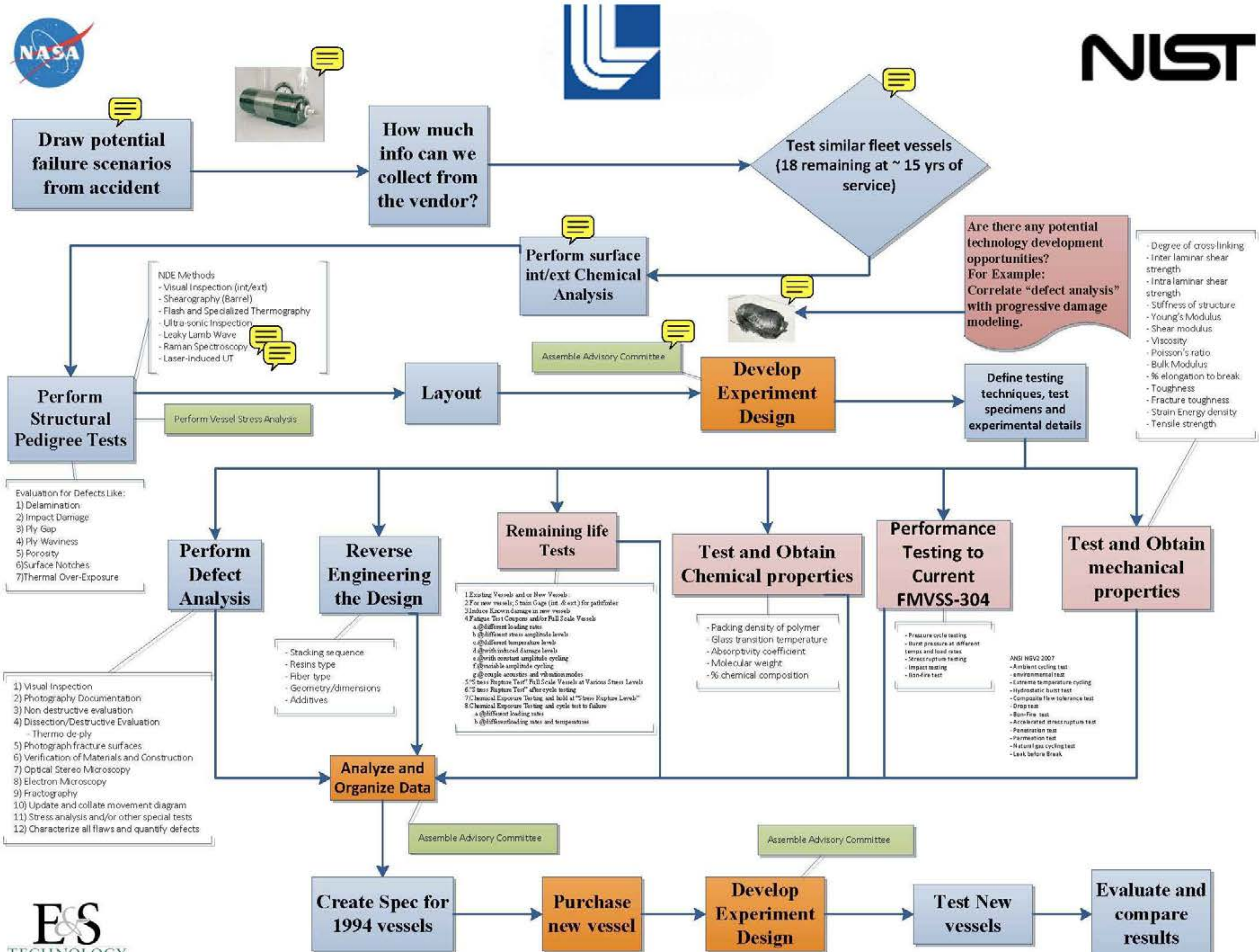
Approach: 3 Phases (stretched out to 4 years) remove technical risks

- **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 knocks out technical risk for all key unknowns : compliance, toughness, strength, permeation, novel phenomena**



Approach: Eliminating All Realistic Failure Mechanisms for Cold Hydrogen Delivery in Novel Composite Pressure Vessel Technology

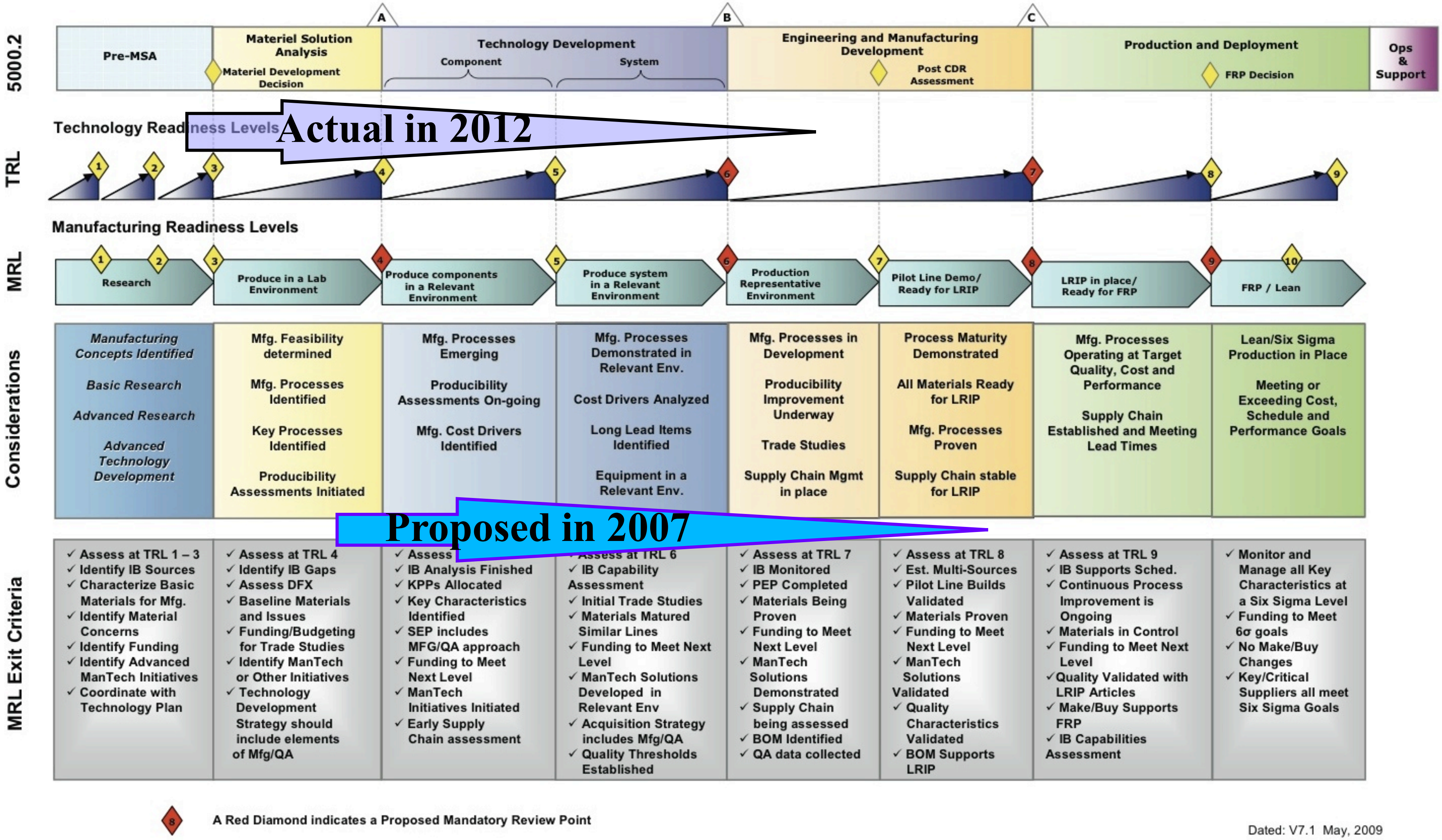
- Program to accomplish this goal – planned and actual testing
- Manufacturing innovation encountered several road blocks
- Ability to engineer this novel technology
  - Risk of wishful thinking counteracted by trial and error
  - Full scale CPV test program found to be necessary to eliminate realistic risks (of actual failures during scale-up)
  - Failure Analysis methods being developed by NASA/DoT
- Proof of Concept tests = hydrostatic burst, P+T cycling, and long duration (weeks) hydrogen permeation ⇨ measure P(t)
  - Very dangerous tests of experimental vessels at high P-H2
  - Site selected and in preparation for > 10 MJ explosive-potential testing, no longer DOE funded or LLNL specified
- New Science required to overcome problems discovered
  - Testing of subscale and full scale test articles → discoveries
- Mathematics required to deal with Stress Rupture likelihood
  - Has very high leverage over capital cost of cold glass fiber



Draw potential failure scenarios from accident
How much info can we collect from the vendor?
Test similar fleet vessels (18 remaining at ~ 15 yrs of service)
Perform surface int/ext Chemical Analysis
Are there any potential technology development opportunities? For Example: Correlate "defect analysis" with progressive damage modeling.
- Degree of cross-linking
- Inter laminar shear strength
- Intra laminar shear strength
- Stiffness of structure
- Young's Modulus
- Shear modulus
- Viscosity
- Poisson's ratio
- Bulk Modulus
- % elongation to break
- Toughness
- Fracture toughness
- Strain Energy density
- Tensile strength
NDE Methods
- Visual Inspection (int/ext)
- Shearography (Barrel)
- Flash and Specialized Thermography
- Ultra-sonic Inspection
- Leaky Lamb Wave
- Raman Spectroscopy
- Laser-induced UT
Assemble Advisory Committee
Perform Structural Pedigree Tests
Perform Vessel Stress Analysis
Layout
Develop Experiment Design
Define testing techniques, test specimens and experimental details
Evaluation for Defects Like:
1) Delamination
2) Impact Damage
3) Ply Gap
4) Ply Waviness
5) Porosity
6)Surface Notches
7)Thermal Over-Exposure
Perform Defect Analysis
Reverse Engineering the Design
Remaining life Tests
Test and Obtain Chemical properties
Performance Testing to Current FMVSS-304
Test and Obtain mechanical properties
1.Existing Vessels and or New Vessels
2.For new vessels; Strain Gage (int. & ext.) for pathfinder
3.Induce Known damage in new vessels
4.Fatigue Test Coupons and/or Full Scale Vessels
a.@different loading rates
b.@different stress amplitude levels
c.@different temperature levels
d.@with induced damage levels
e.@with constant amplitude cycling
f.@variable amplitude cycling
g.@couple acoustics and vibration modes
5."Stress Rupture Test" Full Scale Vessels at Various Stress Levels
6."Stress Rupture Test" after cycle testing
7.Chemical Exposure Testing and hold at "Stress Rupture Levels"
8.Chemical Exposure Testing and cycle test to failure
a.@different loading rates
b.@different loading rates and temperatures
- Packing density of polymer
- Glass transition temperature
- Absorptivity coefficient
- Molecular weight
- % chemical composition
- Pressure cycle testing
- Burst pressure at different temps and load rates
- Stress rupture testing
- Impact testing
- Bon-fire test
ANSI NGV2 2007
- Ambient cycling test
- environmental test
- Extreme temperature cycling
- Hydrostatic burst test
- Composite flaw tolerance test
- Drop test
- Bon-Fire test
- Accelerated stress rupture test
- Penetration test
- Permeation test
- Natural gas cycling test
- Leak before Break
- Stacking sequence
- Resins type
- Fiber type
- Geometry/dimensions
- Additives
1) Visual Inspection
2) Photography Documentation
3) Non destructive evaluation
4) Dissection/Destructive Evaluation
- Thermo de-ply
5) Photograph fracture surfaces
6) Verification of Materials and Construction
7) Optical Stereo Microscopy
8) Electron Microscopy
9) Fractography
10) Update and collate movement diagram
11) Stress analysis and/or other special tests
12) Characterize all flaws and quantify defects
Analyze and Organize Data
Assemble Advisory Committee
Assemble Advisory Committee
Create Spec for 1994 vessels
Purchase new vessel
Develop Experiment Design
Test New vessels
Evaluate and compare results

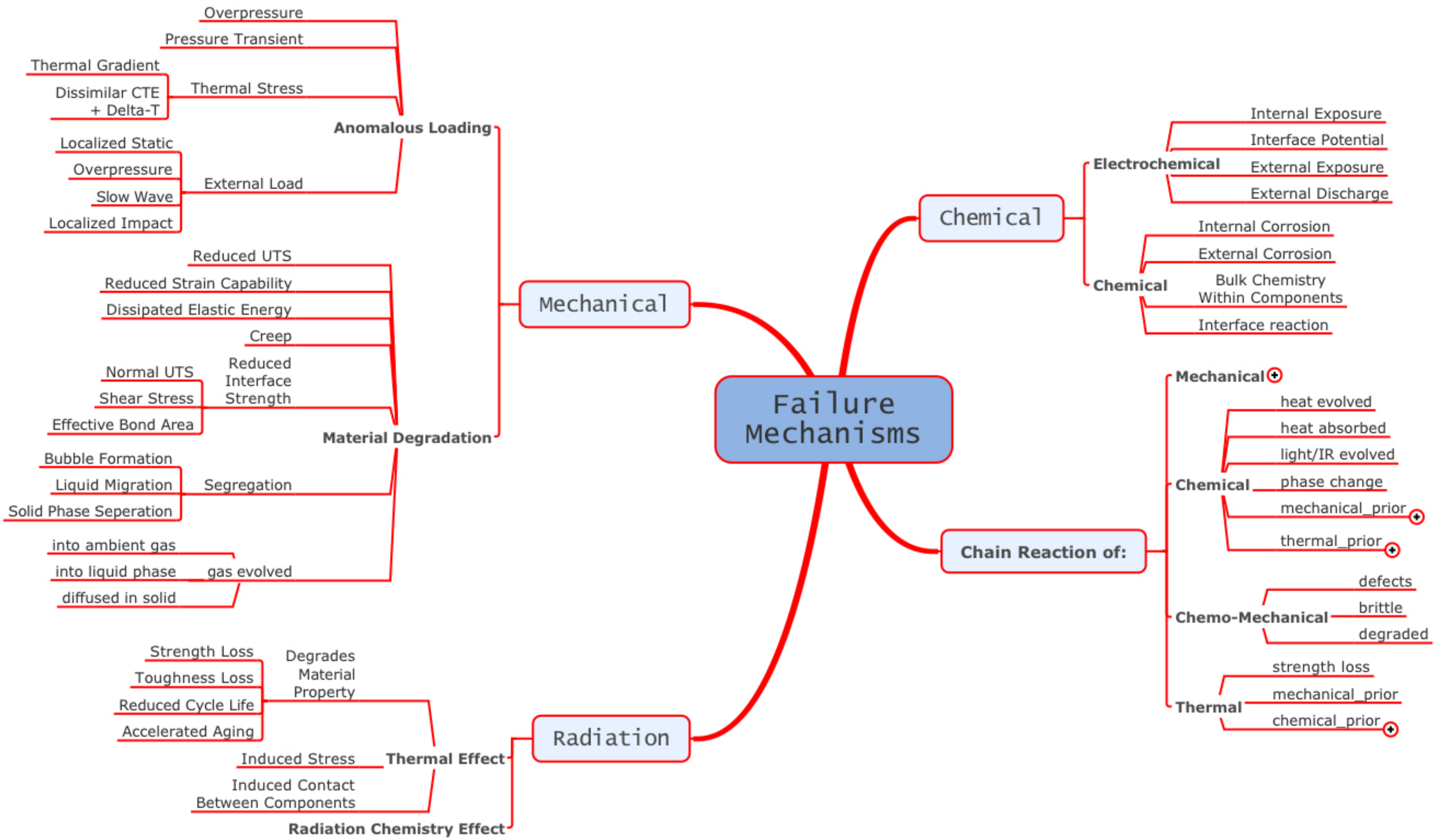
Manufacturing Readiness Levels (MRLs, used by DoD):

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.

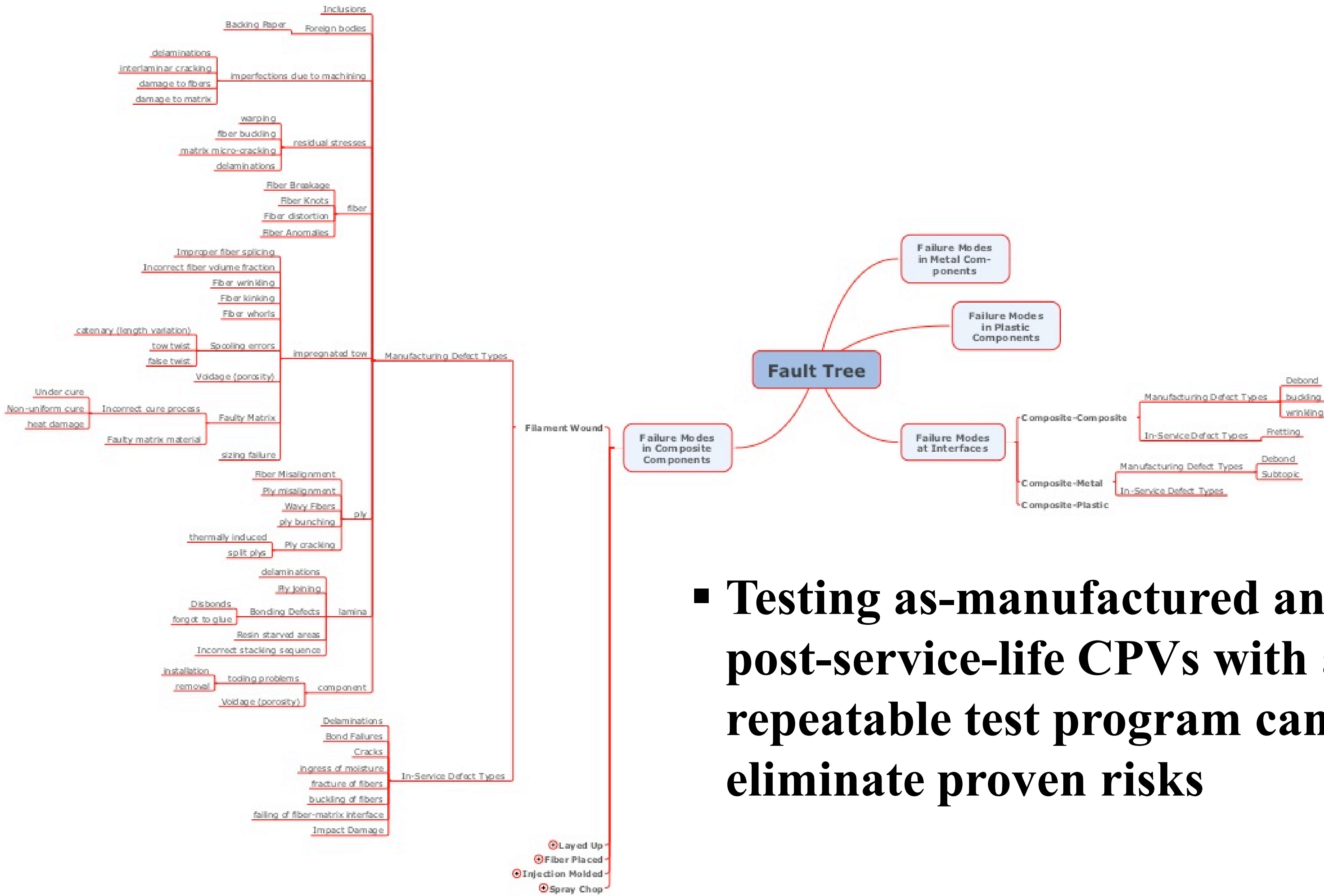


Failure Modes for Composite Pressure Vessels – Ways CPVs Fail

- NASA, DoT, and NIST have been collaborating to catalog and instrument actual CPV failures (both in service in and in labs)
- Ongoing activity has organized them into diagnostic methods



Accomplishments: The First Fault Tree for Fiber Composite Pressure Vessels



- **Testing as-manufactured and post-service-life CPVs with a repeatable test program can eliminate proven risks**

Permeation Test Facility Under Construction to Determine Rate of Hydrogen Escaping from Full Size Tanks Under Maximum Service Pressure at Temperature Extremes ➔ Severe Hazards

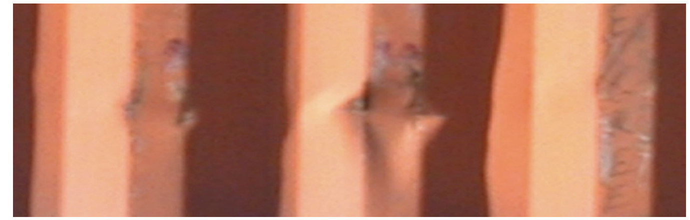
- Transport 'coffin' keeps CPV's clean, allows them to be trucked without impact damage over dirt roads, and lowered into dug 'berm'

permeation test rig in design phase

- Buried in mowed lot, over 100' from trees, in guarded private forest, under > 12” of sand bags atop steel decking plate, for 1-8 weeks/test under T-controlled dry gN2 ambient

Proven Failure Modes of Integrated Trailers ⇨ ISO Containers Optimized to Protect Their Contents vs. Road and Lift Hazards

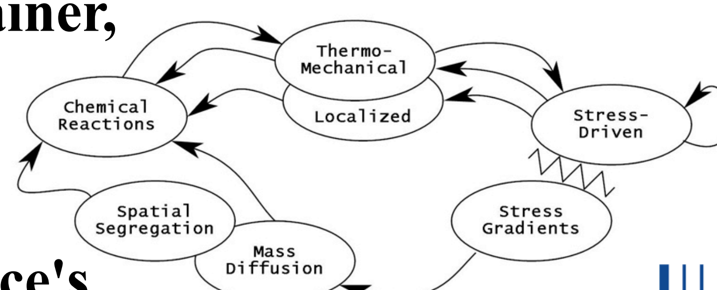
- **Best way to keep contents and their environment from interactions that can damage them (or harm us)**



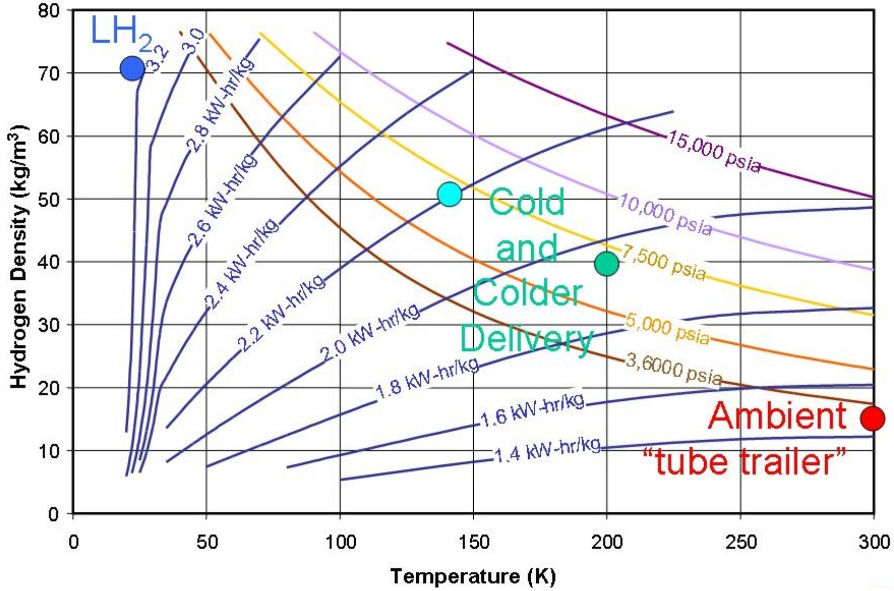
- **Impacts, leaks, large mechanical loads, corrosion, localized loads . . . Designed to be handled, dropped...**

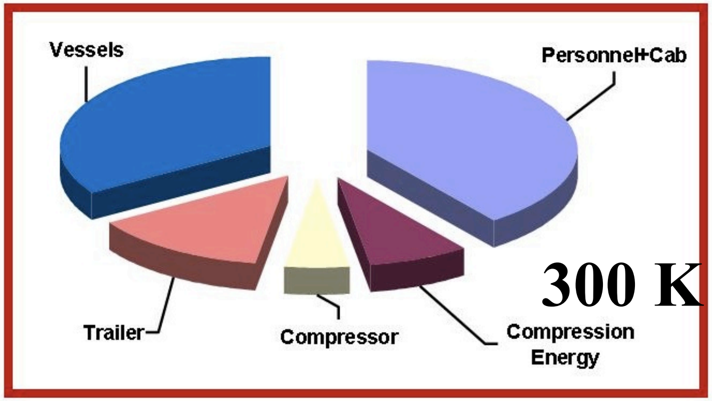
Failure Modes Anticipated for Integrated Trailers = Loss of Cab Propulsion, Loss of Insulation, Fire on Exterior of Container

- **Break up possible Complex Chain Reactions with :**
  CO_2 + slight overpressure inside container,
  Coatings vs. Mass Diffusion
  Suspension of CPV's vs. Shock Loads
  3 Layers of Insulating Tiles
  Redundant + Overlapping Relief Device's



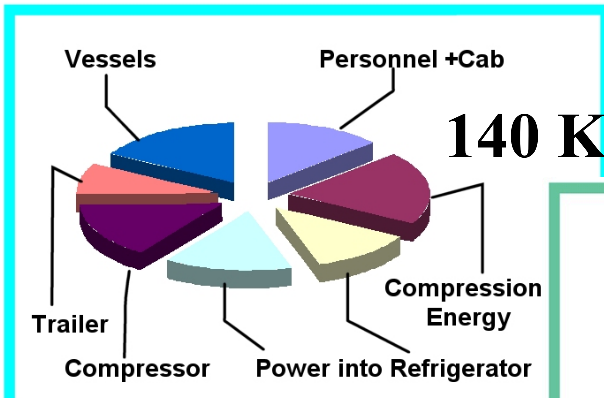
The Refrigeration Problem: a realistic comparison between delivery options calls for an understanding of cooling costs



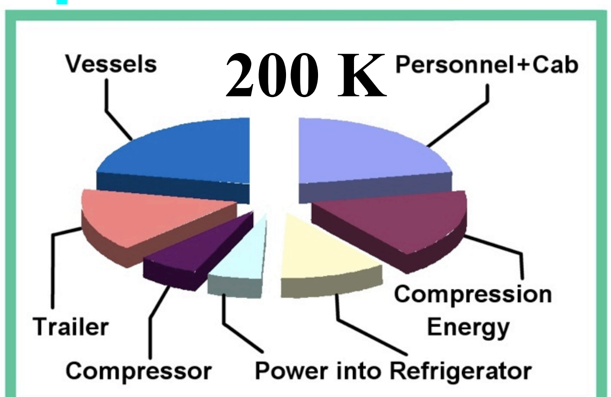


Ambient delivery needs no gas-terminal scale refrigeration

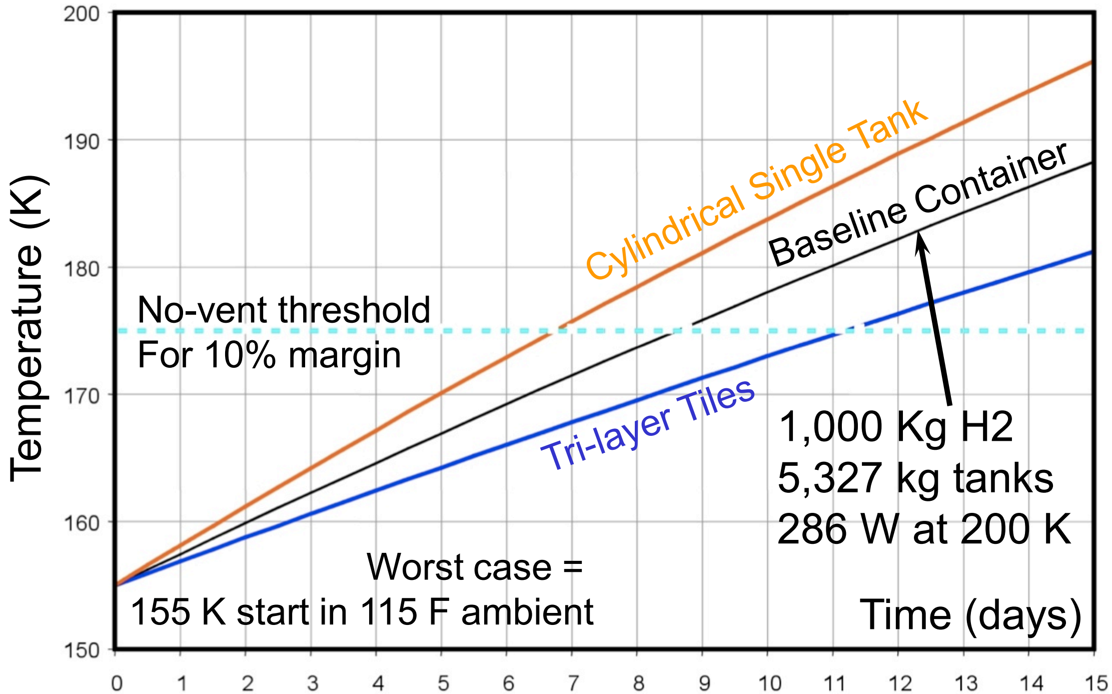
Refrigeration power and capital costs are estimated with a conservative 30% efficiency atop the Carnot refrigerator efficiency times the required exergy to achieve the delivered state



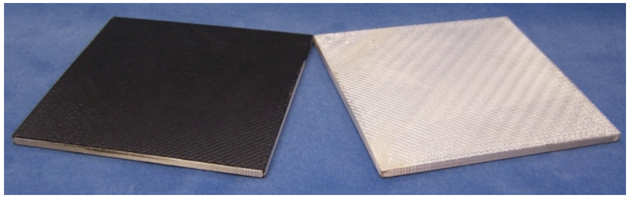
Cold and colder 200 K and 140 K options are shown scaled by $/kg-d

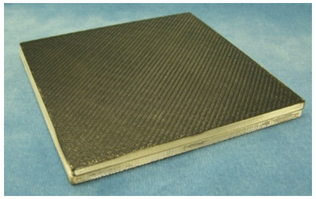


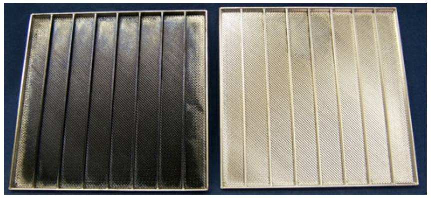
The Insulation Sub-Problem: no risk due to weakening as a result of warming unless stranded for *weeks*



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

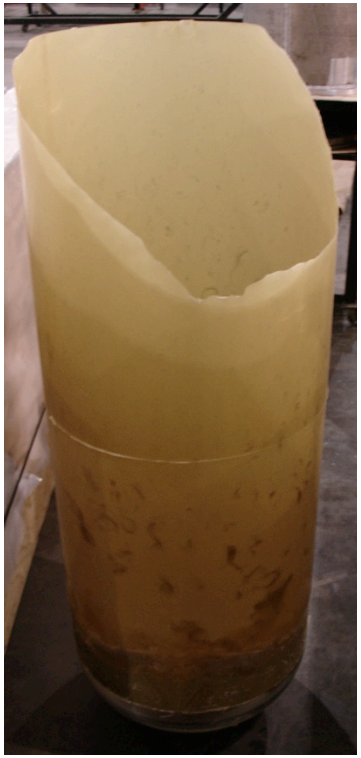


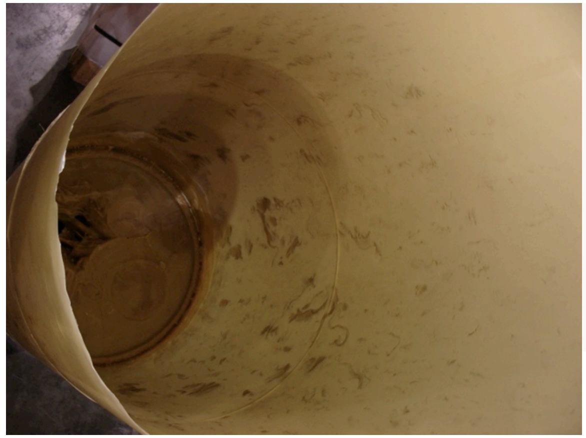


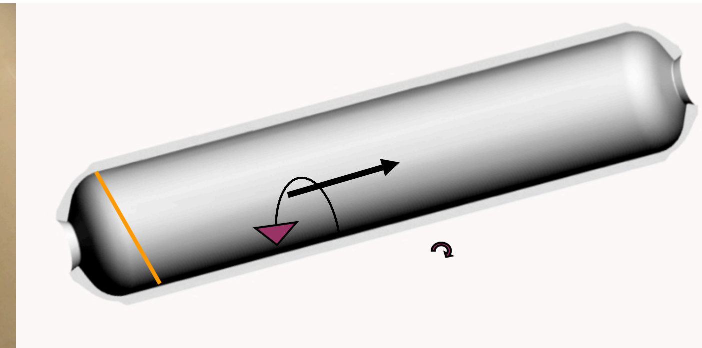


Prototype insulation tile development: low- and high-emissivity faces, outside an internal anti-bending structure, clamp gap width in a planar vacuum (metal foil, welded, no-recharging) inner layer

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

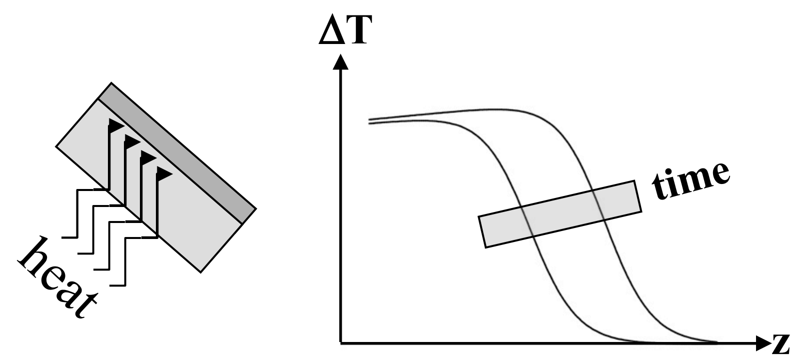






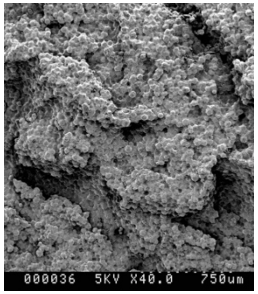
closed mold was poured with a single shot of ambient-T ROMP, then spun on 2 axes

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

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

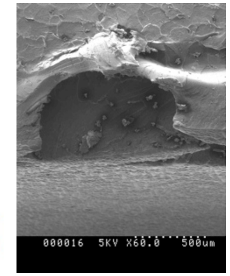


cracks with extreme detail

Ultimate Strain Disagrees with Tensile "Dog Bones"

Mechanical

Chemical



bubbles on crack surfaces

multi-axial strain ε_{max}

novel phenomena

stress concentration

in bulk material

requires extreme anisotropy

differential shrinkage

at interface

material properties discontinuity

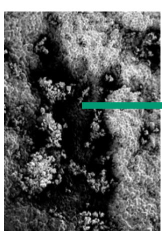
release of partial bond

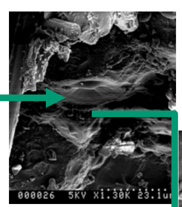
Diffusion time nonuniformity

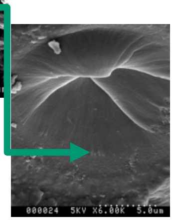
mold seam induced defect

outgassing 'corrosion'

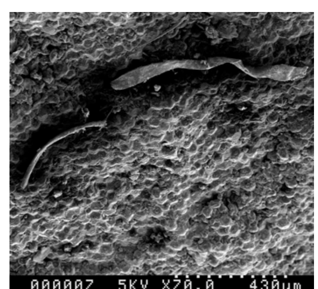
P-dependent chemistry'



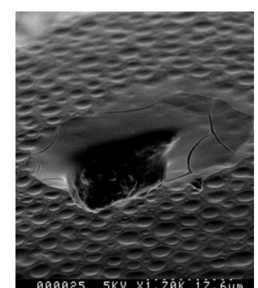




crater with fangs "tells all"

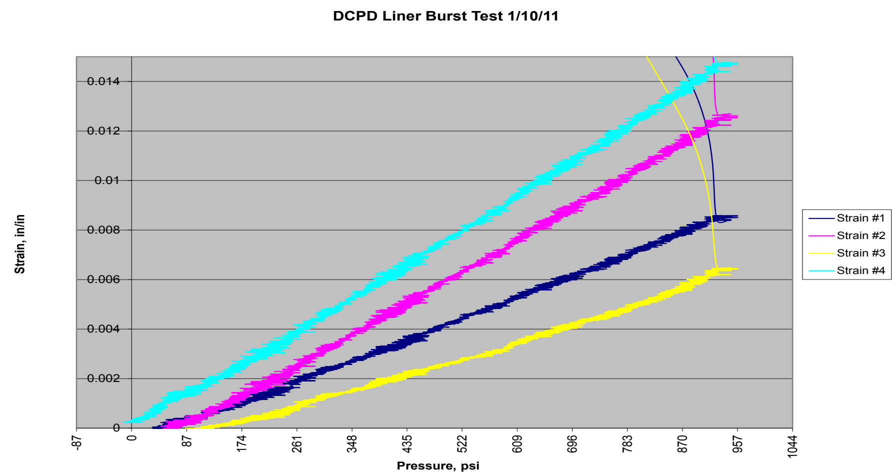


Process-induced defects of many kinds



Second Generation tooling yields first successful burst test of full scale (23” diameter) S Glass fiber pressure vessel

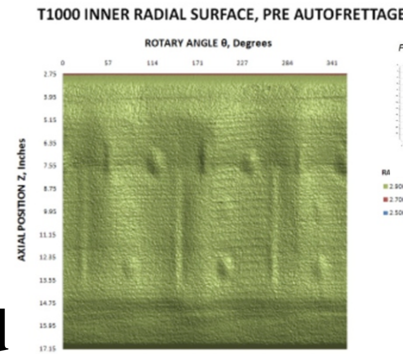
Failure Mode not observed previously in hydroburst testing of composite pressure vessels proves liners and seals operate at strains > trailer design levels

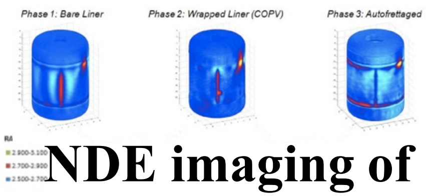


Failure Mode shown with loose failed hoop fiber layer cut away

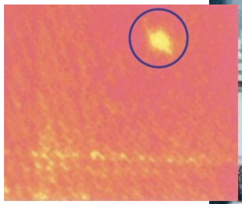
Failure Modes that Might Be Suppressed by Tougher Plastics

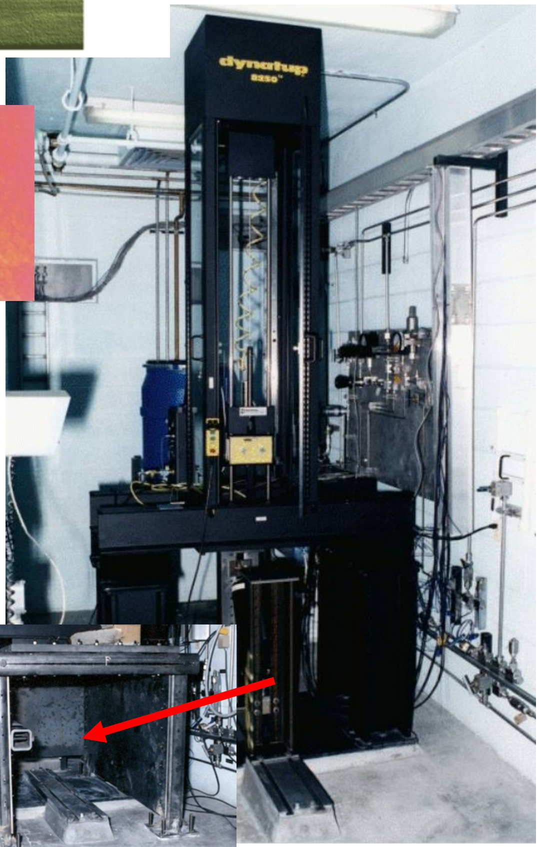
- **Mechanical Damage – major cryptic (not easily noticed) failure modes in low-volume production, during CPV installation, and in service**
- **More prevalent in metal-lined (Types II and III) CPV's, but also very likely in cold, weak HDPE CPV liners**
- **Testing about to commence by impacting 3" ROMP CPV liners at White Sands (NASA lab) Þ toughness at T = 77°K**
- **Blast-shielded room and rig have potential to observe shrapnel emerging from high-Pressure (gas content) bursts**
- **Chain reaction accidents can be precluded by tougher CPV's**





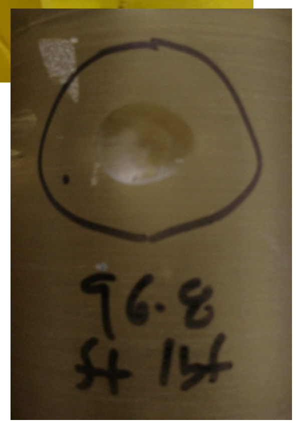
NDE imaging of cryptic damage



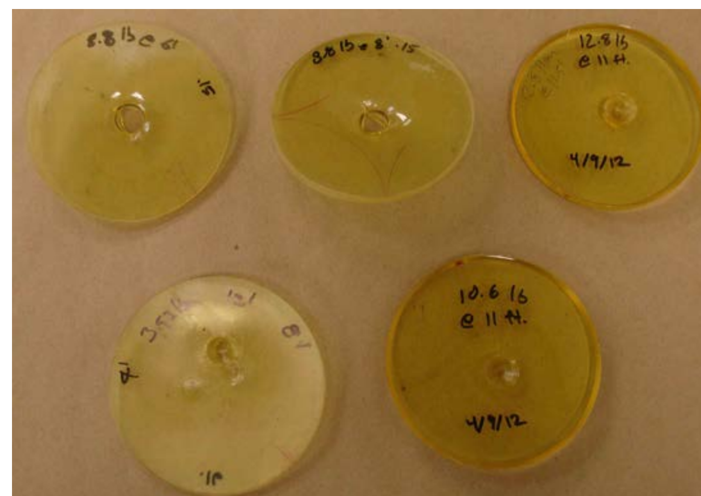


Preliminary Testing Establishes ROMP Plastics are Tougher

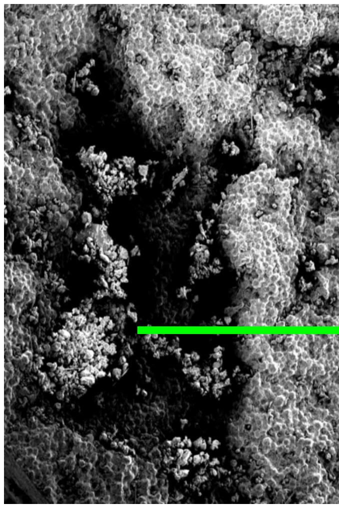
- Test tower at SCC set up to impact 3” subscale ROMP plastic liners and ASTM D5628 flat cast plaques
- Standard 3/8” thick plaques deform but do not crack at 140 ft-lbf impact energy (vs. toughened epoxy at 45 ft-lbf)
- Cylindrical liners withstand ~twice the impact energy vs. thinner flat plaques of the same thickness as liner walls



Practicing LN cool down for WSTF

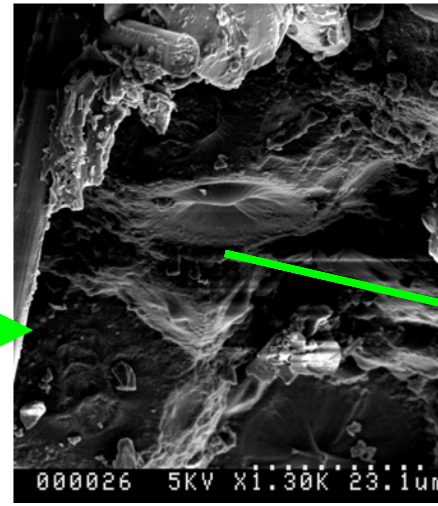


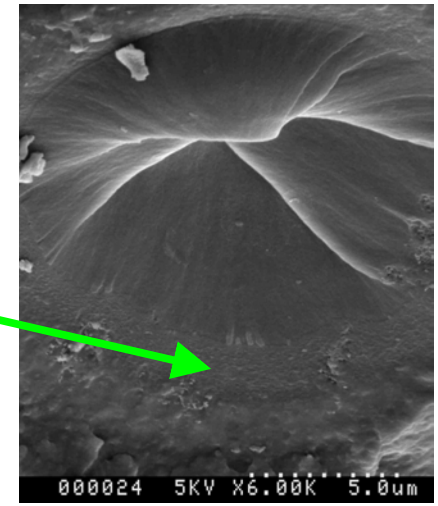
'Nanocracking' – The Manufacturing Failure Mode that cost this project at least one year, may never have been previously observed, and may not occur in non-ROMP plastics (⇨ a Science Spin-Off)

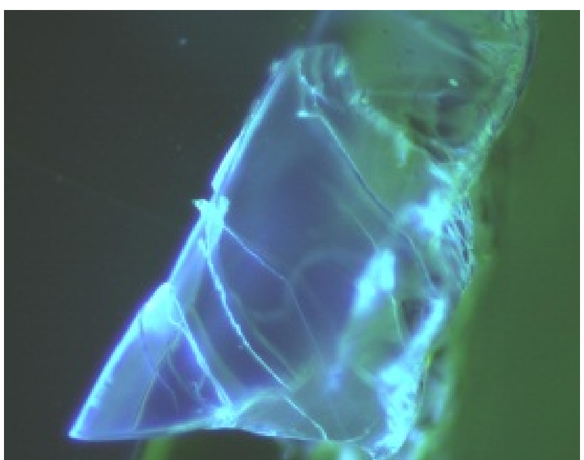


a crater with fangs

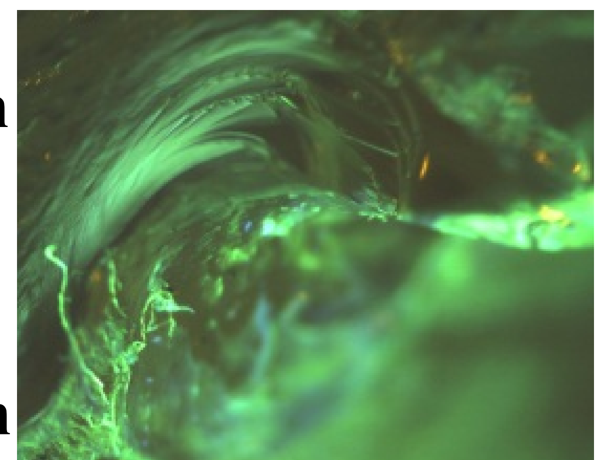
“tells all”





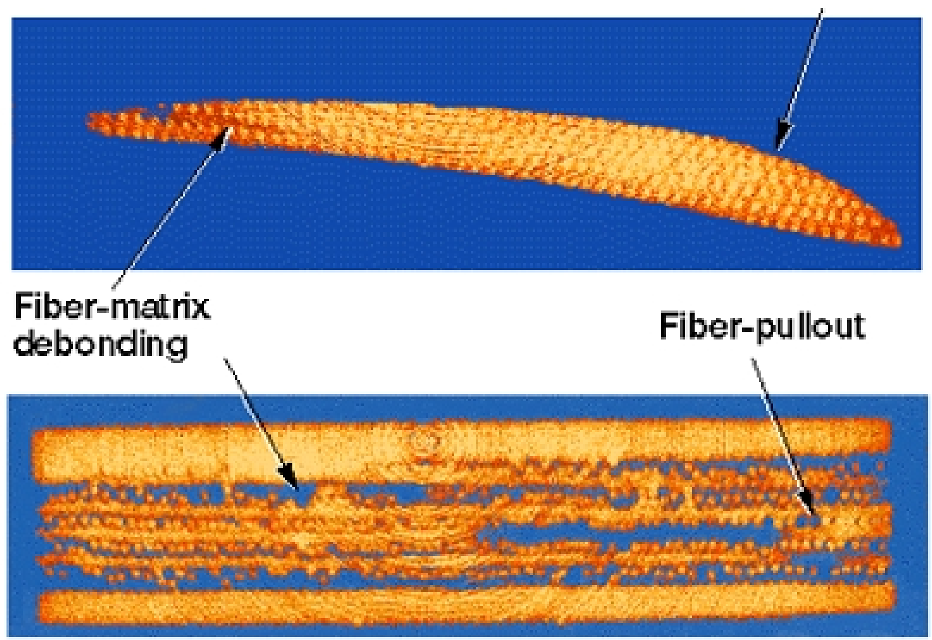


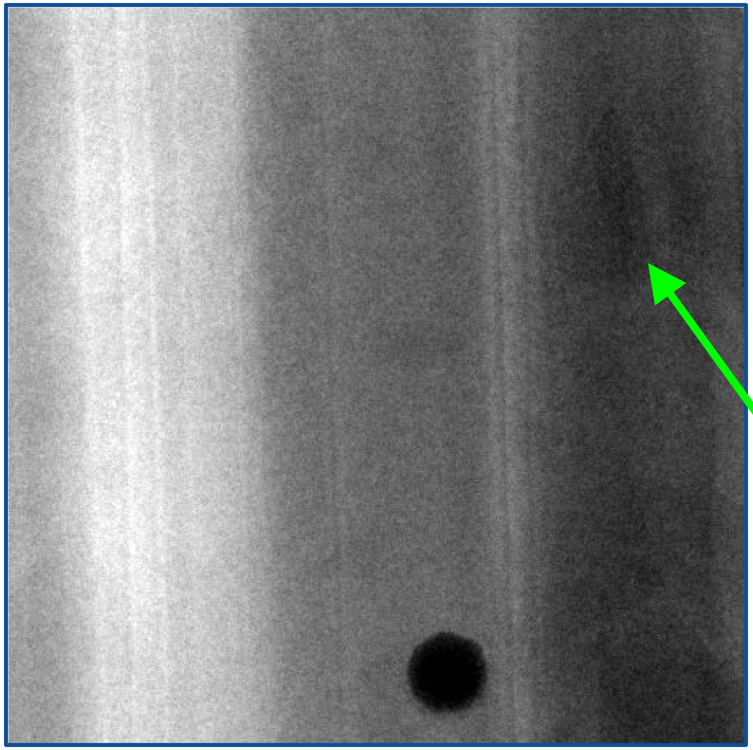
nanocracked region fails with > 30-fold difference between ultimate tensile and shear strain



CAT X-Ray – A Superb Diagnostic Tool vs. Manufacturing Defects

X-rays can image sub-micron patterns of different atoms non-destructively through ~1 centimeter of carbon/epoxy CPV wall, or ~0.5 millimeter of glass/epoxy



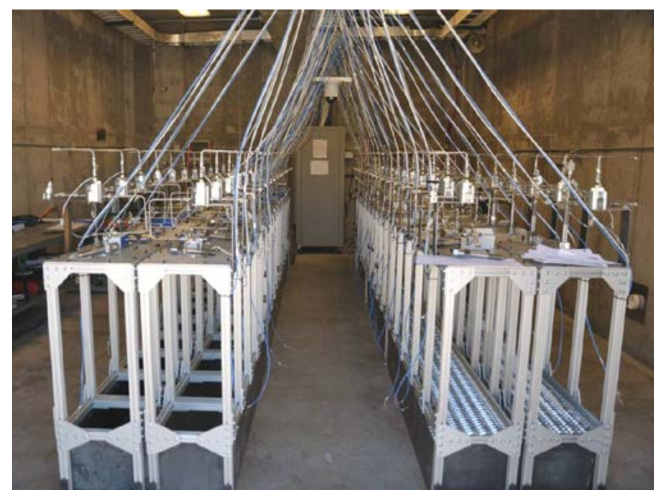


First-ever *nanoscale* image of high-performance S Glass fibers in pultruded epoxy matrix (field of view shown is 16x16 microns) shows innards of one fiber likely segregated !

Soon to be applied to the "smoking gun" crater of nanocracking (see Slide 20)

Stress Rupture – The Widely-Recognized Failure Mode Limiting Glass CPV Service Life (and thereby determining Capital Cost)

- A realistic risk 'proven 'for Glass CPV's by1980s LLNL/DOD testing
- Plate Glass life under load suggests moisture to blame for erroneous LLNL fiberglass service life results
- NASA WSTF is conducting shielded experiments on hundreds of CPVs



- Shields separate CPV's under months of hydro-static testing, ~25 sensors/CPV

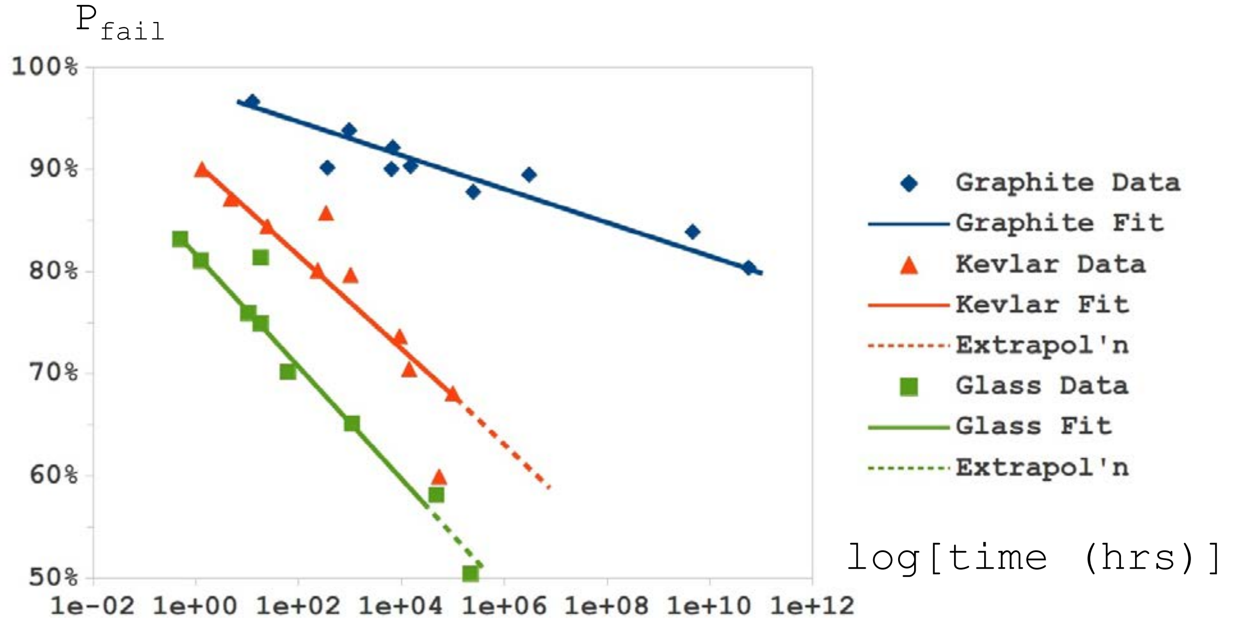
Fitting the Number of Survivors to Weibull's Distribution

- **Originally claimed to be "ad hoc", The Weibull Distribution is one of only two Extreme Value Distributions**

$$\Pr\left\{x_{sampled} \le x\right\} = 1 - \exp\left[-\left(\frac{x-\mu}{\sigma}\right)^m\right]$$

- **Generations of grad students taught the links-in-a-chain metaphor for large numbers of identical risks, never taught to examine the assumptions leading to EVD's**

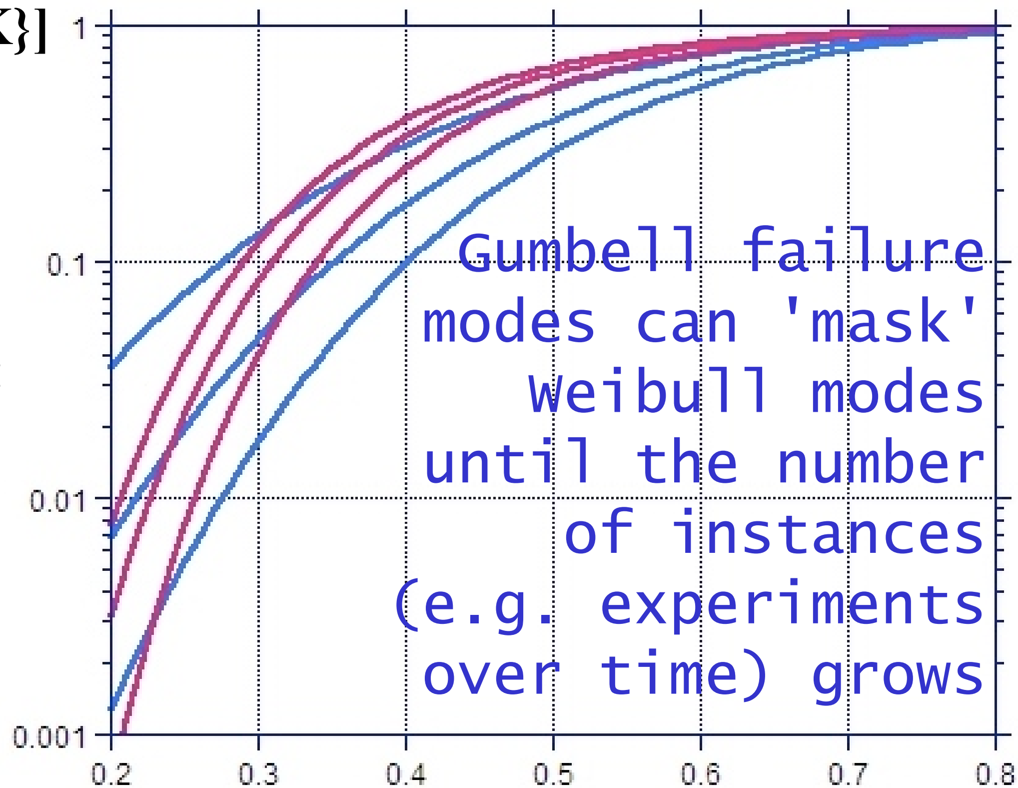
- ***Artificial Materials* can *violate these assumptions***



Kevlar is a registered trademark of E. I. du Pont de Nemours and Company

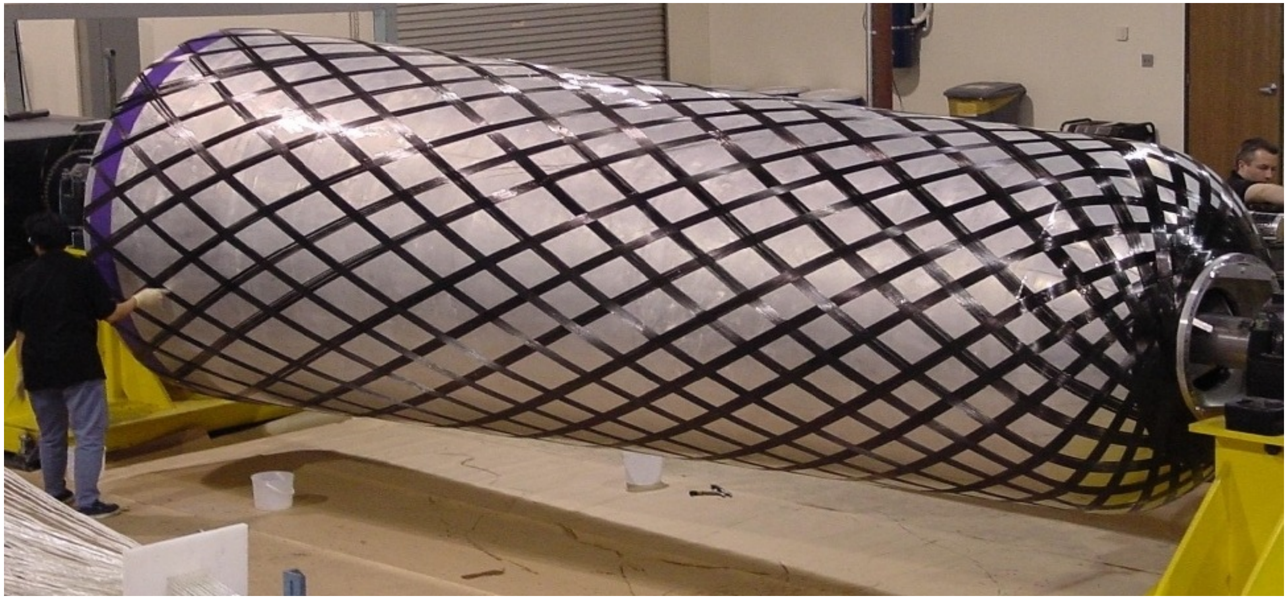
What Escapes Notice Until More Time and More Units-Under Test

- **Multiple failure modes are realistic in most engineering**
- **If independent, their logarithms of Pr(OK = unfailed) add together in situations where the system fails if one or more of the instances of every failure mode fail (since their individual probabilities-of-not-failing multiply)**
- **Plotted against some other axis that failure modes depend on (such as applied stress) :**
- **Weibull modes (and all power-law, fat-tail modes) combine into an overall Weibull**

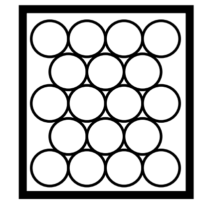


- **Gumbell (the other, much-more-well-behaved Extreme Value Distribution) combine into an overall Gumbell**

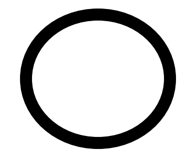
Collaborations: LLNL is teamed with rocket innovators eager and able to develop novel, *very large composite parts*



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**

Proposed future work: Joint DOE/DoT Cold-cH_2 Field Demonstration

- **Located contacts with potential DoT Program Managers likely to be regulators of cold safety subsystem requirements**
- **Building Industrial Partnerships: eager-to-adopt gas vendors, trailer integrators, CPV and materials intellectual property**
- **Materials Research and Development efforts must continue for hydrogen-specific and cold-specific applications :**
  - **strength, compliance, permeation vs. T ⇨ test + improve**
  - **stress rupture life(T) testing (a by-product of trailer tests)**
- **Expect further beneficial changes to properties : toughness, hydrogen and water permeation, lack of FC-poisons' leaching**
  - **(subscale vessels and mitigation layers permeation testing)**
- **Expecting ROMP plastics commercial availability in 2012**
- **Design and modeling efforts required: insulating tiles, acceleration-loaded CPV suspension, expansion isolation from container, economic modeling of built trailer costs and tooling improvements at production-line quantities**

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**
- **Third batch currently being manufactured is full Type V CPV with 25 ksi LN-service-compatible PTFE-over-316 seals**
- **Graphite epoxy version of third batch (designed 10 ksi burst) currently undergoing full ASME X Standard qualification**
- **Successfully (water) burst tested full scale 24" vessel at 300K with earlier seal design sufficient for P(burst) at 20,000 psi**
- **Third batch seal design in 6" subscale (full Type V CPV) currently in cycle testing; safe enough for H_2 permeation test shrapnel-safe plan for 300K, then 100K *(not by LLNL/DOE)***
- **Proceeding to scale up to single-cylinder ISO-scale vessels *without DOE funding*, likely to require until 2013 to prove**
- **Expecting new ROMP plastics commercial availability in 2012**
- **Development pathway for large vessel delivery underway**