Advanced Concepts for Containment of Hydrogen and Hydrogen Storage Materials

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Project ID # STP36

This presentation does not contain any proprietary or confidential information

Overview

Timeline

- Start date: **October 2003**
- End date: **September 2008**
- Percent complete: **50%**

Barriers

- **B. Weight and volume**
- **H. Sufficient fuel storage for acceptable vehicle range**
- **I. Materials**
- **M. Hydrogen capacity and reversibility**

Targets

- **2007 DOE weight and volume target**

Budget

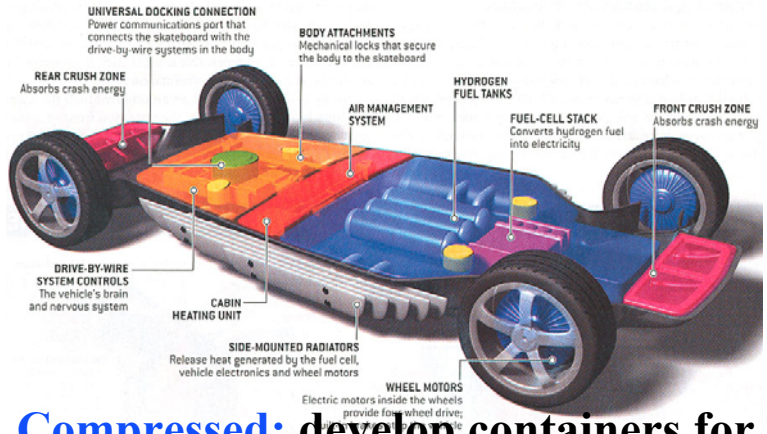
- Funding received in FY05: **$500 k**
- Funding for FY06: **$400 k**

Partners

- **Spencer composites,** CRADA **with Automotive Composites Consortium,** aerospace work funded by **DARPA**
- Collaboration with many **Universities**
- Demonstrating cryotank technology (**SCI, SunLine,** funded by **SCAQMD**)

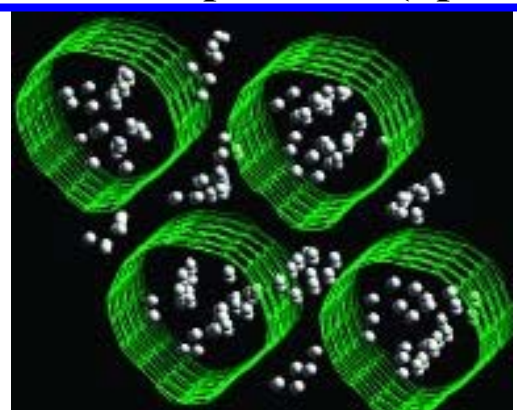
Objectives: We are developing high performance conformable containers that can operate under extreme conditions, as needed for hydrogen and hydrogen storage material containment

Liquid: develop conformable containers that can operate at extremely low temperature (20 K) and wide range of pressures (100-5000 psi)



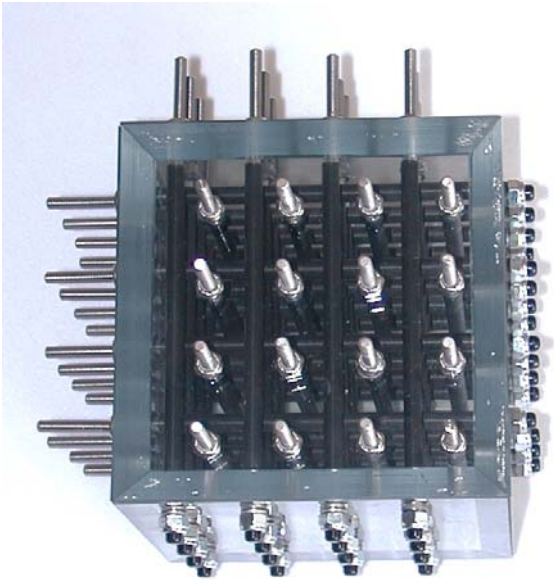
Compressed: develop containers for very high pressure (10,000 psi) and moderate temperature (up to 100°C)

Chemisorbed: develop conformable containers for high temperature operation and efficient thermal management



Physisorbed: develop compact containers that operate over wide range of conditions and provide efficient thermal management

Approach: we are developing innovative concepts for hydrogen and hydrogen storage material containment for efficient thermal management at cryogenic or high temperatures



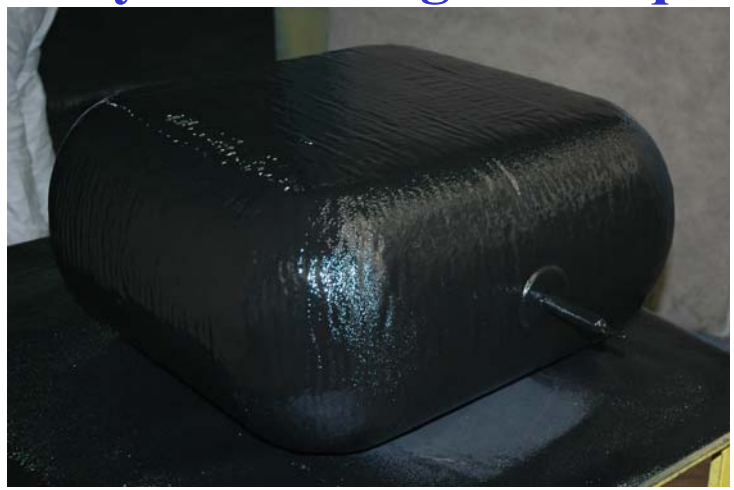
Filament wound containers support stresses on the outer skin. Geometric features are efficiently used for reducing bending moments

Macrolattices use an internal structure to contain the pressure forces. **Struts** provide heat transfer paths for efficient thermal management

Replicants also use an internal structure. Structure is made of small components that are bonded to each other.

Accomplishments: We have built two filament wound conformable vessel segments with flat ends (pillow tanks)
First vessel was built to verify feasibility of winding techniques

1. Machine foam mandrel



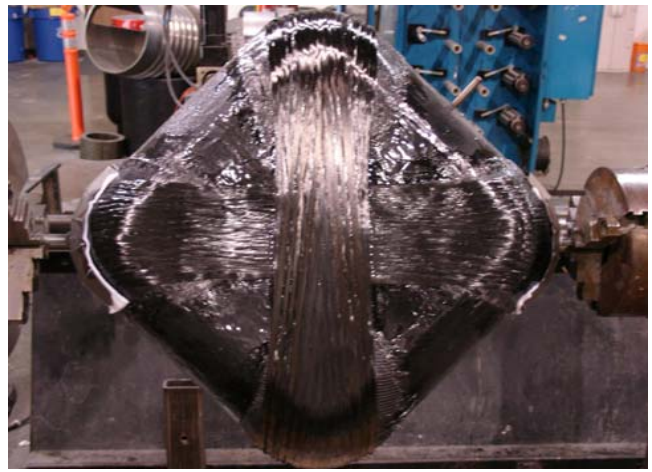
2. Install boss and apply layer of polyurea

3. Apply layer of composite mat

4. Wind

Our second pillow tank has improved reinforcement of corners for better performance

1. Winding of corners in first diagonal



2. Winding of second diagonal

3. Winding of elliptical sides

4. Finished vessel

We have instrumented and pressure tested two pillow tanks

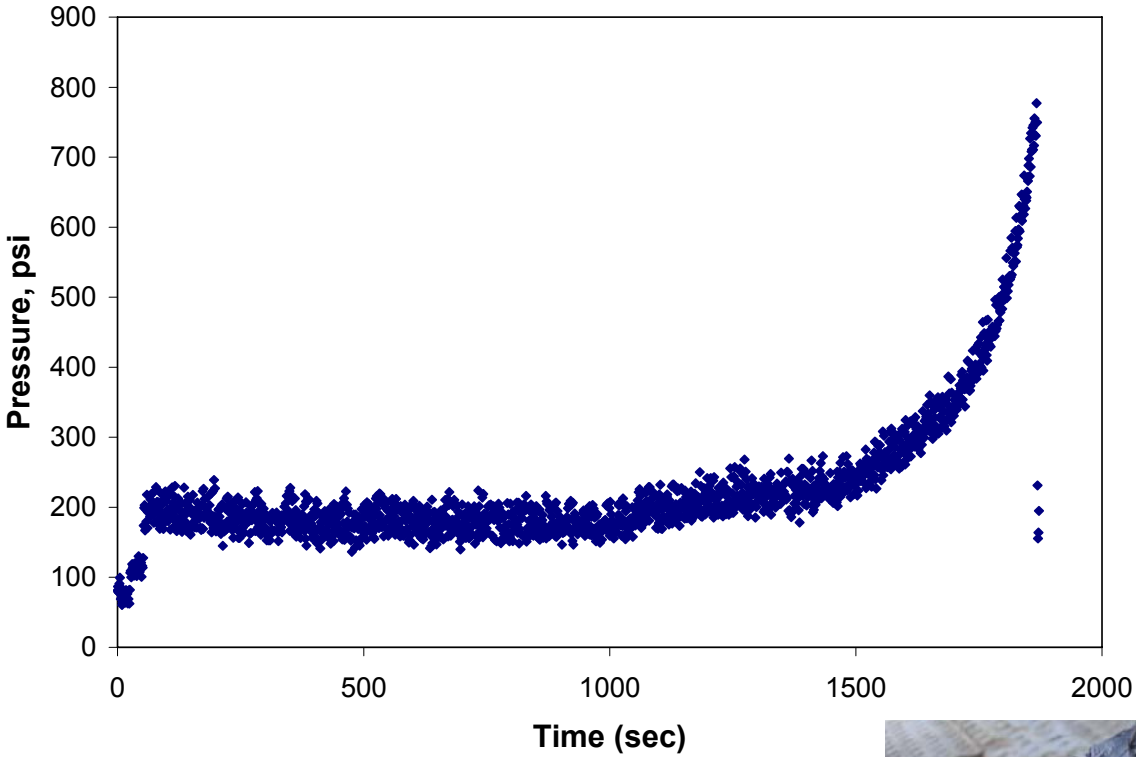
1. Instrument vessel with multiple strain gages

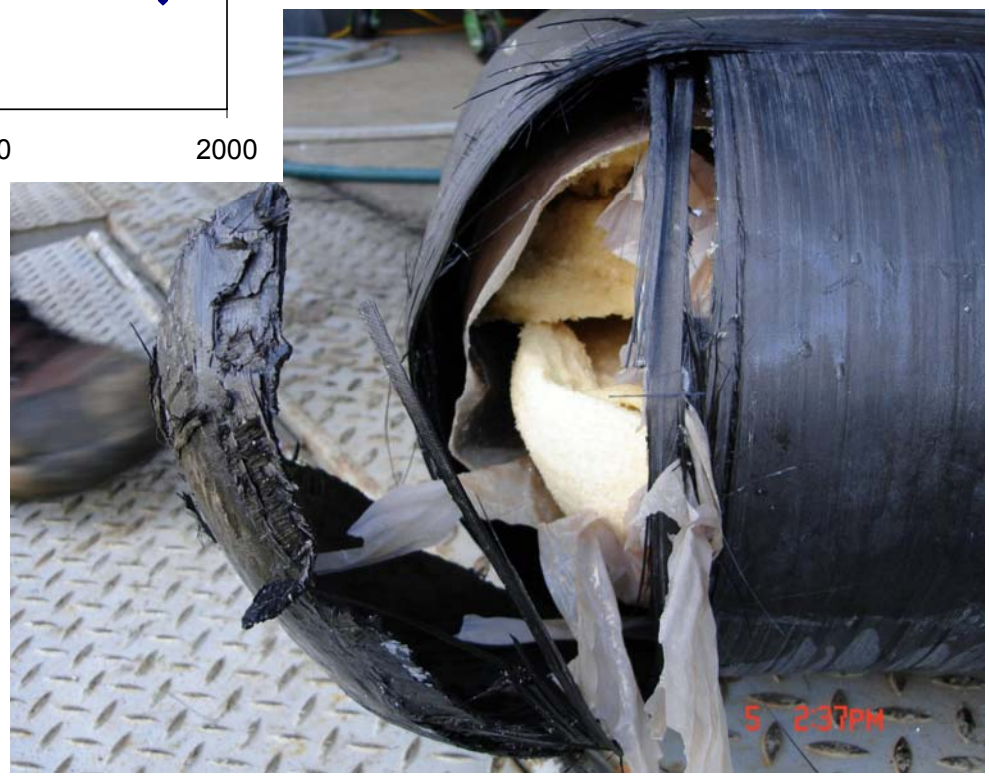
2. Install vessel inside sandwich support

3. Burst test

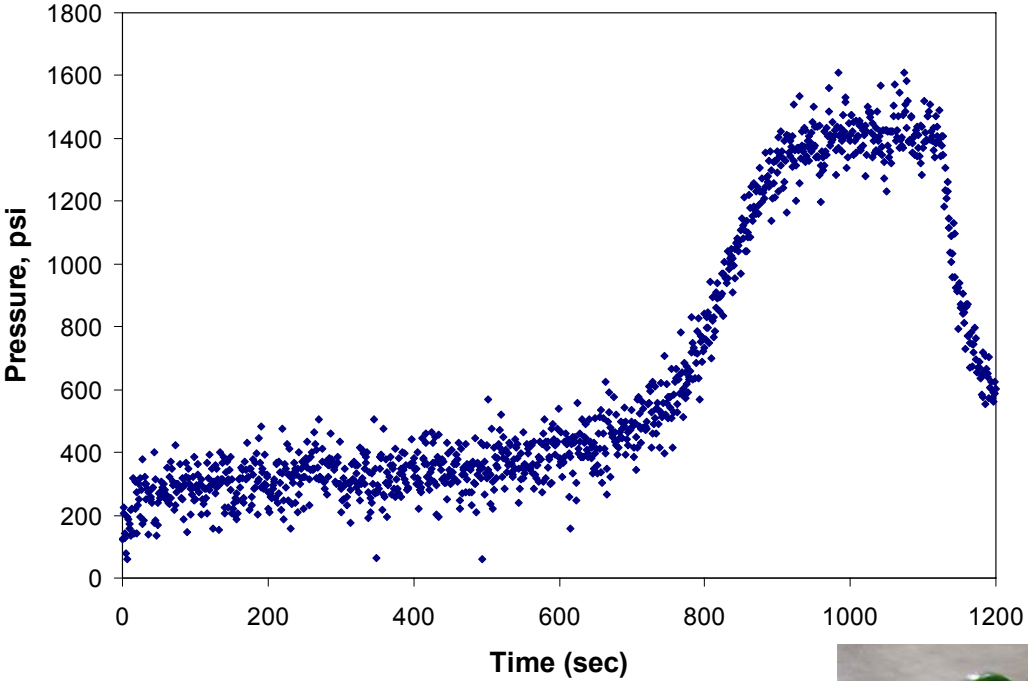
4. Saw vessel to analyze failure mode

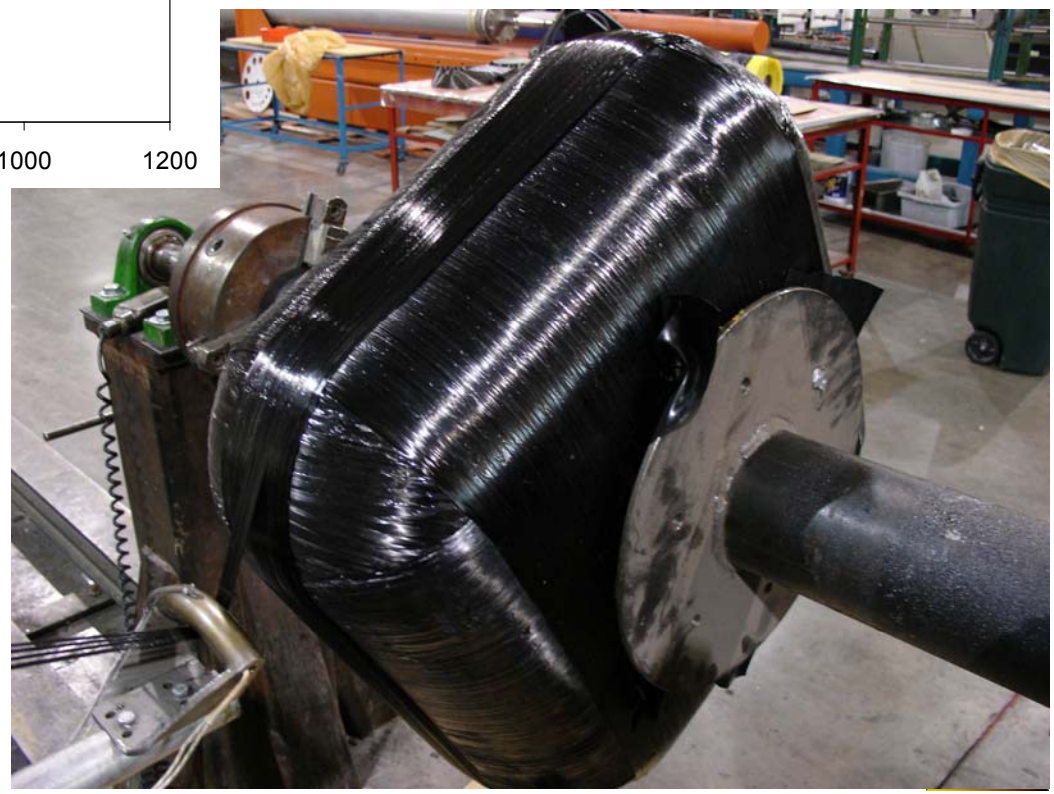
The first pillow tank failed at a corner at 800 psi





Second pillow tank leaked through the boss at 1600 psi. Reinforced corners were able to support pressure





Macrolattice Containers

- Pillow tanks design and re-purpose proven fabrication processes and materials to approach conformability
- Replicates are a mass-production alternative strategy => new processes
- Potential for full volumetric efficiency recovery in rectangular shapes

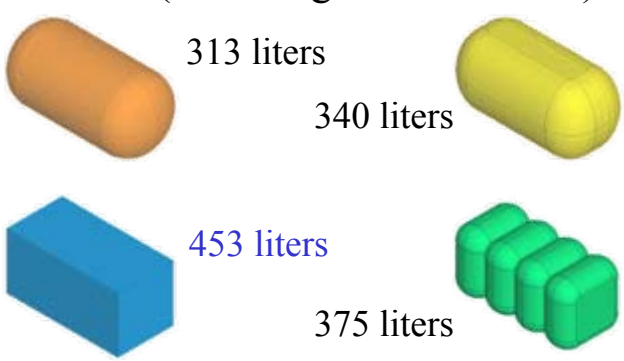
η_{vol} = rectangular volumetric efficiency (H2-volume/rect-envelope vol.)

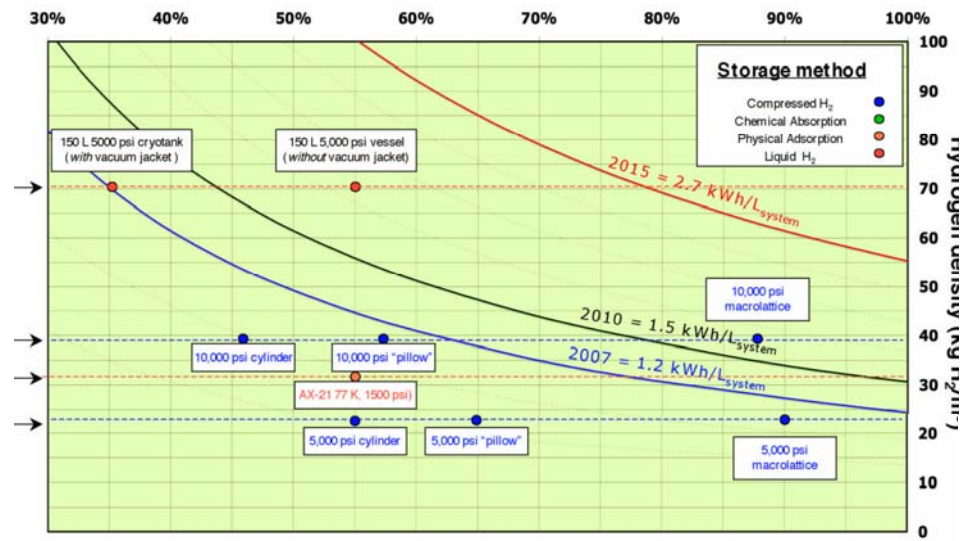
~60% for conventional tanks (including 12% structure volume, plotted below on axis --->)

vs. ~75% for pillows

vs. > 85% macrolattices

(including 12% structure)





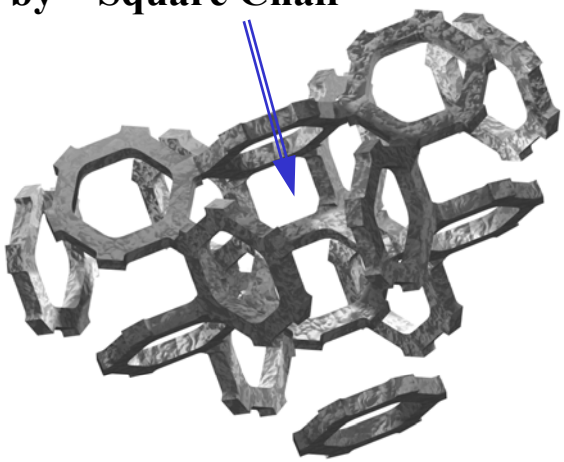
- A new way of using strong materials creates opportunities for new hydrogen storage features in 2 directions: thermal control and crash safety
- A related project which conducted macrolattice R+D for an improved Hydrogen Delivery Infrastructure started in Aug05 and halted in Jan06

Core structural components of an optimized Infrastructure container are shaped by one particular choice of lattice geometry

Vertex Hexagon

Many possible shapes of replicated elements can realize these Space Groups

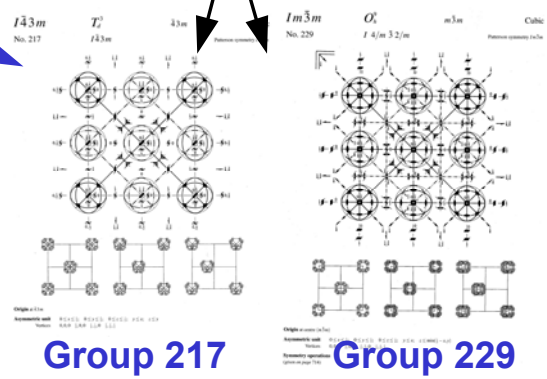
Currently competition for best mobile infrastructure replicate shape is being won by "Square Chair"

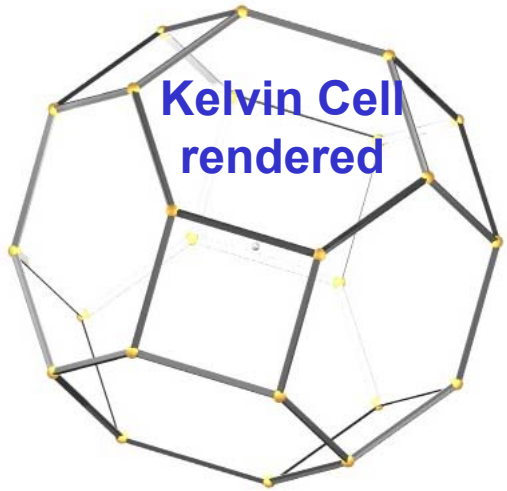


230 Space Groups

Crystal Classes > Cubic Subset

replicated "Kelvin Cells" pack space

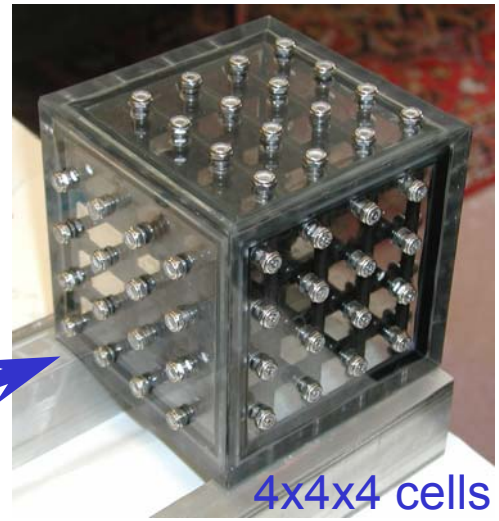




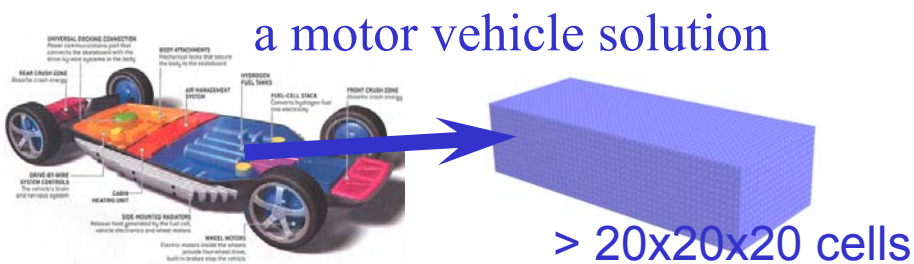
Note: lattice geometries have arbitrary cell size, force balance (sizes lattice struts) is also scale-invariant, but connector and bend shapes are very scale-dependent

When hexagon replicates were thought best, the possibility that some connection schemes could preclude their 'assemblability' called for rapid prototyping, which has since been used to assist enumeration of required skin tile variants

Through-Strut Replicants are Likely Best Lattice for Motor Vehicle Hydrogen Storage

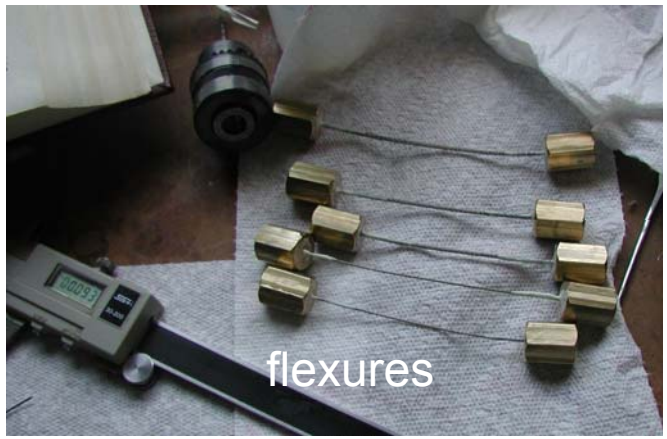


- Deliberately minimize vessel shear strength
- Rationale for 3 generations of development:
  - Limited development resources so triage risk
  - Gen-0 demonstrated Existence of a solution
  - Gen-1 is Engineering a mass-efficient skin
  - Gen-2 intends to prove an advantageous solution is fully Feasible
- Design and construction of macrolattices is a very under-constrained problem so prototypes are guaranteed to be suboptimal – they have been scaled to enable affordable for R+D, they are not examples of a motor vehicle solution



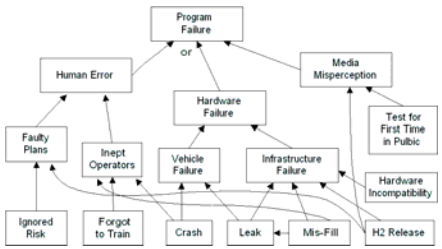
- Gen-2 material and process research (procured by LLNL) is already underway at Spencer Composites -> pultrude 80%-by-volume Basalt fiber composite

Technical and Economic Risks are Targets of LLNL Information Capture, with Unknown Unknowns emerging routinely in hot pursuit of experiments



Photos show initial tensile testing experiments intended to qualify strut bonds

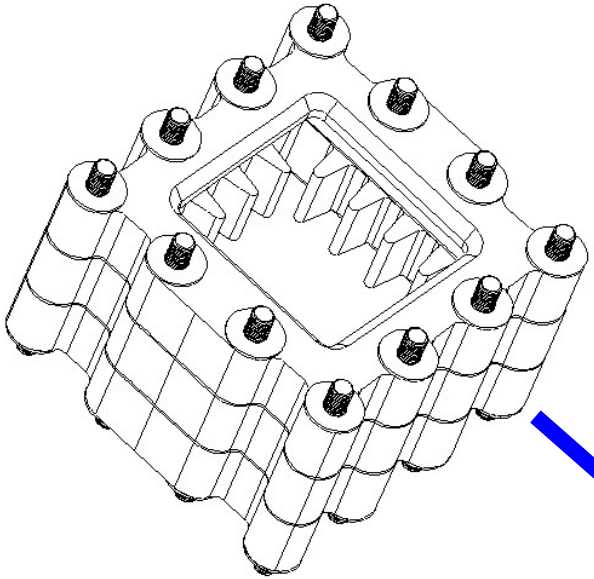
Loading stabilization struts (flexures) were first to require $\sigma_{tensile}$ failure statistics



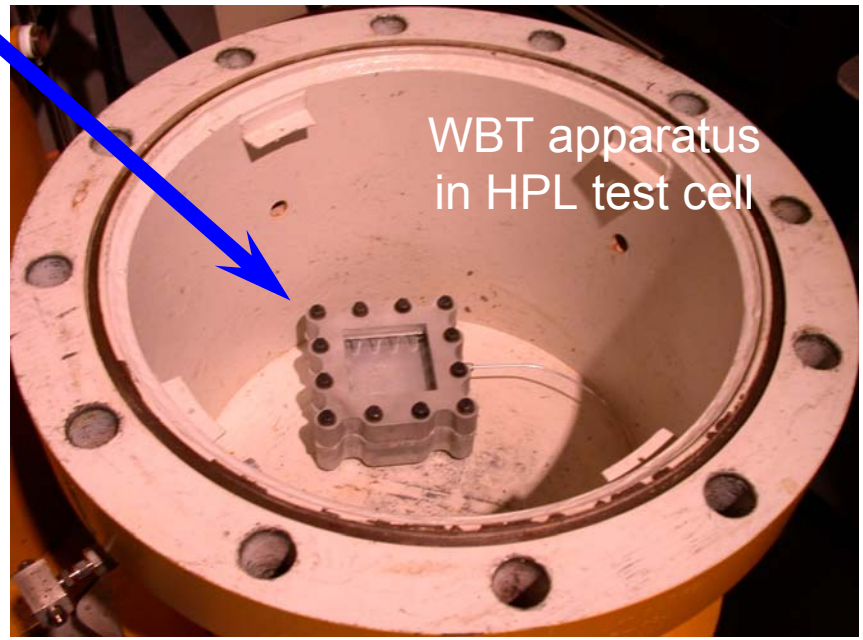
Fault Trees captured during debugging become FMEA

"Window Blow-out" Test provided an unexpected testbed for Gen-1 seals

Window Blow Out Test is ready to acquire failure data from Gen-0 (machined) Face (full-sized-part mimics)

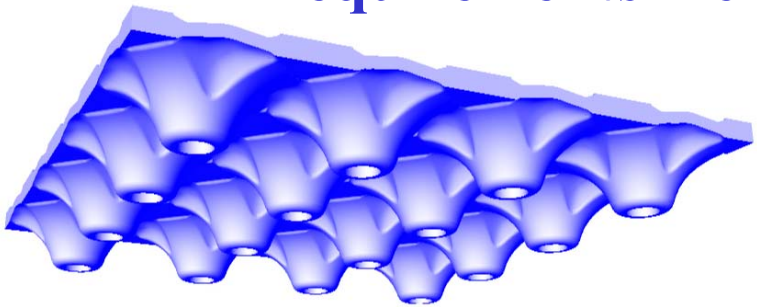


Design for this apparatus was found to be necessary because neither LLNL High Pressure Lab nor commercial facilities had suitable fixtures for ~6”-square windows



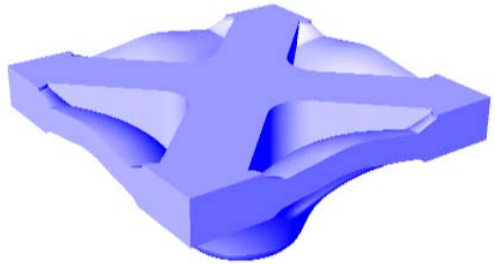
The apparatus shown here grew from a Tech Team suggestion into a learning instrument. Although the relevance of its expected results is problematic, it has acquired teaching and fab R+D roles

A Fully-Plausible Solution for Gen-1 that fulfils requirements including scalability to Gen-2



Rendering of Gen-1 skin tiles in 4x4 face array viewed from inside cube

Single skin tile (outside view)

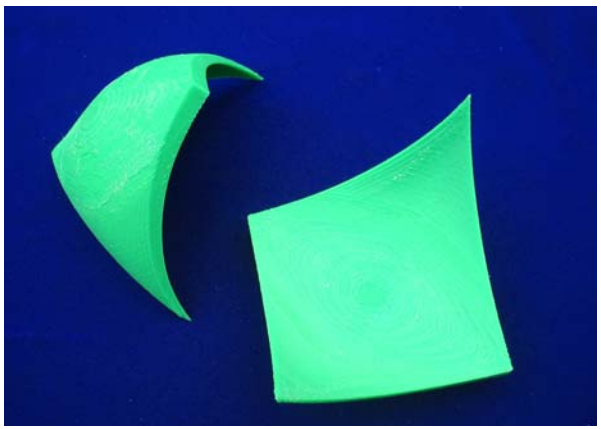


Tree epoxied onto struts

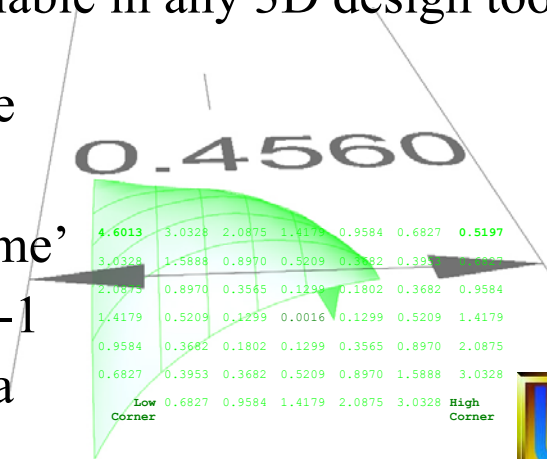
Renderings of Gen-1 skin tiles designed to anchor "Dog Bone" core struts

Math ⇒ Applied (3 D) Geometry ⇒ Data Structures ⇒ C++ Code ⇒ .3dm Files ⇒ Existing Tools ⇒ Visualization + Prototyping

Novel software enables shape creation steps not available in any 3D design tool

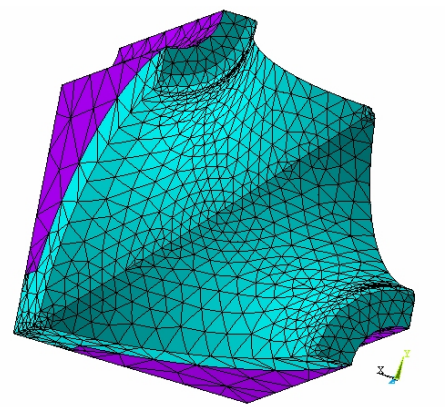


Isotensile surface shape approximates a constant-thickness 'dome' covering ~70% of Gen-1 Face part's surface area

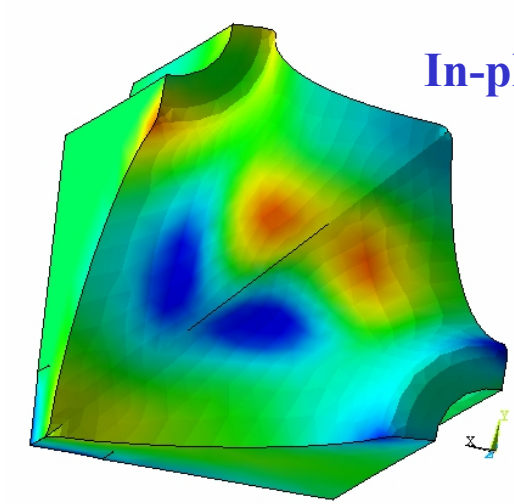


Earliest Finite Element Analysis of Skin Tile

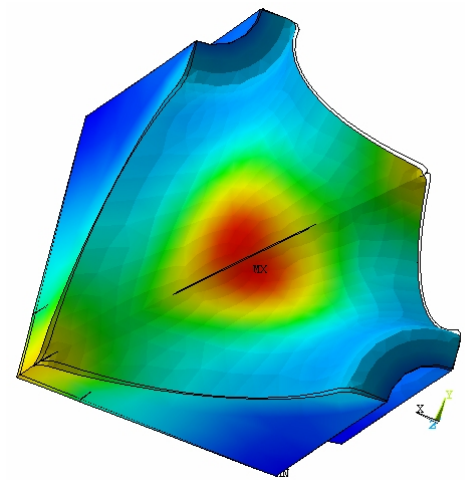
ANSYS finite elements



In-plane X deflection

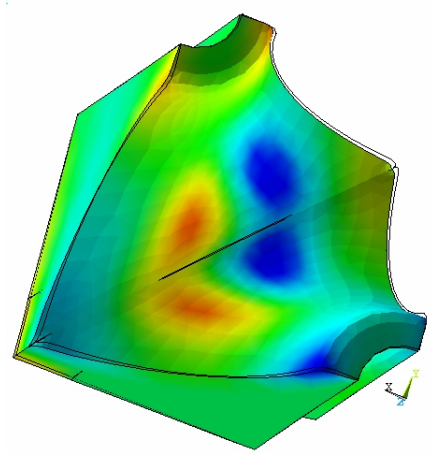


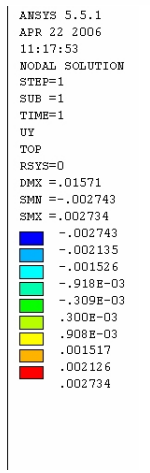
Outward Z deflection



- This replicant geometric shape is mirrored and copied in a 4x4 array to form the face of a physical (cast PET plastic) component.
- That component face is actually cast as one connected solid with 5 other faces, 12 edges of 3 flavors, and 2 kinds of different corners.
- This FEA solution presumes periodic boundary conditions on the in-plane edges of the surface tile, and a pressure differential across the skin balanced by tension conducted inward by the strut.

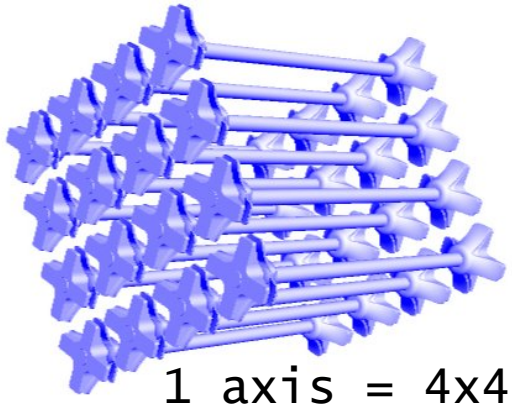
In-plane Y deflection



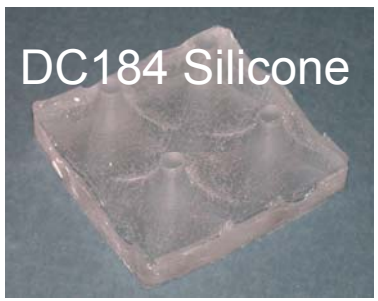


Tree elements

Converging Process Developments for Gen-1



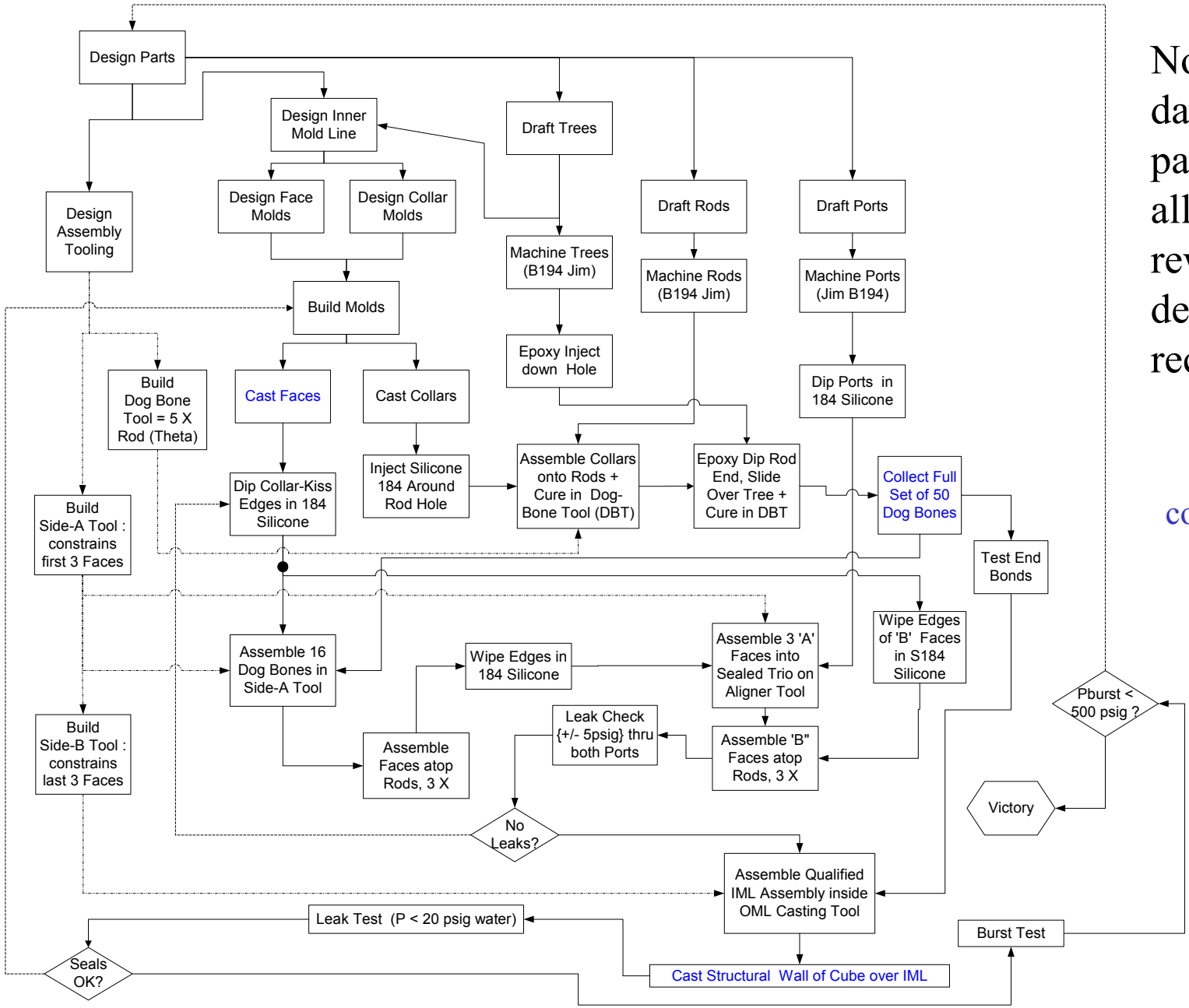
Photos and renderings of Dog Bones with Trees and Crosses on ends



Rapid prototyped ABS
=> DC184 Silicone copy
=> plaster copy, modify
to smooth => PET copy

Photos of molding processes – building a structural skin from cast plastic

Gen-1 Fabrication Sequence in Flow Chart Form



Note: dashed pathways allow partial rework and design error recoveries

color code: blue process steps are illustrated in active development on the previous slide

Future Work

- Pillow Tank
  - Iterate build and burst test design cycle to achieve ~80% of ideal
  - Repeat fabrication process without changes 3X and gang-test
  - As-built FEA (Finite Element Analysis) by both Spencer and LNLL
  - Design and build contoured liners (likely with tooling) -> flat faces
  - Design, build, and test composite end plates to complete 3rd axis
  - Test pillow tanks onboard LLNL Prius (Hydrogen Demo Vehicle)
- Macrolattice
  - Gen-0 compliance testing with external loading of entire faces
  - Gen-0 thermal diffusion testing with resistor point heat source
  - Gen-1 debug entire fabrication process, build #1 clear, #2 x-lucent
  - Gen-1 pressure test compliance and proof pressure to confirm FEA
  - Gen-1 permit to operate demonstration at 20% of proof pressure (air)
  - Gen-1 permeation testing with low pressure hydrogen fill
  - Gen-2 scale down tile design 3X to match basalt composite strut strength
  - Gen-2 structural bond qualification, proving the last and riskiest load path
  - Gen-2 cast aluminum skin made from unpolished jewlers wax ~ Gen-1
  - Gen-2 composite (biaxial) tape along edge seams completes load path
  - Pultrusion fabrication studies to flare strut ends, lose matrix, model costs

Project summary

- **Built two prototype conformable vessel segment (pillow) tanks.**

- **Pillow tanks were pressure tested. Considerably higher burst pressure was obtained with an improved fiber layout pattern**

- **Window blowup test ready to take data. Apparatus has already served a process research role. Its silicone gasket designs solved Gen-1 seal issues. Re-use of this apparatus is currently anticipated as a mid-Gen-1 testbed for anchoring single dog-bon-ends into cast PET face-tiles.**

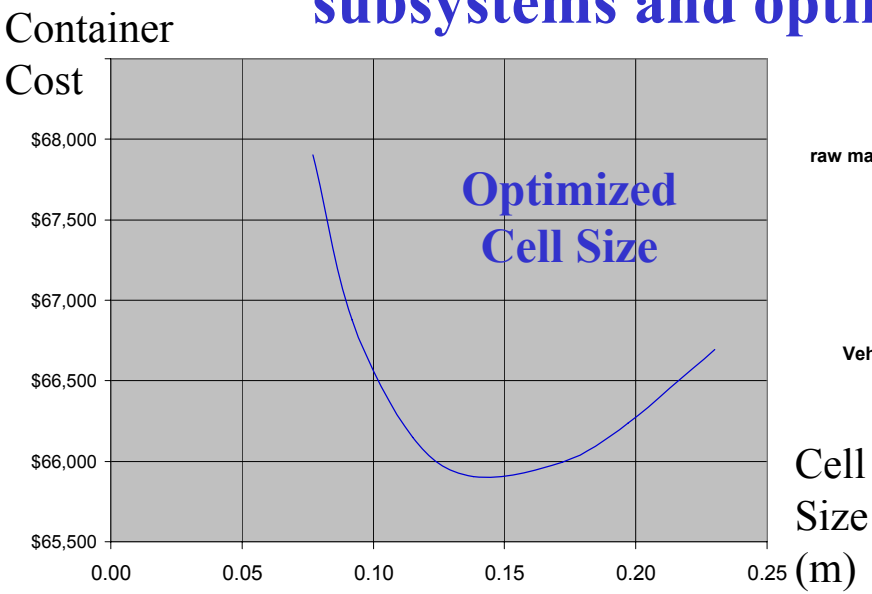
- **Macrolattice Gen-1 has completed ~ 75% of a converging design process, including compatible process specifications. Technical risks have been minimized in a generation expected to survive over 1500 psi with a transparent skin. Geometry and stress ratios in this Gen-1 design yield a smooth scaling plan for Gen-2.**

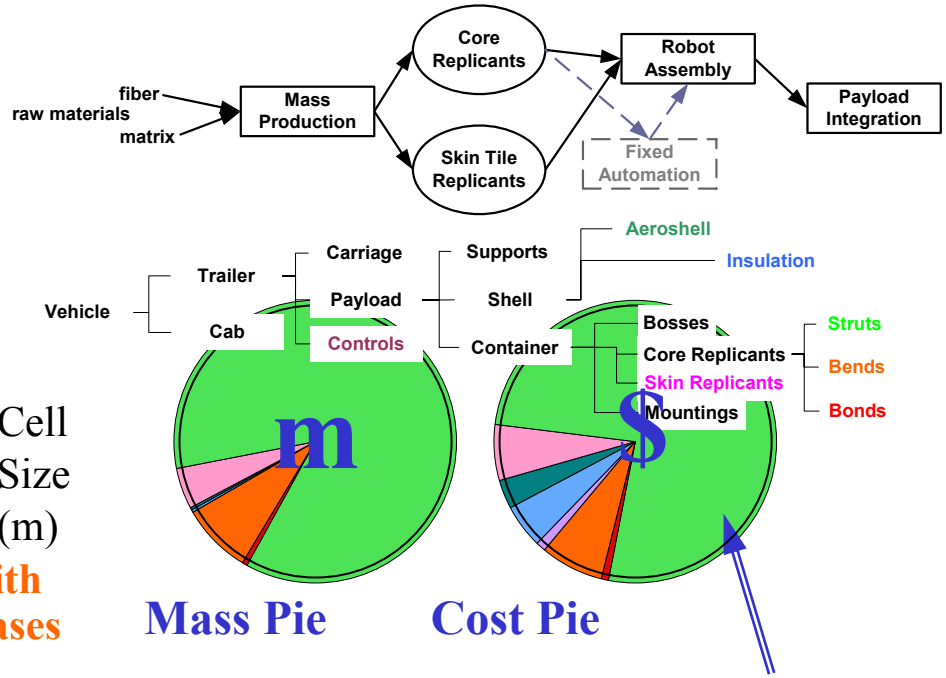
Supplemental slides

Responses to reviewers' comments:

- *Conformable containers need to be demonstrated.* **We have built and pressure tested two pillow tank and a macrolattice tank.**
- *Testing results are not presented yet.* **We are now presenting test results for the two concepts being pursued**
- *It is nice to see the model of the macrolattice vessel, but what are the plans for testing?* **We have pressure tested the macrolattice vessel. Future testing will help establish the benefit of the internal structure.**
- *PI might benefit to collaborate with tank builders for future work.* **We are working closely with Structural Composites Industries and with Quantum on developing our next generation of cryo-compressed pressure vessels. We are working closely with Spencer Composites on pillow tank processes and designs, as well as trial production of Gen-2 macrolattice core strut materials**

Cost accounting for LLNL's proposed macrolattice container truck begins with a hierarchical breakdown of subsystems and optimizes lattice cell size





Connector mass+cost fractions decrease with cell size, but skin mass+cost fraction increases

Cost calibration based on DOE 2000 Goals specified by LLNL and achieved

Quantities : optimized container requires 14470 core cells and 7569 skin tiles

Manufacturing economies of scale pay back the cost of tooling and capital for mass production with relatively few total trucks produced due to the high replicant count

Learning curves can be applied to model cost of large quantities, but have not been accounted for yet, since learning rate depends on mfg. process choices

Publications and presentations

Patents

- **Lightweight Cryogenic-Compatible Pressure Vessels for Vehicular Fuel Storage,** Salvador M. Aceves, Gene Berry, Andrew H. Weisberg, US Patent 6,708,502 B1, March 23, 2004. World Patent WO 2004/029503 A2, April 8 2004.
- **Storage of H2 by Absorption and/or Mixture within a Fluid,** Gene Berry and Salvador Aceves, World Patent WO 2005/015076 A1, February 24, 2005.

Publications in Books and Technical Journals

- **Hydrogen Storage and Transportation,** Gene Berry, Joel Martinez-Frias, Francisco Espinoza-Loza, Salvador Aceves, Invited chapter, Encyclopedia of Energy, Volume 3, pp. 267-281, Elsevier Academic Press, New York, 2004.
- **Hydrogen Production,** Gene Berry, Invited chapter, Encyclopedia of Energy, Volume 3, pp. 282-294, Elsevier Academic Press, New York, 2004.
- **The Case for Hydrogen in a Carbon Constrained World,** Gene D. Berry and Salvador M. Aceves, Invited discussion paper, ASME Journal of Energy Resources Technology, 2005.
- **Vehicular Storage of Hydrogen in Insulated Pressure Vessels,** Salvador M. Aceves, Gene D. Berry, Joel Martinez-Frias, Francisco Espinosa-Loza, Accepted for publication, International Journal of Hydrogen Energy, 2006.
- **Liner Materials for Composite Tanks**, Andrew Weisberg, Invited paper for "Materials for the Hydrogen Economy," CRC Press, 2005.

Publication in Refereed Proceedings

- **Development and Demonstration of Insulated Pressure Vessels for Vehicular Hydrogen Storage,** Salvador M. Aceves, Gene D. Berry, Proceedings of the 15th World Hydrogen Energy Conference, Yokohama, Japan, June 27-July 2, 2004.
- **Advanced Concepts for Vehicular Containment of Compressed and Cryogenic Hydrogen,** Salvador M. Aceves, Gene D. Berry, Andrew Weisberg, Francisco Espinosa-Loza, Scott Perfect, Proceedings of the 16th World Hydrogen Energy Conference, Lyon, France, 2006

Technical Report

- **Hydrogen Absorption in Fluids: An Unexplored Solution for Onboard Hydrogen Storage,** Gene D. Berry, Lawrence Livermore National Laboratory Report UCRL-TR-209650, Livermore, CA, February 2005.
- **Proposed Standards for Hydrogen and Liquefied Natural Gas Insulated Pressure Vessels,** Report to the South Coast Air Quality Management District August 2004

Presentations

- **Advanced Hydrogen Containers,** Andrew Weisberg, Invited presentation, American Physical Society, March 2005.
- **Cryogenic Hydrogen Storage**, Salvador Aceves, Invited Presentation, Materials for the Hydrogen Economy, September 2005

Critical Assumptions and Issues

- ***Need to demonstrate high performance pillow tanks***
- ***Need the ability to consistently manufacture pillow tanks***
  - ***requires 3 or more units bursting at closely-spaced pressures to prove success***
- ***Must complete the pressure load path along the pillow's Z axis***
  - ***this is 1/3rd of the structure problem, which end-plates solve for 1..n pillows***
  - ***only composite end-plates and tie-rod-equivalent-bands will enable pillow tanks to be competitive with conventional wound tanks in fiber mass costs. {Metal Z-axis load path hardware ruins the pillow container's %-by-mass-H_2.}***
- ***Macrolattices appear costly because:***
  - ***their mass-production costs are now merely extrapolations based on related processes. {Need cost bases acquired from closely analogous processes.}***
  - ***witnesses to early prototyping see a lot of effort and skill lavished on 'models', which are far smaller than motor vehicles require. {Prototypes are mistaken for for examples of advocated hydrogen storage solutions. LLNL prototypes' designs minimize costly staff effort, building just enough replicates to encounter the full list of challenges that optimal macrolattices will face.}***