# III.A.3 Next-Generation Physical Hydrogen Storage

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## Objectives

- Improve useable density of physical hydrogen storage through conformability
- Adapt new structural designs and material technologies to reduce cost by ~60%
- Develop fundamental understanding of structural storage in various geometries
- Demonstrate safety innovations at component level with rupture experiments
- Contribute expertise to regulatory processes reflecting the results of research

## Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- H. Sufficient Fuel Storage for Acceptable Vehicle Range
- A. Cost
- B. Weight and Volume
- J. Lack of Tank Performance Data
- F. Codes and Standards

## Approach

- New theoretical ability to perform trade-offs between mass, volume, and cost
- University libraries and trade shows yield new materials and design innovations
- Development of mass-producible components that enable assembled tanks
- Acquisition of data on the statistical behavior of molded composite components
- Collection of suitable data to enable statistical engineering of burst probabilities

## Accomplishments

- Dimensionless formalism that combines mass, volume, and cost expressed in C++
- More statistical qualification performed on pressure vessel structural components
- Exploration of Weibull and Gaussian statistical distributions used by ASTM tests
- Exhausted core geometries capable of carrying structure loads through replicates
- Selected best structural geometries for mass-producible composite replicate cores

## Future Directions

- Prototype the best core and skin structures for safest motor vehicle replicant tanks

- Match dimensionless theory to actual burst performance of replicated structures
- Extend statistical methods to burst testing of small pressure vessel prototypes
- Acquire data on the unexplored tensor debonding waves in "turn to dust" bursts

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- Learn to engineer tailored elasticity tensor and rupture loci for better crash safety

## Introduction

Physical containment of hydrogen has been accomplished successfully by tanks for the past few decades. Compressed hydrogen gas at ambient temperature, contained in strong structures, allows motor vehicles to store hydrogen in Type IV pressure vessels (commonly called tanks) that are already available and getting better. Compressed hydrogen storage thus provides a near-term solution based on already-solved problems, with well-understood performance limitations. Current and next-generation hydrogen tanks are on track to deliver the next two objectives (2005 and 2010 targets) in the Hydrogen, Fuel Cells and Infrastructure Technologies Multi-Year Research, Development and Demonstration (R,D&D) Plan. The relative absence of further technical risks in these two generations of tanks provides near-term opportunities to reduce their costs significantly by taking calculated risks on new ways to build them.

The most advanced (Type IV) hydrogen tanks built with current technology have the potential for a cost reduction of roughly a factor of two (at any specific production volume), enabled by the reduction of costly materials and by statistical process control (SPC) techniques. Proving that potential formed the basis for planning advanced tank development experiments at Lawrence Livermore National Laboratory (LLNL) in FY 2002. On the way to those experiments, fundamental discoveries emerged which foretell several directions for expansion of the frontiers of physical containment. Tanks are *not* the only structures suitable for physical storage of compressed hydrogen – many of the newly discovered structural container geometries should be able do the same job better, providing greater range, utilization of volume through conformability, as well as lower cost. Departing from the prior art in advanced hydrogen tanks can make physical containment of hydrogen a strong contender for meeting the 2015 R,D&D Plan objectives.

## Approach

LLNL advanced tank development efforts followed a deliberate plan intended to reduce the cost of hydrogen storage tanks twofold. Most of those savings are expected to derive from a change in qualification methods applied after manufacture. Replacing arbitrary safety factors with real failure statistics (using SPC) can save roughly 30% of costly structural mass. Such SPC is applied routinely in mass-produced high-technology products like tires and semiconductors. The underlying data that enables SPC must come from statistical testing of significant quantities of nominally identical test articles. LLNL has located a new industrial partner capable of cost-effective burst testing of entire small pressure vessels (replacing the collaboration anticipated with Professor Ronald Humble, a pioneer of rocket testing who died unexpectedly in 2003). Even more informative, three accredited ASTM testing labs capable of extracting rupture data from small structural components within an accuracy of ~2% were interviewed and provided decades of unpublished expertise in the statistics of composite failure.

The composite structural components which were tested to failure in early 2004 employed a new matrix material (shown in Figure 1). LLNL expects to obtain data (paid for by a private company under contract to the Defense Advanced Research Projects Agency) from bursting small prototype tanks in the next fiscal year. Some of that test data will capture the performance of the new matrix material, although sufficient statistics will only be obtained for epoxy matrix variants. These tests will provide experience and some publishable statistical data on materials and process innovations in preparation for realistic planning to test an attractive alternative to conventional tanks.

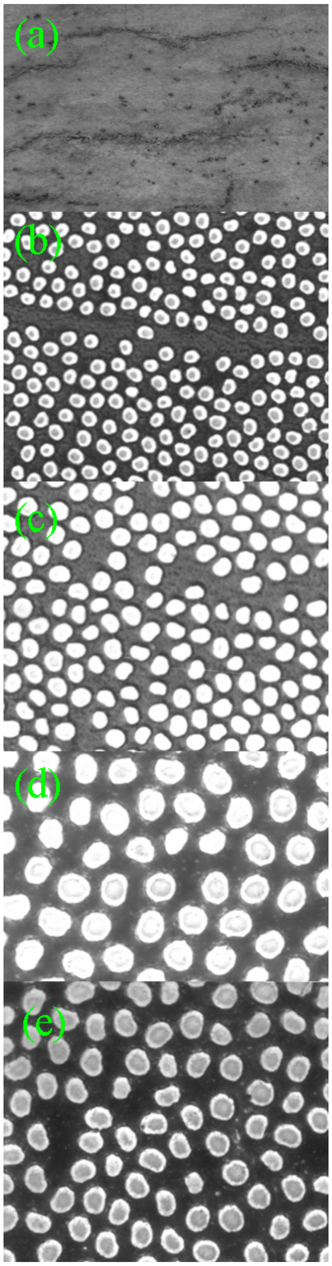
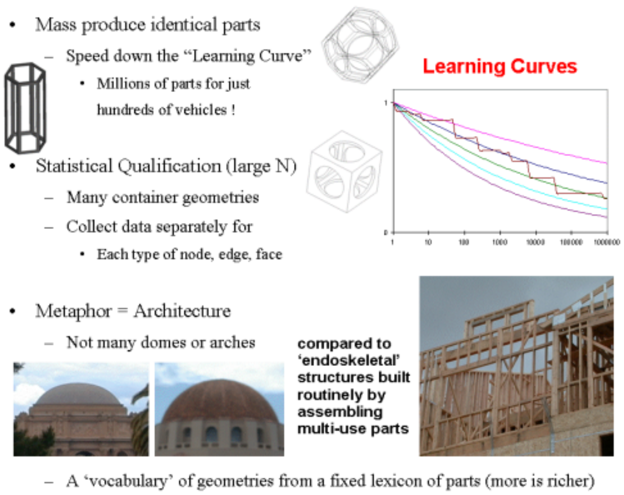


**Figure 1.** Process experimentation with a new composite matrix material that can 'grow' across interfaces could eliminate the intrinsically weaker bonds obtainable with adhesives or fasteners.

Conventional tanks are wound with composite layers built from uninterrupted fiber. A new kind of container that hardly resembles conventional tanks can be made by assembling replicated structural components. This approach was re-discovered by searching through the literature of composites innovations of the 1980's. Containing compressed fluids by carrying almost all structural loads through the inside of the container, this 'macrolattice' approach (shown in Figure 2) is inherently mass-producible. Containers built with this approach are labeled 'replicant' tanks due to their construction from replicated structural components, and their assembly can result in extreme conformability with volumetric efficiencies above 90%. The limitations of physical hydrogen storage are thus no longer imposed by a highly developed prior art in advanced (wound composite) tanks and must be replaced by models based on raw materials structural properties and feasible mass-producible component geometries. This new approach to containing compressed hydrogen is undergoing design, analyses, and prototyping at LLNL.



- Mass produce identical parts
  - Speed down the "Learning Curve"
    - Millions of parts for just hundreds of vehicles !
- Statistical Qualification (large N)
  - Many container geometries
  - Collect data separately for
    - Each type of node, edge, face
- Metaphor = Architecture
  - Not many domes or arches
  - A 'vocabulary' of geometries from a fixed lexicon of parts (more is richer)

**compared to 'endoskeletal' structures built routinely by assembling multi-use parts**

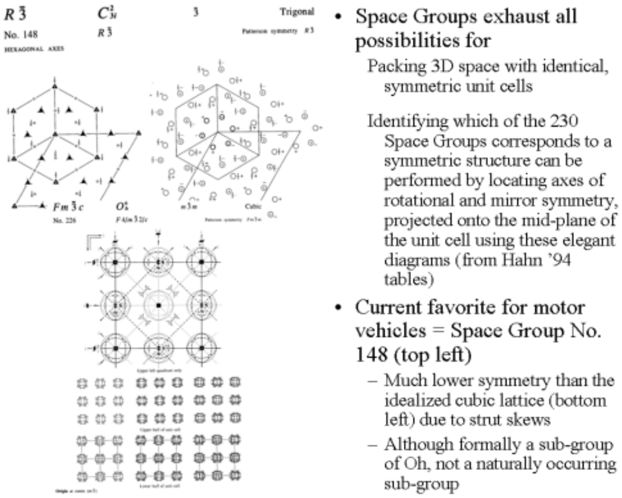
**Figure 2.** Macrolattices are built from a large number of replicated structural components known as 'replicants', are highly symmetric due to identical parts, and have Architecture analogs.

## Results

Attractive geometries and materials options for 'replicant' hydrogen containers were explored this year. A materials innovation that substitutes a proprietary plastic for the conventional epoxy in graphite-epoxy composites was the target of preliminary process research. Cross-sections of some of the first matrix infusion attempts are shown in Figure 1. Packing replicated structural components together (as illustrated in Figure 2) was found to offer even more potential statistical advantages due to the possibility of single-point-failure tolerance. Modeling of 'replicant' tank performance was conducted with newly built computational models based on the dimensionless formalism developed in FY 2003, predicting storage mass, volume, and cost closely comparable (within ~15%) to conventional tanks.

Nearly arbitrary conformability may be possible with 'replicant' tanks but appears to be disadvantageous. Collections of convex, almost rectangular (as viewed from all 3 axes) shapes could be plumbed together to achieve arbitrary conformability (as well as disjoint containment volume shapes) and will probably prove superior to roughly doubling the number of different 'replicants' to build concave shapes. All possible macrolattices were explored, assuming only that they would be assembled from identical components, by exhausting the 230 Space Groups of Crystallography that partially describe the geometry of the replicated macrolattice's core.

Because identical parts pack space with local translational symmetry, the possible geometries for a macrolattice are limited to the 230 Space Groups. All of these symmetry groups were surveyed for manufacturability, and many shortcomings emerged relying on Group Theory as a sufficient description. As a necessary level of description, the 230 Space Groups provide a taxonomy for possible 'replicants' and allowed a very illuminating consideration of the elasticity tensor. At least four variants of Group Theory were explored, with the crystallographers providing the most relevant descriptions of possible symmetries while the physicists can use those symmetries to reduce Cartesian tensors to deduce mechanical properties. Consideration of the elasticity tensor of possible macrolattices enabled a major safety innovation that deliberately reduces the off-axis (shear) terms in the unit cell (or in the quasi-continuum average) elasticity tensor.



- Space Groups exhaust all possibilities for
  - Packing 3D space with identical, symmetric unit cells
  - Identifying which of the 230 Space Groups corresponds to a symmetric structure can be performed by locating axes of rotational and mirror symmetry, projected onto the mid-plane of the unit cell using these elegant diagrams (from Hahn '94 tables)
- Current favorite for motor vehicles = Space Group No. 148 (top left)
  - Much lower symmetry than the idealized cubic lattice (bottom left) due to strut skews
  - Although formally a sub-group of Oh, not a naturally occurring sub-group

**Figure 3.** Crystallography provides a taxonomy and all permitted Group Theoretic operations that partially describe all possible space-packing symmetric macrolattice core geometries.

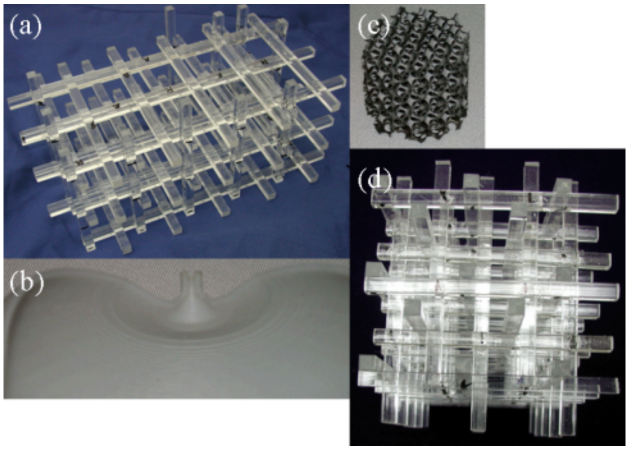


**Figure 4.** Photographs show small prototypes of macrolattice components: (a) shows the first assembled macrolattice, (b) shows a rapid prototyped liner detail with cutaway into the tank boss inlet, (c) shows a sintered metal macrolattice built for an unknown purpose at LLNL before 1980, and (d) shows assembly alignment defects in the end view of (a) that demanded improved tooling.

Replicant tanks that are deliberately very weak in shear endorsed the selection of the best Space Groups as those with rectangular geometries when viewed from all 3 axes. Figure 3 shows this deduced 'best' Space Group for motor vehicle crashworthiness, while Figures 4 and 5 show early attempts to visualize and learn to assemble this geometry. Figure 5 also shows a biological macrolattice, which lacks the symmetry of identical components in its core but shows that a different structure is necessary in the skin that surrounds the core (which in this case has more fluid transport functions than structural functions). (Another form of engineered metal

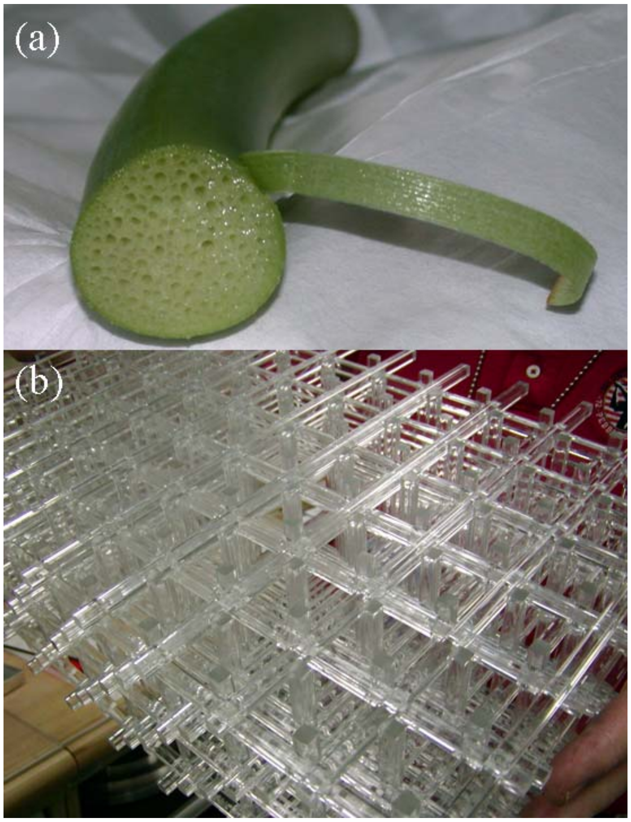
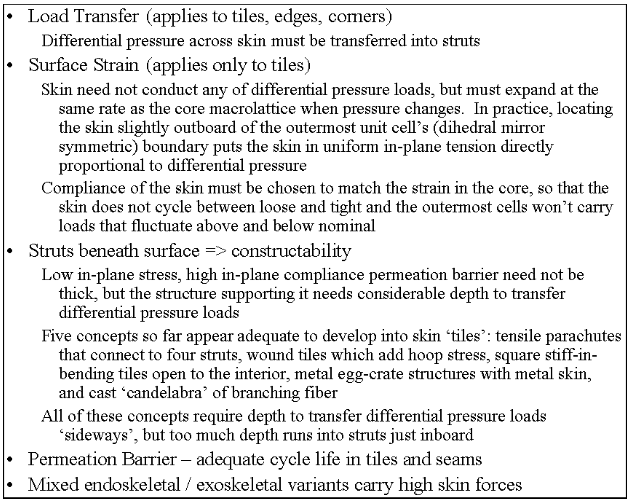


**Figure 5.** Second-generation macrolattice core geometry prototype (of the best Space Group for motor vehicle applications) demonstrated sufficient assembly accuracy to extend the process over arbitrary scale, duplicates the occupied volume fraction that safely contains 10,000 psi (MEOP, Safety Factor 2.25) using current T-700/epoxy composite to build its struts, and is shown beneath an example of a naturally occurring macrolattice.



- Load Transfer (applies to tiles, edges, corners)
    - Differential pressure across skin must be transferred into struts
- Surface Strain (applies only to tiles)
    - Skin need not conduct any of differential pressure loads, but must expand at the same rate as the core macrolattice when pressure changes. In practice, locating the skin slightly outboard of the outermost unit cell's (dihedral mirror symmetric) boundary puts the skin in uniform in-plane tension directly proportional to differential pressure
    - Compliance of the skin must be chosen to match the strain in the core, so that the skin does not cycle between loose and tight and the outermost cells won't carry loads that fluctuate above and below nominal
- Struts beneath surface => constructability
    - Low in-plane stress, high in-plane compliance permeation barrier need not be thick, but the structure supporting it needs considerable depth to transfer differential pressure loads
    - Five concepts so far appear adequate to develop into skin 'tiles': tensile parachutes that connect to four struts, wound tiles which add hoop stress, square stiff-in-bending tiles open to the interior, metal egg-crate structures with metal skin, and cast 'candelabra' of branching fiber
    - All of these concepts require depth to transfer differential pressure loads 'sideways', but too much depth runs into struts just inboard
- Permeation Barrier – adequate cycle life in tiles and seams
- Mixed endoskeletal / exoskeletal variants carry high skin forces

**Figure 6.** Skin technology matches core geometry to complete the container of a 'replicant' tank, but must satisfy diverse engineering requirements and poses numerous unexplored design issues.

macrolattice has been found by literature-searching whose core functions mostly to transfer heat.) The skin poses the majority of technical risk to the feasibility of 'replicant' tanks but accounts for very little (roughly 10%) of their mass and even less of their material costs. Some of the complex engineering requirements (used as a term of art in aerospace system integration) that must be solved to develop an adequate skin for the 'replicants' are described in Figure 6.

## Conclusions

- The frontier of performance for physical hydrogen storage has been re-opened.
- Statistical Process Research has been initially demonstrated for hydrogen storage.
- Statistical methods can limit probabilities of failure to required (~0.1 ppm) levels.
- Mass production and innovative 'replicant' structures can improve crash safety.

## FY 2004 Publications/Presentations

1. Next Generation Physical Hydrogen Storage, DOE Annual Hydrogen, Fuel Cells and Infrastructure Technologies Program Review, Philadelphia, PA, May 25, 2004.