

Next Generation Physical Hydrogen Storage



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- **Find and investigate the best structural alternatives for storing hydrogen.**
- **Evaluate the most attractive performance and manufacturing processes capable of improving upon conventional tanks in hydrogen fueled motor vehicle applications.**
- **Seek fundamental safety innovations enabled by compressed hydrogen storage.**

Budget for FY04



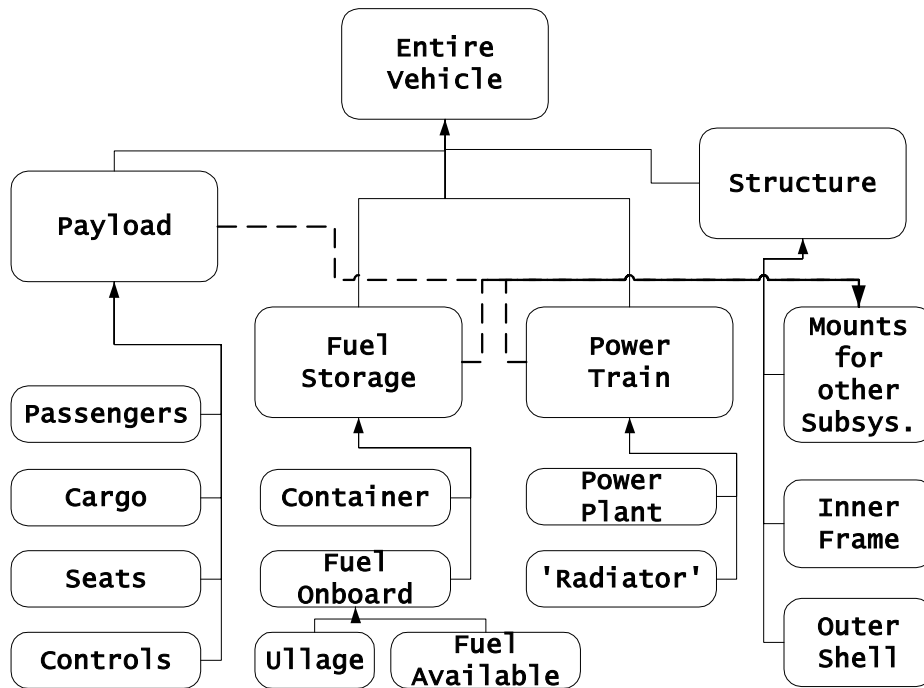
- **\$225K portion of \$500K B&R**
- **Taxes decrease discretionary spending to < \$200K**
- **LLNL is an expensive place to work, so seek “industrial partners”**
- **Rent and small supplies/expenses and travel leave ~\$160K**
- **Roughly \$20K spent on experiments = minimal but significant**
 - **Large surplus of good ideas, but not of the ability to develop them**
 - **Limited hardware validation enables valid planning of future efforts**
 - **Finding commercial sources for components, processes and qualification testing is on the critical path to ‘Proof of Concept’ experiments that would complete the proof of replicants feasibility.**

Approach



- **Theory** (specifically requested by Tech Team)
 - **Re-purposed concepts from related fields:**
Architecture, Aerospace, Materials Science, Applied Mathematics, Industrial Engineering
 - **Fresh formulation, physically correct**
Dimensionless analyses mix mass and volume, optimize both
- **Experiments**
 - **Focussed (selecting a route to “Proof of Concept”)**
Key parameters: σ_{ult}/ρ , $\sigma_{ult}/\sigma_{shear}$, E (modulii), ν (Poisson’s ratio)
New Processes: bonding for connectors, insert molding
 - **Generic (useful independent of structural design)**
ASTM Testing Labs – the only source for publishable data
Rapid turnaround, vendor-performed hydroburst testing
Techniques for making testable coupons and subscale analogs
- **Outreach** Journal articles: AIAAJ, Applied Math, Design News

Mass and Volume Partitioned at Vehicle Level



- **Each major subsystem is partitioned by function (Requirements tree)**
 - **Payload delivers value to the vehicle user**
 - Must be constrained constant for 'fair' comparisons of performance
 - **Fuel satisfies Mass Conservation, supplies energy for propulsion**
 - **Power Train satisfies Energy Conservation from sources -> losses -> sinks**
 - **Structure satisfies Momentum Conservation, withstands all forces:**
 - Gravity, acceleration, and drag forces are withstood by structure
 - Structure is further partitioned to securely mount other subsystems

Statistical Research



- **Actual Failure Data collected from assembly failure forces** **The first installment of structural testing wherein a nearly identical collection of samples is broken**

Diameter	N	material	form	Epoxy	Shear Strength
0.840"	1	composite	tube	Vendor 1	200 psi
0.450"	4	composite	rings	Vendor 1	460-870 psi
0.335"	3	Mg	discs	Vendor 2	880-1025 psi
0.335"	5	Mg	discs	Vendor 1	380-670 psi

- **Sample Size ‘identifies’ Weibull Distribution** **Weibull distribution** **The other “extreme value” distribution (vs. Gaussian) correct in the limit of the minimum of a large series of positive random values**
- $$P(\sigma) = 1 - e^{-(\sigma/\sigma_c)^m}$$
- **Risk of ‘suppressed’ failure modes with higher variance is neglected in current safety standards – not good enough for thousands in service!**
- $p(\sigma) = \partial P / \partial \sigma$
- Overlap of 1/m=.05 and 1/m=.08 with “safety factor” of 1.3**
- **Recommend insurance requirements, European-required batch testing**

Statistical Experiments



- Intended to confirm utility of Statistical Process Control methods in use for many high-tech products [i.e. semiconductors, tires, light bulbs, biotech...]



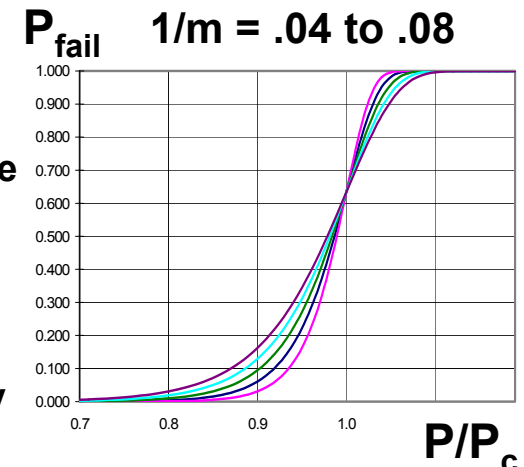
Sensors
measure
Pburst



Assembled
Test Tank

- Method relies on samples from batch built under identical process parameters
- Parameters to Vary depend on Production method:
 - For wound tanks the most crucial parameters are cure Temperature, wind tension (affects both prepreg laminate compression and fiber pre-strain), and stress ratio (helical-to-hoop) – less crucial but potential sources of performance impairment from liner pressurization, helical angles, step back (each of which can introduce ~10 parameters)
 - For assembled tanks parameters include 2 or 3 fab temperatures, direct control of compression and pre-strain
 - Thermoplastic and metal matrix composites are affected by local heating geometry (size and timing of affected zone)

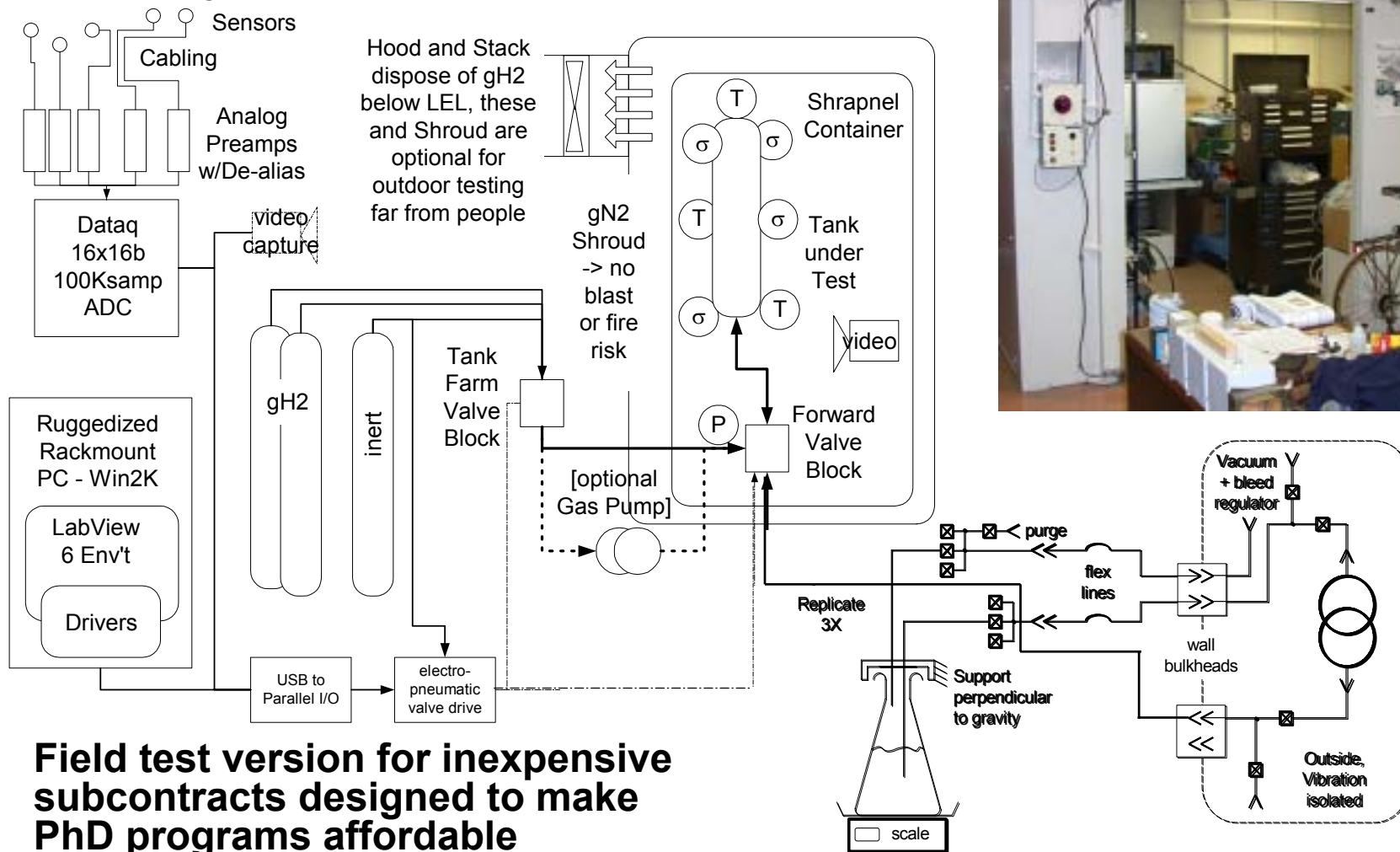
- Measurements' scatter 'identifies' Weibull Distribution
 $1/m = .04$ to $.08$



High Pressure Experimental Facility

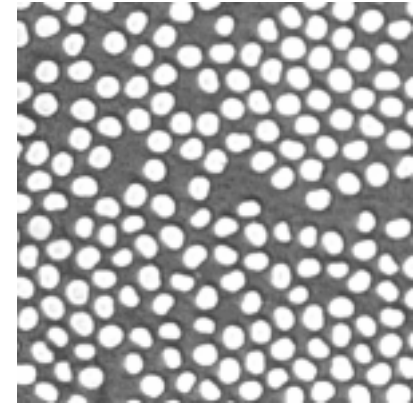
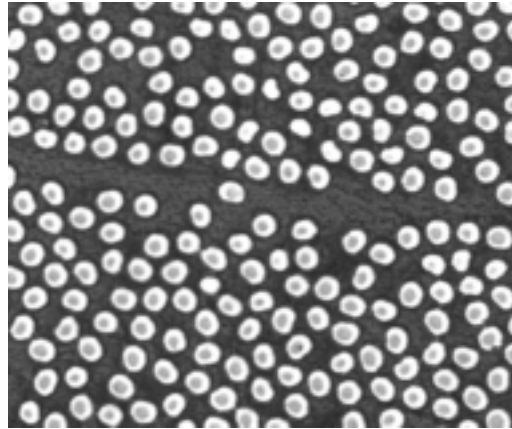
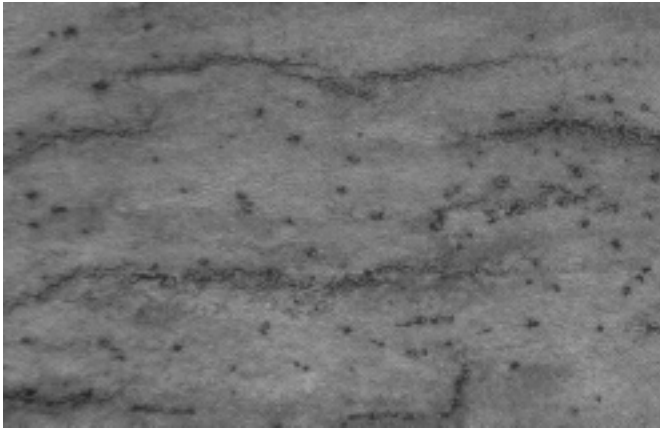


- **Experimental capabilities to burst test tanks, determine PbV/W [mass and volume efficiency] within 1%, observe fast failure phenomenology, test for cycle life, test permeation – to 50 ksi H2**

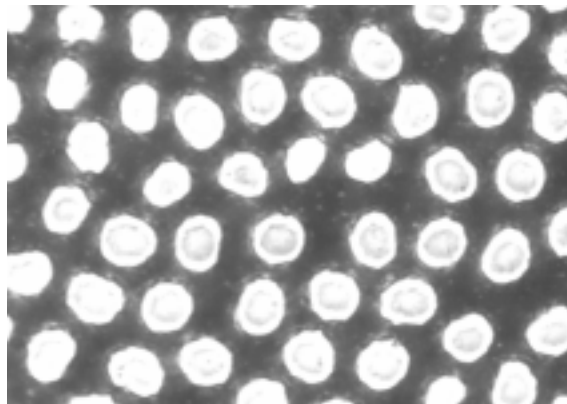


- **Field test version for inexpensive subcontracts designed to make PhD programs affordable**

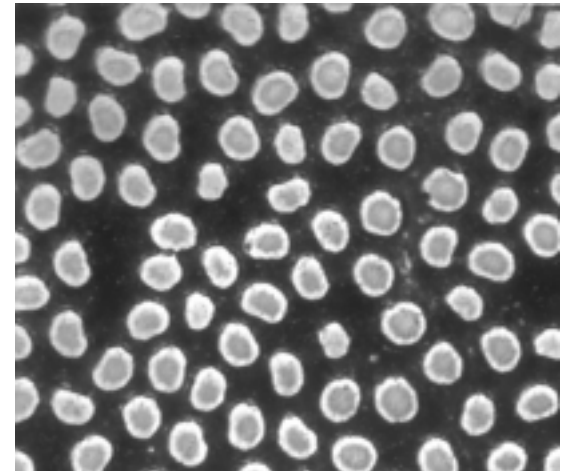
Composite Materials Process Experimentation



Nonuniformities (orig. 50X) Laminated plies photographed at 500X

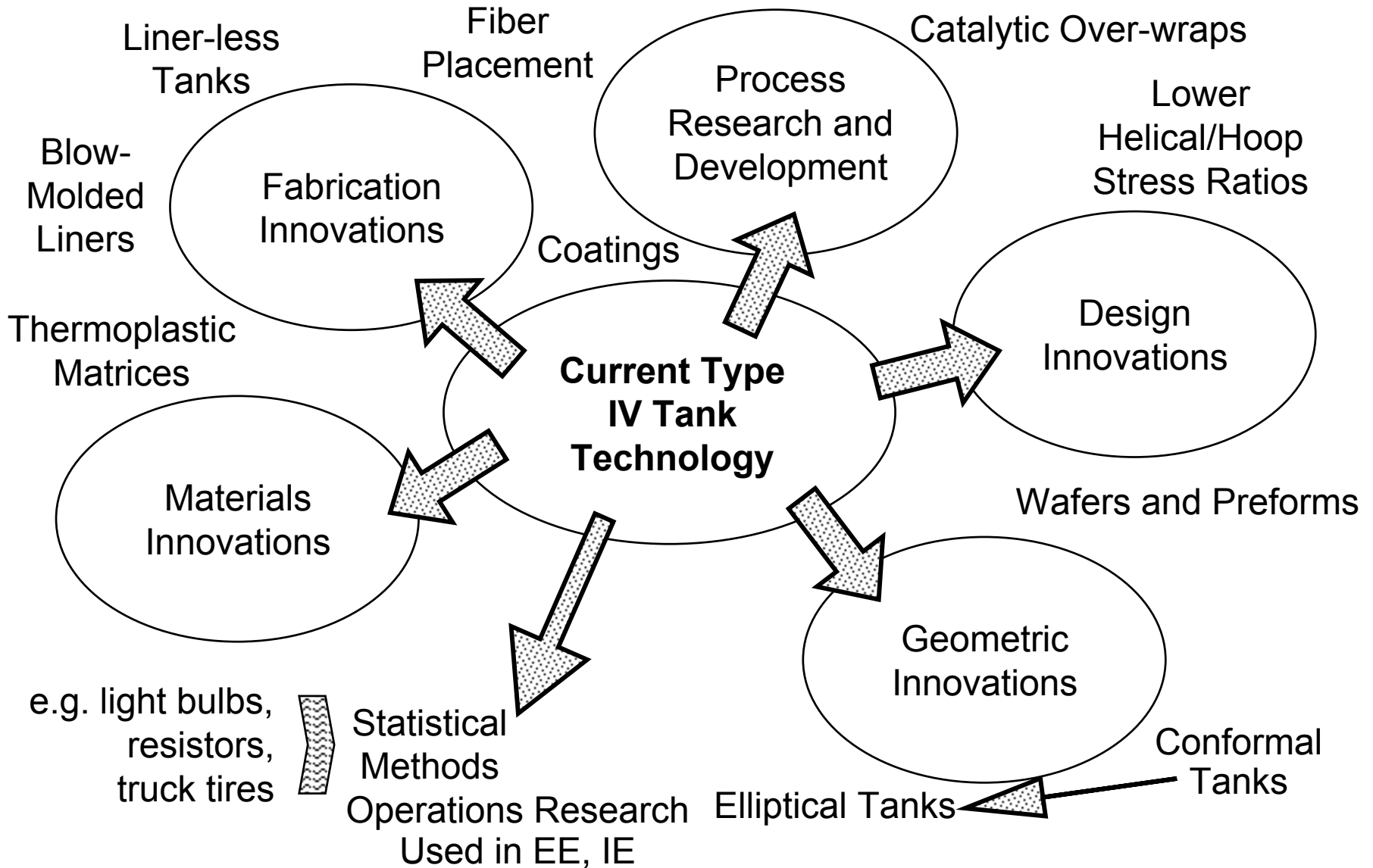


All Photos of metallographically prepared specimens with new matrix material that might reduce fabrication costs by ~30% vs. epoxy



Fiber Area Density -> potential for approaching 75% at 1000X

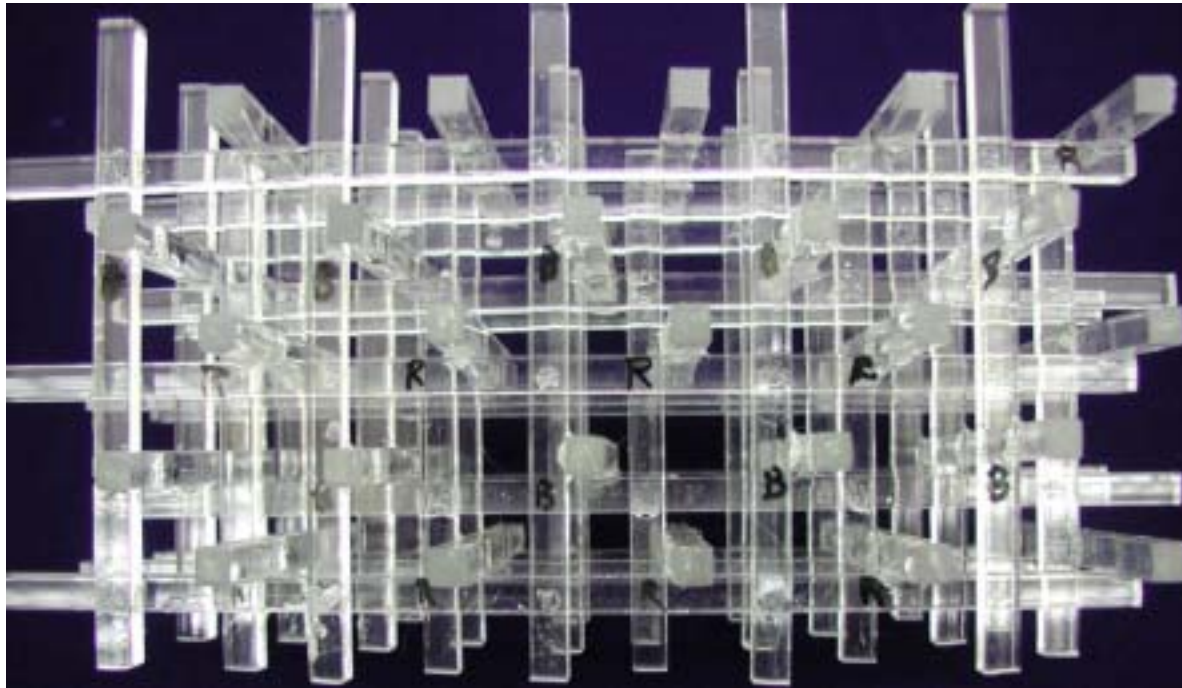
Avenues for Improvement [Projected in FY01]



Macrolattices – Adapted for Motor Vehicles



- **Weak in Shear**
 - Assumption from Solar Rechargeable Aircraft application that good tanks were stronger than the balance of vehicle structure – so they ought to function as vehicle structure – not true for motor vehicles due to safety



- **Access for Assembly**
 - Robot hand takes straight, unblocked path through open corridors to bond just 2 struts at each 'cross' location

Macrolattice Replicates – Rediscovered in 2003



- 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

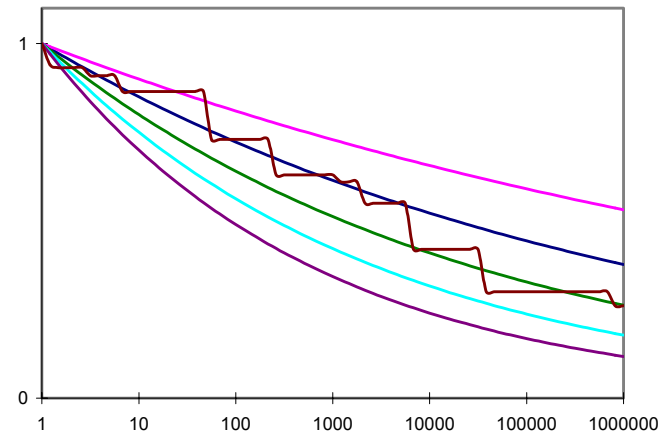
- Not many domes or arches



compared to
‘endoskeletal’
structures built
routinely by
assembling
multi-use parts



Learning Curves

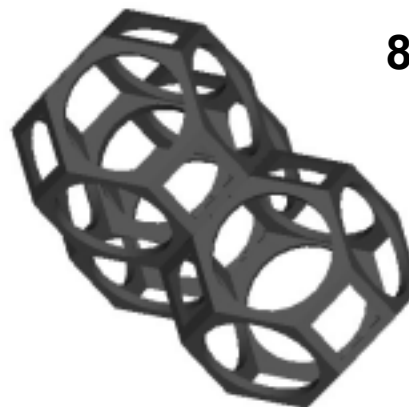


- A ‘vocabulary’ of geometries from a fixed lexicon of parts (more is richer)

Less-Advantageous Replicants – FY04 Update



- Initially believed fabrication easiest for hexagonal facets of truncated octahedral cells
- Discovered that curvature at corners of closed-trajectory faces is locus of excessive shear stresses that would fail matrix



8 ‘wound’ faces (nearly rings) can assemble to fill space



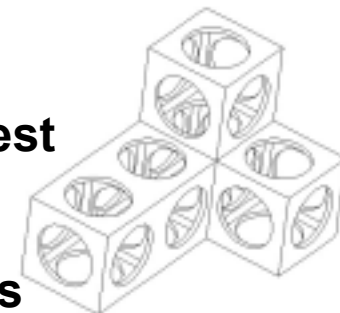
- Problems with radii of curvature are avoided by trusses whose replicated fiber struts **don’t cross**



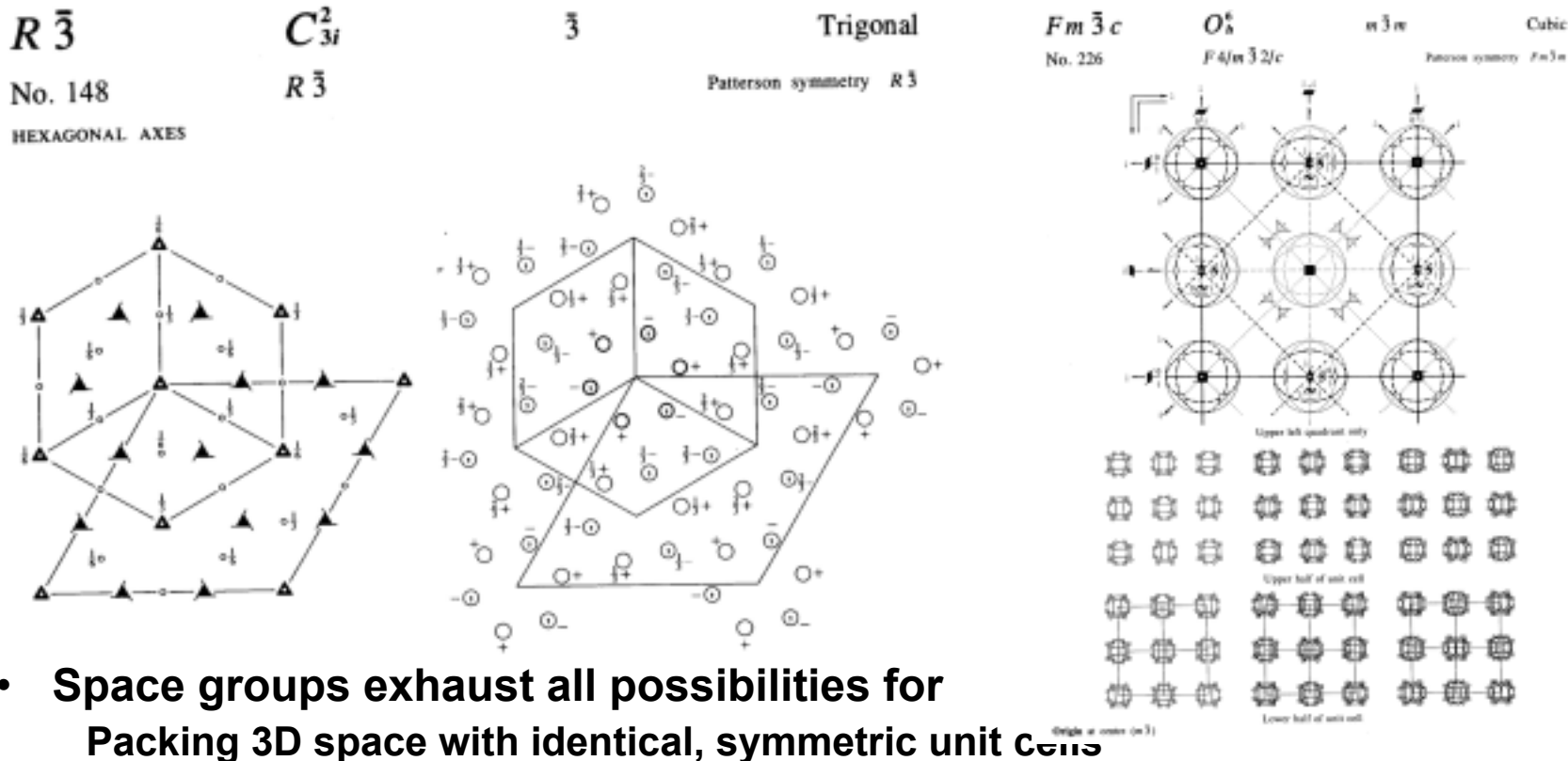
- Fuller’s “Octet Truss” is strong in shear, which is no longer considered to be **safer in collisions**

- Solid modeling of replicants is non-trivial, hexagonal-closed-packed cell was easiest to render in FY03, builds slabs with skins

- Cubic is best for strong biaxial composites



Crystallography Describes Macrolattice Cores



- Space groups exhaust all possibilities for Packing 3D space with identical, symmetric unit $c_{\infty}m_{\infty}3$
- 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 = No. 148 (above left)
 - Much lower symmetry than the idealized cubic lattice due to strut skews
 - Although formally a sub-group of O_h , not a naturally occurring sub-group

Skin Requirements and Preliminary Design Issues



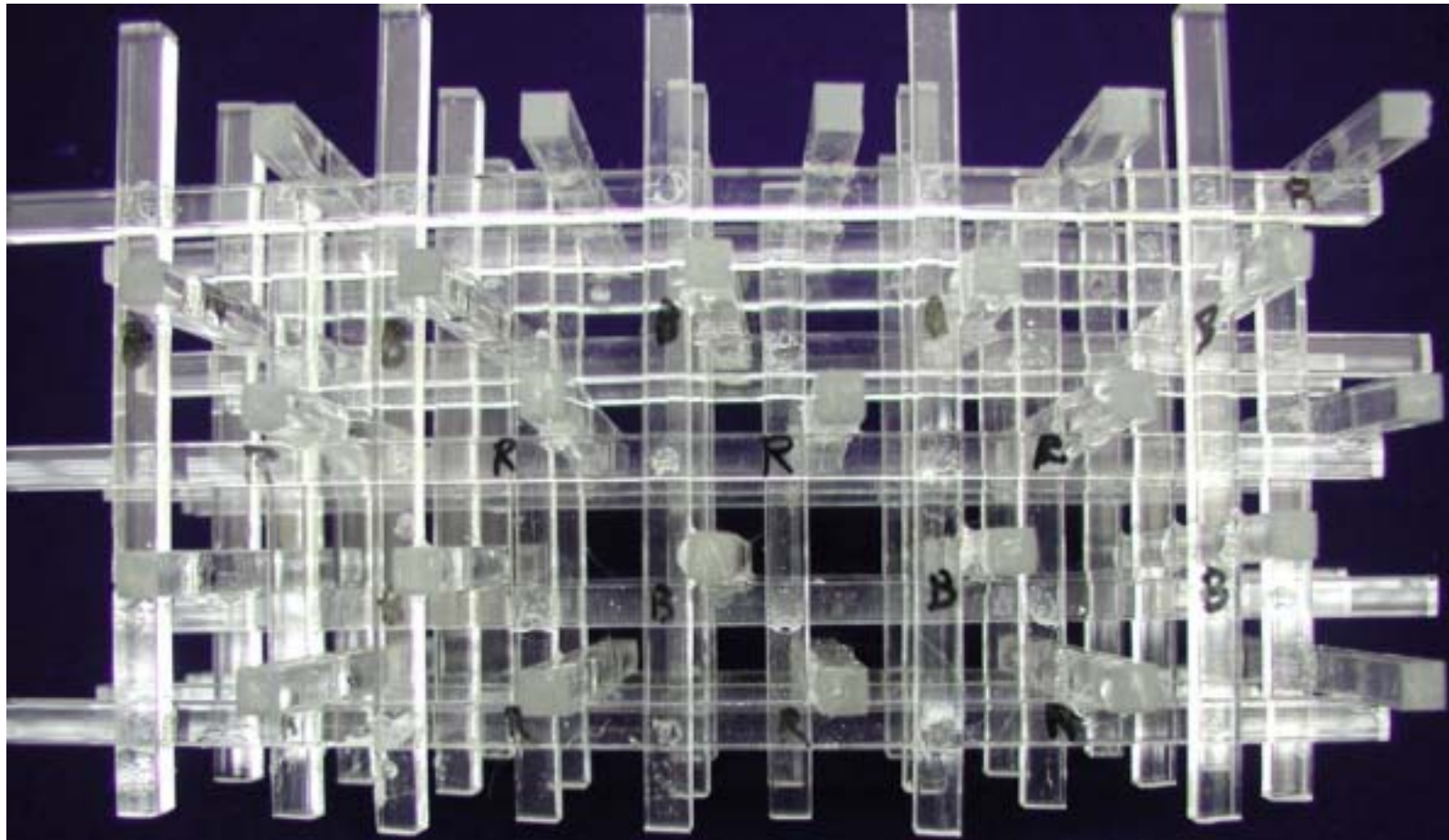
- **Load Transfer** (applies to tiles, edges, corners)
Differential pressure across skin must be transferred into struts
- **Surface Strain** (applies only to tiles)
Skin need not conduct any of differential pressure loads, but must expand at the same rate as the core macrolattice when pressure changes. 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**

Limits of Crystallography



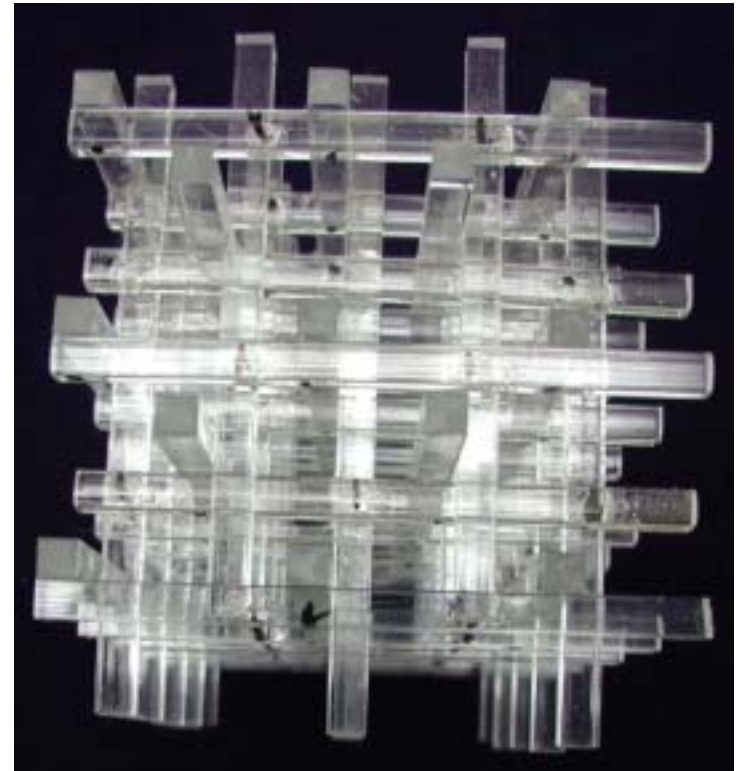
- **Continuity of load paths**
 - Most of stress "flows along" fibers, can't stop 'abruptly'
 - Curvature limited by strength of matrix in shear
 - Can be thought of as additional continuity requirements on facets
- **Solid models not fully represented by points or lines**
 - If boundary representations could be correctly reduced to vectors, CAD would not need these richer descriptions to assemble 3D entities
- **Connection of 3D to 2D and 1D and 0D elements**
 - Demands strong intervention into the closed operations of a group
 - Possible to embed a partial lattice inside a ring group, but is it helpful?
- **Micro-to-Macro matching of solutions**
 - Know how to do this for atoms and metal lattices, not for 3D structures
- **Defect load path**
 - Much larger variety of defects in macrolattices than in regular crystals
- **Full FEM useful – computational experiments solve periodic BC's**
- **Probably obeys Physics (version of Group Theory) decomposition of Cartesian Tensors into irreducible form, using spherical harmonics**
- **Correlated failure modes – nothing similar in Materials Science (yet)**

Models of Advantageous Groups



- **This truss geometry is currently the conceptual front runner for motor vehicle applications, enabling nearly rectangular containers**
- **Bonds between struts are not in differential pressure load path so they can be designed as mechanical fuses, mitigating crash risks**

Experiments in Assembled Structures



Metaphors Derived from Diverse Disciplines



- **Architecture** - a 'vocabulary' of structural elements
 - (Successful 15 year regulatory transition to distributed-load designs)
- **Applied Mathematics**
 - **Differential Geometry** Curvature limits on composite assembly
 - **Group Theory** Generation and description of lattices
 - **Trajectory Optimization** Vehicle optimization with constraints
- **Aero/Astro**
 - **Composites** Topics shared with ME and Mat. Sci.
 - (Successful 15 year experience getting the most from fiber winding)
 - **System Integration Methods** Subsystems Partitioning, mass accounting
- **Operations Research** Reliability Theory
- **Industrial Engineering** Manufacturing, process research
- **Design of Experiments** Minimize test program costs
- **Ballistics** Shock propagation and shrapnel
- **Crystallography** An obvious metaphor, some utility
- **Collision Kinetics** Understanding crash mechanics
- **CAM** Robot Assembly of replicants

Safety Innovations Worth Pursuing



- **Several attractive possibilities have emerged in last 3 years:**
 - **Strain energy in compressed storage could be advantageous**

Megajoules stored in elasticity and dozens of kilojoules of PdV work are released by failure [vs. Gigajoules of chemical energy in stored hydrogen]

That stored energy can power deliberately designed ‘fail-first’ structural elements
 - **Sonic Disposer ‘Nozzles’ could thereby eliminate most of the eliminate ~5% probability that a vehicle crash catches fire**

Hydrogen is very difficult to ignite, its flame speed is easily exceeded by sonic jets from cracks acting like transient rockets

Controlling how a container breaks could enable fundamental improvements in vehicle fire safety, only available from hydrogen
 - **Dust instead of shrapnel observed in > 3 different programs**

Likely a new Physical Instability that could be engineered to dissipate most of the megajoules of stored strain energy
 - **Crash Test program who should collect shrapnel ?**
 - **Collaboration with auto companies on shapes and stiffness**
 - **Survey locations for tanks that won’t burst in low speed crashes**

“Turn to Dust” Failure Modes



Successful (mass record set in June 2000) tanks turned to dust in a single frame on high speed cameras

This potentially *benign* failure mode displayed almost no localized fracture, releasing fine ‘shrapnel’ that can be easily stopped by thin shielding

The “missing 7%” *may* be understood

Stress ratio (helical / hoop) “too high”

Dome failure activated – high dispersion

Real manufacturing problems on dome

A poor trade off : wider tows cost less but imply more severe 3D effects in dome

This is a repeatable class of failure modes with the potential for new Science and Engineering (designer failure modes)!



Collaborations



The PI (Principal Investigator) is under contract to DARPA to provide technical supervision of awarded Water Rocket contracts with Hamilton Sunstrand and Proton Energy; responding to renewed DARPA interest.

Two other DARPA projects have been under way over the past year with contributions from the PI (the launch-on-demand vehicle RASCAL and advanced composites aerospace tank development under SBIR).

On both of these later DARPA projects, the PI is working closely with two uniquely-skilled commercial suppliers of advanced materials technology (Spencer Composites and Cymetech). In pursuit of quantitative structural performance measurements on these contracts, the PI has become acquainted with the unique capabilities of 3 ASTM-certified testing labs. These labs have proven to be valuable repositories of the aerospace composites development efforts over the past 30 years, and LLNL expects to work with several of these labs to establish the performance and value of new matrix materials and fabrication methods.

Long term collaborations with academics have been underway with Stanford, Berkeley, and Purdue. The small tankage prototyping and test program LLNL has planned is intended to re-ignite academic research into containment structures. Private sector vendors are learning to furnish liners, and entire test rigs, enabling ~one-PhD-per-\$100K proposals. Other sponsoring agencies besides DOE have mandates to fund academic advances in Mechanical Engineering, Material Sciences, and Computer Science by sponsoring research at the PhD level.



- **Theory**
 - **Scholarship**
 - Literature Searching
 - **Vehicle Modelling** – built and exercising software tools for static vehicle Optimization including range and specific power constraints
 - **Preferred forms for Macrolattices**
 - Crystallography, Chemists' and Physicists' Group Theories
 - **Point design for current materials**
 - Enabled model with correct density and scale of struts
 - Fundamental advance in relaxed assumption of identical strut length
 - enabled ~4X smaller unit cell size for lattices, nearly total conformability
- **Experiments**
 - **Learn how to build macrolattices**
 - Using humans as assembly robots, developing the tools to locate struts
 - **Consider bonding techniques**
 - Both UV-cured cast composite parts and thermoplastic matrix compression molding have been prototyped for the first time, and thermoplastic matrix lap joint connectors will be fabricated to prove one of the leading contenders for inter-strut and strut-to-tile connectors.
 - **Downselect what to prototype** {still plenty of shopping to do}
 - **New collaborators** (Spencer and Cymetech and 3 ASTM Test Labs)

Plans for Future Work



- **Publication: AIAAJ, then Applied Math, then Design News**
- **Model Building – lucite, then composite, illustrate core + skin**
 - **Core first, then alternative skin substructures {3D modeling}**
- **Breaking Representative Structures, with Statistics**
- **Investigate sonic disposal of hydrogen**
- **‘New’ Physical Instability → basic research + safe disassembly**
 - **Tensor ‘debonding’ waves presumed to dissipate strain energy**
 - **Faster than 4,000 frame/sec cameras → arduous instrumentation**
 - Accelerometers and optical attenuation sensors affordable >100 KHz
- **Chance to break the Mass Record again (~16%) in 4” test bottles**
- **Permeation – hydrogen diffuses through most materials**
 - **Curves fit to 5,000 psi (insufficient for optimal structural storage)**
 - Diffuses as protons through metals, diatoms through plastics
 - but what does it do in organo-metallics, densified xerogels?
 - **Designs for textured foils that can take the strain (< 1.5%)**
 - Ideal for low mass skin on macrolattices, but cycle life unproven
 - **Cycle life of permeation = good to the end of service life?**
 - No testing being done on permeation after cycling ~ “safety factor”
 - As pressure ratings rise, current liners will cycle above yield stress