Hydrogen Storage Using Lightweight Tanks

Andrew H. Weisberg, Blake Myers, and Gene Berry
Lawrence Livermore National Laboratory
7000 East Ave. L-477, Livermore, CA 94551-0808 weisberg1@llnl.gov

Abstract

As tooling was being designed for compressed hydrogen tank experiments, a series of discoveries were made. The issues uncovered are difficult to translate into the vocabulary of any single technical discipline, ranging from computational geometry to exotic materials. Dimensionless system performance models powerful enough to evaluate the new, wider range of structural geometries and materials are formulated. Their preliminary results may change the best solutions to hydrogen storage.

Recent Progress

LLNL tank design was progressing through a welter of CAD/CAM (Computer Aided Design / Computer Aided Manufacture) languages when the first hints of unmodeled effects were noticed. Questions about the simplifying assumptions made initially seemed to apply only to methods from the 1970's that pre-dated finite elements (FEA). Ordinary differential equations (ODE) that balanced internal pressure with fiber tension transition to surfaces that can't be physical, as their solution progresses up the "balanced ovaloid" dome contour from the cylinder toward the boss. This transition occurs in the same region where wound fiber builds up (on the ends of tanks) into a basket weave pattern around the axial bosses.

Another ODE for fiber buildup also had to be solved to calculate displacements on either side of the nominal dome contour, in order to derive the final tooling shape for molding tank liners. It also went singular as the contour approached the boss. LLNL researchers had been shown proprietary fiber build up models used by manufacturers in their much costlier (FEA) design calculations. Neither LLNL solutions nor the best industrial models explicitly take into account the lack of axial symmetry in actual fiber trajectories. Getting the dome contour wrong turns out to be very costly, and real wound fibers can't follow idealized axisymmetric trajectories.

Examination of real fiber trajectories in 3D (three dimensions) extended the discovery process beyond familiar tank geometries. The region near the boss design where the pair of 1D dome contour ODE's (that derive the balanced ovaloid from Classical Lamination Theory) go singular has negative curvature. LLNL researchers have been proposing building toroidal composite tanks for spacecraft since a fundamental analysis (performed for AFRL in 1997) showed their mass savings. Toroidal tanks have negative curvature over a large portion of their surfaces. Aerospace-style 'inverted' bulkheads have a small but crucial negative curvature transition ring, and can be nested to increase vehicle density. Curiosity about which shapes of container surfaces that could contain pressure most effectively led to an exploration of arbitrary geodesic trajectories.

Real wound fibers can disobey the geodesic (no shear) constraint because other fibers can restrain them from slipping sideways (with friction and the high viscosity of wet epoxy matrix). It turns out that real fibers must violate this constraint to get past one another where they build up end domes. But there are other trajectories that don't build up. Some of them can fill space with nesting surfaces. This led to foam-of-tanks concepts, followed by structural containment concepts that need not look like 'tanks' at all. When LLNL colleagues started asking about the mass and volume penalties of filling space with large numbers of identical structural elements, a

new theory of dimensionless performance models was formulated. It has sufficient generality to compare the many ways that structural strength could be used to store hydrogen.

This widely applicable theoretical formalism quantifies the utility of mass, volume, and cost performance of any hydrogen (or other fuel) storage subsystem, and was derived just in time to present at the Annual Hydrogen Program review (APR, Denver West, Co May 16, 2002). More formality will be exercised to present this theory in mathematical (as opposed to viewgraph) form herein. Much of this theory was motivated by more fundamental and detailed modeling contributed by Gene Berry (in preparation for a textbook chapter on Hydrogen Fueled Aircraft). Preliminary results that combine volume effects with mass and cost overhead for various forms of structural containment suggest that the best way to store hydrogen has changed.

Context of Discoveries

Although there are many ways to present the succession of discoveries made at LLNL in the period ~December 2001 through May 2002, this document approximates the order of topics delivered by viewgraph at the APR. It begins with the Statement of Work that DOE reviewers were already cognizant of, moves through what actually happened in tank research, to the geometric problems that research uncovered, to the theory motivated by colleagues' questions, and on to that theory's preliminary implications. The APR presentation returned to recap the full range of research LLNL was reporting to DOE, but this report has distributed that recap throughout for a logical flow from experiments to theory to implications. This report has much to cover, and regrettably cannot cover its topics with the thoroughness their consequences demand.

The LLNL strategy for DOE tankage research justifies working on statistical quantities of small tanks (see below), but also contributes to other sponsors' goals. What can currently-available innovations contribute to storing hydrogen onboard vehicles? The advanced tankage effort at LLNL began (in 1992) by applying the best aerospace structural technologies to storing hydrogen (and oxygen) aboard solar rechargeable aircraft. A long list of LLNL high performance vehicle designs have subsequently been enabled (cars, spacecraft, blimps, SUV's, busses, scooters, . . .) by applying extremely mass efficient aerospace composite structural technology. Current aerospace production methods that wind the best tanks (Type IV composite pressure vessels) are being adopted in the current generation of hydrogen fueled demonstration vehicles (c.f. Quantum Technologies current work for DOE under a solicitation specified by LLNL), but the expertise that created this technology across the 1970's has dwindled.

In the course of this Report, many topics of research will be re-opened that 'expired' 1-2 decades ago. Those innovations were never pursued, not because they lacked merit, but because proven methods (e.g. epoxy-T1000 composites) were already performing in the most demanding, lucrative, and risk-averse aerospace applications adequately (the Trident and SRB rocket motor cases). Times have changed, providing copious computer power, better strong materials, and a few new processes. Yet the fiber technology conferences stop in the early 1990's. Hydrogen's path to adoption in many applications (from portable electronics to ocean surface to air cargo, including ultimately motor vehicles and giant stationary storage) may justify revivals of several 'abandoned' innovations of the 1980's.

Goals and Objectives

The LLNL tankage research effort has been tasked by DOE to learn how to build and operate the best hydrogen container technologies. Before the research reported herein, Type IV (plastic lined, composite wrapped) pressure vessels were the proven 'best' way to hold hydrogen onboard vehicles where container mass matters more than container volume.

Optimality is hard to quantify among the fundamentally different approaches to hydrogen containment: structural strength (compressed), thermodynamics (cryogenic), and chemistry (hydrides, nanotubes, etc.). Researchers and industry have sufficient vested interests to preclude such a broad optimization, but within the more limited competition among structural options, LLNL can optimize with a cost function that allows the consumer to mix desiderata of containment mass, volume, and cost. This report contains the first methodology that can combine these desiderata arbitrarily. That methodology can handle the plethora of recently rediscovered structural geometries, and appears powerful enough to include thermodynamic containment options.

LLNL objectives therefore are seeking the best structural containment options for hydrogen across a range of conventional, new, and rediscovered geometries; a range of storage scales and vehicle types; and the full range of hydrogen's Equation of State (EOS). To meet this objective, LLNL expects to augment computer models to include the 3D effects recently discovered during conventional tank design, to conserve fibers along fiber trajectories, and to predict the limitations on high pressure storage that are likely consequences of matrix shear strength effects along actual (non-geodesic) fiber trajectories.

LLNL has planned and is executing experimental activities to implement these goals. A return to the frontiers of mass performance will allow affordable retrodiction of the "missing 7%" of fiber failure strain observed in prior (record setting, much costlier) experiments. Prototyping small tanks will allow LLNL experimenters to push the envelope in mass, volume, and cost at minimal expense. Planned experiments range from real Science (a new physical instability) to Statistical Process Research which should save ~30% in structural containment mass and cost.

The "science project" which seems likely to observe a new class of waves could also supply very valuable fundamental improvements in hydrogen containment safety. If this new class of waves can be engineered (i.e. grenades and avalanche diodes), "designer fragmentation" could provide a safe way to dissipate structural stored energy. To generate such understanding, LLNL hopes to collect data on acoustics, hydrodynamic shock, and debris morphology. Other safety innovations can make use of compressed hydrogen's fractional megajoules of mechanical stored energy to safely dispose of its fractional gigajoules of chemical stored energy. Continued experimentation with affordable test articles and rigs is targeted at reviving academic research contributions to advanced composite manufacture and extremely strong materials.

Rationale for Small Tanks

The primary reason LLNL has been prototyping small tanks is to make further research affordable. Advanced tanks directly applicable in buses, SUVs, and cars formed the backbone of tankage research at LLNL up to the record-breaking results of June 2000. Each of the high performance test articles burst in that effort was designed to contain 5 kg of hydrogen, and cost ~$10,000 to build. The final two experiments on these car-sized tanks cost roughly triple that much to hydroburst test (at Thiokol) with full diagnostics. Those experiments left crucial mysteries surrounding a repeatable 7% performance loss, and a failure mode whose further observation may be quite valuable for enhancing burst safety.

The obvious next steps to continue this line of fundamental tankage research call for variation of manufacturing process parameters. A new experimental program was conceived in late 2000 that relies on the small size of tanks suitable for scooters, motorcycles, wheelchairs, skidoos, etc. This scale of tanks uses just $15 of costly fiber to collect data that can be validly extrapolated at all larger scales. A tank has been designed at this scale that can be affordable produced and burst in sufficient quantities to do science and statistics.

Statistics are critical to understanding whether a particular set of manufacturing process conditions are adequate. Safe bursting implies predictable burst pressures, since excessive variance in burst pressures leaves too much probability in the tail of statistical distributions, causing uninsurable and industry-crippling premature bursts in too high a fraction (parts per million?) of tanks that can be expected (numerically predicted) to burst prematurely. The end dome region is the locus for burst phenomena with a variance as high as 20% in conventional wound tanks, an unacceptable risk(except for expendable munitions onboard unmanned vehicles). By arranging for excess strength in the dome regions, good tank design will burst in the cylinder wall with variances around 3%, close to the strength dispersion in the fiber itself. Obtaining enough burst data to extract statistics can fully validate a particular tank design and manufacturing sequence, and save both cost and mass that would otherwise be sacrificed to unused "safety factor".

Besides cost savings that can come from real statistics, the low cost of a minimal fiber vessel makes it enabling to low volume small vehicle and portable applications. It may not make great sense to build small tanks on performance grounds alone, but their relatively poor (per unit mass of hydrogen) economic and mass efficiencies should still prove enabling for applications that currently have *no* viable hydrogen storage options. The thermal containment required for cryogenic or chemical hydrogen storage scales down even more poorly than does compressed storage fluid connection and permeation reduction mass overheads. Because there are essentially no good hydrogen storage options in this mass class, no existing commercial entities will be harmed by DOE's funding of this approach to hydrogen tank research. The use of minimal fiber, combined with adequately low variance in burst pressure, constrains small tank diameters to be larger than ~4", and a diameter of 4.5" was chosen due its (hearsay) optimality for adoption in scooters.

Experimental Progress

LLNL small tank prototyping allows national laboratories, universities, and industry to return to significant experiments with high performance tanks. Besides making scientific experiments (described below) affordable, engineering 4.5" diameter test pressure vessels which use the minimum amount of expensive fiber and design sophistication also enables non-incremental progress in design and manufacturing techniques. Statistical Process Control, of the sort practiced on semiconductors and light bulbs, can be demonstrated for hydrogen tanks and is expected to deliver roughly 30% of the 50% savings in tank cost LLNL has forecast for next generation (mass produced) hydrogen tankage.

Because LLNL and DOE could not afford the full sophistication of the best current tank design procedures, non-proprietary techniques that were the state of the art in the 1970's have been employed. Over half a decade working with many of the most capable pressure vessel manufacturers has allowed LLNL tankage researchers to observe the capabilities and methods of proprietary design software. The detailed nature of most of those tools is protected by Nondisclosure Agreements (NDAs), but its safe to say that finite element analysis (FEA) provides the stress and strain prediction in state of the art composite design tools. LLNL's prototyping effort could afford the consultants to price such analyses, and concluded that ~$15,000 of analysis per point design would cripple the ability to iterate on early designs.

Instead, LLNL invoked to the membrane approximation and "balanced ovaloid" dome contours. Outdated methods made sense as an economy measure, not as a basis for investigating design models. One person had to comprehend enough of the design issues to specify mold tooling for prototyping, and that comprehension was more valuable if it could be discussed without violating NDAs. Several percent mass performance could be expected to be lost by using the older methods, but when they began misbehaving, it appeared at first unlikely that their

problems would persist to plague state of the art FEA methods. Whatever performance premium the fully comprehended older methods cost, they would at least allow academic research (PhD programs) with the prototypes.

The design process was brought to sufficient completion at LLNL by these older methods, which solve a trio of ordinary differential equations (ODEs) for the shape of the end dome. This shape, once its design is frozen, will determine burst pressure for a particular fiber manufacturing process and winding pattern. Because the liner mold tooling that will be built to implement a particular dome shape is costly, can take several months of project schedule, and constrains the structural performance of many potential future winding patters – it was important to check it thoroughly. The ODE that balances pressure forces with fiber tension has a singularity, that led to the entire range of discoveries reported here, but initially appear trivial.

LLNL obtained the first iteration of tank design and ODE solutions from very capable and cost effective consultants. Classical Lamination Theory was applicable in analytic form because using the minimum amount of costly fiber that would lead to representative experiments required just two identical plies of helical fibers. A diameter of 4.5" was initially selected based on hearsay market research for the most popular tank diameter that could be easily applicable to scooters in Asia.

Using T700s fiber, the cost performance leader among current composites, and Thiokol's TCR prepreg matrix (available from at least 3 of LLNL's candidate tank winding subcontractors, its density is not proprietary), LLNL's small tank design is predicted to burst at 5.6 ksi in the hoop winding, not the helical plies. The same design and liner dome contour are intended to perform sufficiently well with three times as much fiber wound on the liners to burst at >15,000 psi. Some alterations in the boss, and more detailed analysis with FEA may be required to perform a wide range of material science experiments (e.g. hydrogen permeation, liner creep) that will determine the near term feasibility of the best hydrogen storage options considered below.

Once liner mold tooling is finalized, the remainder of tank manufacturing operations have already been specified (discussed below) and can be executed with schedules delays of a few weeks at most per process step. Burst testing is the near term target of LLNL prototyping, because it confirms or falsifies modeling, and provides a platform for science of potential extreme value as safety innovations. Figure 1 below shows a schematic diagram that mixes electronic, fluidic, and mechanical blocks to portray LLNL's approach to outdoor hydroburst testing. Outdoor tests are anticipated at LLNL, to calibrate a FEDEX-shippable test rig, to be continued at one or more private rocket test subcontractors. LLNL experimental plans are holding course with a projected cost of $100 per burst test data point (sufficiently low to afford statistics).

Experimental Backgrounds

Figure 2 below shows the most informative single frame photographed during the penultimate test LLNL performed on 18" diameter x 48" long tanks in June of 2000. This effort set the current record for mass performance in hydrogen storage at 11.3% hydrogen by weight, using T1000G fiber (which is currently 5 times more expensive and ~3.5 times less cost effective than T700S). The burst morphology turned this tank, and a previous test article that burst at essentially identical fiber strain, to dust with very few macroscopic remnants. That transformation happened in a single frame of the fastest observation Thiokol could then perform. None of the 15 'experts' present at these tests had seen this morphology before, could explain the consistent 7% low fiber strain at failure, nor had the presence of mind to collect the dust.

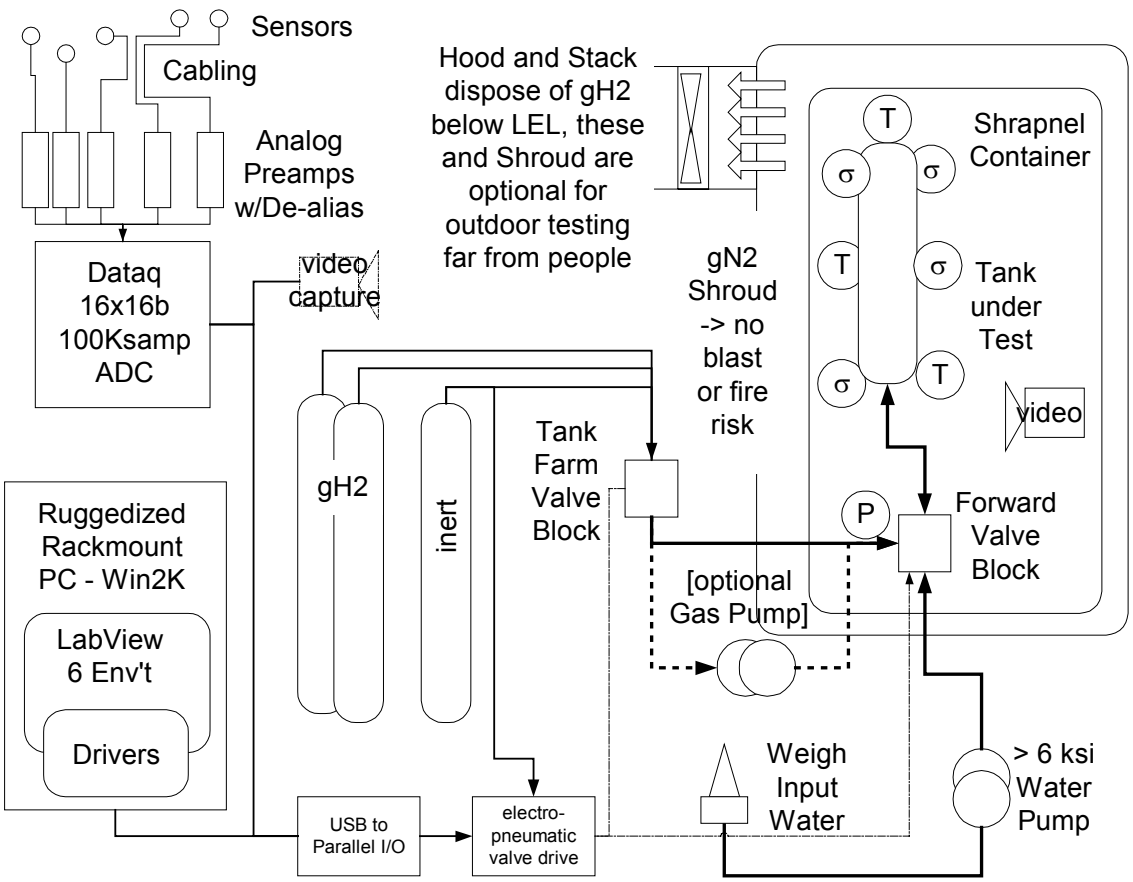

Figure 1 – LLNL Field Test Rig capable of measuring PV/W to 0.5%, safe vs. shrapnel

Since those costly tests in Thiokol's indoor burst test outbuildings, the turn to dust failure modes have been observed in two other situations, both with T700S. High performance (PbV/W = burst pressure * contained volume / total weight) was the goal of one tank design that failed multiple times with the "turn to dust" morphology, while the other was a previous generation (~4% hydrogen by weight) design that was assaulted at Sandia with kinetic energies from a dropped impacting rod comparable to a mortar round (several kilojoules, more than an order of magnitude more than bullets would impart). The Sandia tests were observed with 4000 frame per second cameras, and this failure mode still occurred far faster than a single frame. Although full details of these both T700S experiments are protected by NDA, neither of these later failure types were accompanied by observed loss in fiber strain at failure, while the LLNL record breaking tank broke twice at strains 7% lower than >10,000 Thiokol data points from T1000G.

Thiokol's experts didn't have any viable options to offer for continued experimentation, because what wasn't understood would be very costly to probe. Thiokol's film streak cameras cost nearly $8,000 to instrument the last burst, and couldn't temporally resolve it. Varying the tanks manufacturing parameters at $10,000 per test article to perform what they called a "science project" wouldn't get DOE very far. Thiokol test experts considered it unlikely that the failure was local, since an onset in one spot would kick a relatively intact piece off the other side. This problem wasn't moot, since LLNL had not quite made it to the 12% goal line and nobody knew why.

Figure 2 – Best 2.5 millisecond photograph of June 2000 mass record burst

The DOE hydrogen community treated the Sandia results as bad news, and they were not followed up. LLNL proposals to continue those experiments and collect crucial data from "turn to dust" failure modes found no audience. But prior experience with performing safe experiments that might generate shrapnel had been acquired by LLNL staff (under AFRL funding in 1997), and it was clear that tanks turning into dust is good news. This is a potentially *benign* failure mode. Not only is if fundamentally new Physics, dust can be stopped with very little mass while macroscopic shrapnel requires significant mass per unit area to dissipate its kinetic energy. The possibility of designer fragmentation could be a fundamentally improve hydrogen containment safety.

Results from the geometric tank design work described below present a strong hypothesis that can account for the lost strength, but only further experiments can determine its likelihood. The ratio between stress in the helical and hoop windings was boosted to help LNL acheive the record mass, and this could have allowed a failure to begin in the end dome. A failure in the end dome could easily be repeatable, if it derives from the discrepancy between designed and actual stress. If current LLNL understanding of non-3D effects in the end dome is adequate, real manufacturing problems were exacerbated by Thiokol's manufacturing process (which wound very wide fibers 'tows'). The repeatability of many failure transition phenomena, including the hypothesized wave of destruction that might carry a local failure throughout the vessel in a few dozen microseconds, is a necessary condition for any such hypothesis to explain a repeatable strength loss. LLNL hopes to add non-imaging (fiber light occlusion and

acceleration) sensors (with the ~megahertz bandwdith and data acquisition required) to observe this failure mode in real time.

Prototype Manufacturing Process

All experimental compressed gas storage test articles contemplated in LLNL research plans before March of 2002 have been Type IV composite pressure vessels. These are the highest (mass) performance tanks suitable for containing hydrogen that can currently be built with proven processes and industrial capabilities. Figure 3 below shows a cross section of LLNL's current prototype small tank design. It is a snapshot from the design process midway between computer models and drafting tools. Two further computational transformation convert those models into tooling which will constrain the performance of any tank that can be wound on this contour.

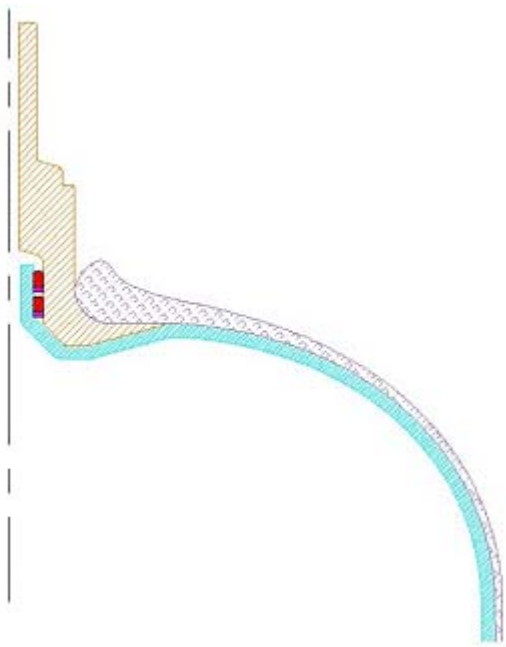

Figure 3 – Cross section of LLNL prototype 4.5" diameter tank showing liner (aqua), boss (brown), two layers of helical composite overwrap (gray), and dual o-ring seal (red)

Production begins with molding liners. LLNL plans to mold liners two ways, from at least three materials. The first and most economic way to mold liners is rotational molding (rotamolding), where tooling is projected to cost $5000 and take three weeks to manufacture. LLNL will use tooling manufacture for rotamolding to practice fabricating the most exacting part of a tool for blow molding, which would cost $20,000 and 6 weeks to manufacture ab initio. LLNL may be able to use the same capability to save cost and time on that exacting part – the contoured metal liner exterior surface. Because of the high costs and time lost if these tools are built incorrectly, much analysis has gone into the contours. Solid models have also been generated as an intermediate between drafting and implementation of the molding tools. Plastic stereolithography models that realize those solid models were brought to the APR, and reflect LLNL's current progress beyond a frozen design, just short of issuing tooling fabrication contracts.

The remainder of LLNL's prototype fabrication sequence is already in position, specified to match actual subcontractor capabilities. Liners are molded from their tooling, shipped to LLNL, where they are glued onto their seals with catalytically vulcanizing silicone adhesive and

pressure tested. This liner design is capable of holding pressure without composite overwrap, in order to enable experimentation with prestressed liners. The boss fits into a commercial VCR fitting for pressure certification to ~60 psi, then batches of 5 liners ready for wrapping are shipped to fiber winding subcontractors. At least three candidates should answer LLNL's solicitation to wrap these batches of five identical tanks, at least one should bid ~$5000 per tank. With ~$15 of Thiokol TCR prepreg and ~ 2 hours of wind time (on a ~$250K dollar machine), even lower prices are quite likely. Identical hydroburst testing, with later tests exercising more optional instrumentation, is anticipated to convert at least 25 tanks into dust.

Design Procedures

Without FEA, LLNL derived the end dome contour from earlier analytic methods. The membrane approximation leads to very slight errors everywhere except right over the boss, since a minimum fiber design will have very thin walls. Because the end dome could not be covered with a single ply of helical wrap without risking anomalous statistics from the lack of structural support for point defects, two identical plies were the fewest the contour design could presume. With easy to form tows of T700S prepreg taking their smallest form at 0.016" thick by 0.140" wide, even a tank as small as 4" in diameter would depart < 2% form the infinitely thin membrane approximation.

That approximation breaks down as helical plies approach the boss from their full radius transition from a single curved axis in the tanks cylindrical section. Before the helical fibers pile up, they follow a pair of coupled ODEs. The first of these conserves angular momentum, presuming that no external shear forces are available to deflect the tow as it wraps over the axisymmetric end dome contour. This assumption now appears to be routinely violated as tows have to thread over and under one another to cross in three dimensions (3D) near the boss. The second ODE balances the stresses due to pressure inside the contour acting perpendicular to its surface with a constant tensile force in each fiber. This results in the contour known as a Balanced Ovaloid.

The Balanced Ovaloid is flatter than an ellipse, and departures from it threaten the integrity of the composite. Because the matrix rather than the extremely strong fibers must carry all shear stress, it takes long distances (~0.2") to transfer stresses into or out of fibers from adjacent composite. Thus the zero shear stress and constant fiber tension analytic approximations make sense as bases for a contour solution that can achieve the highest burst pressures for a given amount of fiber. The ODEs are easy to integrate inward from the tangent condition where helical wraps become cylindrical, almost all the way to the minimum radius where fibers must turn around to clear the boss.

As those integrations (performed with 4th Order Runga Kutta) proceed inward, they reach an inflection point beyond which they rapidly go singular. Real fiber has no problem following any geodesic (zero shear) path over an axisymmetric dome as Figure 4 below illustrates. But as the ovaloid solutions passes through an inflection point (at about 0.78" radius), they go from convex to concave and shortly thereafter explode in a singularity that could not be physically realized. The question remains whether these concave out surfaces, which are much more abrupt than the nipples on architectural onion domes, remain valid solutions.

Numerous routine examples of surfaces have more benign flavors of negative curvature. Any nipple structure that connects a plumbing port to a tank wall must have negative curvature at least locally. Rocket nozzles have concave-outward throat sections that can be composite wound (usually with glass-phenolic). Figure 5 below show two examples reflecting this condition. Toroids (idealized doughnuts) are the most familiar examples of surfaces with negative curvature, where one axis bends 'out' while the other bends 'in'. These surfaces could

be very important to compressed hydrogen storage, as suggested by an early analysis LLNL performed for the Air Force in 1997. Toroidal tanks have often been advocated and even implemented in spacecraft where mass savings and compactness are most desirable. The absence of poorly utilized structure in an end dome give toroidal tanks most of the mass advantage of infinite cylinders.

Figure 4 – Example of geodesic (zero shear) trajectories on arbitrary convex surface

Figure 5 – Examples of axisymmetric surfaces with negative curvature

Experimental fiber tow trajectories were wound on variety of curved surfaces to confirm that the singularity in the axisymmetric ODE wasn't a barrier to real solutions inside the inflection point radius. At these radii, too much fiber stress 'flows' over the end dome to be balanced by pressure and inward curvature, but the composite can be prevented from collapsing inward by the boss. With a boss design that supports these loads and a thick build up of the helical wrap whose strength in bending also prevents the curved fiber from collapsing inward under its own tension, its clear that real ovaloid fiber trajectories in 3D can take a safe, nearly flat path inside the inflection radius. The third ODE predicts fiber thickness buildup, and it also goes singular inside the inflection point radius in a way that can't be physical, since there's only so much fiber that can pile up.

After the pile up equation was sufficiently approximated to conserve fiber, so that fibers in a tow were neither created nor destroyed along their trajectory, the workable design in Figure 3 was ready for computer drafting. Figure 6 below shows that design two steps further along towards liner tooling manufacture. Computer tools developed over the last ten years provided the basis

for LLNL assumptions that tanks development could be performed with much greater productivity by exporting calculations as computer files to computer –aided manufacturing (CAM) subcontractors to convert them into metal mold tooling and winding machine instructions. In practice, this chain of computerized tools remains cumbersome, and ~350 man-hours have been spent in a wide variety of software languages to advance the LLNL to the state shown in Figure 5, and to the solid plastic stereolithographic models brought to the APR.

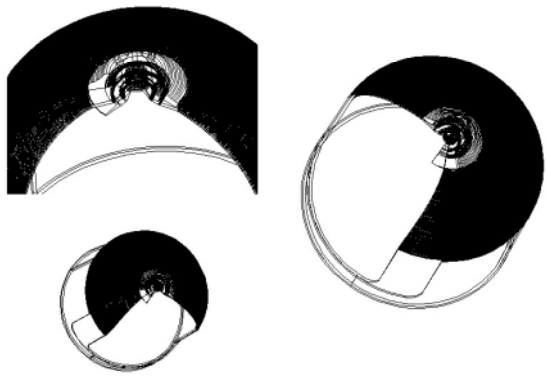

Figure 6 – Visualizations of solid models that capture 3D shapes of LLNL tank design

As fit check aids, physical renderings of solid models have served to validate the tolerances and assembly sequence of liner, bosses, and overwrap. In order to get this far, spread sheet results (that solved the ODEs) had to be translated into scripts for a drafting package (in Visual Basic = VBA), which were translated two more times through DWG and into STL representations. Modern software tools appear nearly adequate to support CAM for these prototypes, but a wide variety of 3D and surface operations are simply not available in any of the advanced drafting or design tools. The equivalent of wrapping flexible components over surfaces could be solved purely geometrically (without computing stresses), but no tool appears able to compute even such idealized fiber trajectories.

Actual Fiber Trajectories

The problems that LLNL considered in validating its prototype design led to more detailed examination of real wound tanks to see what trajectories actual wound helical fiber follow. They build up in a “basket weave” pattern of layer atop layer, as shown below in Figure 7. These investigations showed the value of an even number of two widths around the circumference, so tows entering the dome could leave (cross back over the tangent circle that separates the cylinder from an end dome) with overlapping. Following tows through the overlaps showed that the fiber buildup ODE must break down even at radii larger than the minimum (boss port) radius because fibers couldn’t be created or destroyed. Fiber conservation makes structural sense, but the ODE’s violate it whenever some axisymmetric solutions have some fiber trajectories go purely circumferential.

Examination of actual trajectories showed that state of the art fiber buildup models were also failing to model 3D effects. The proprietary fiber build up models used for state of the art design were also trying to shoehorn trajectories into axial symmetry that actual fibers can’t follow. The more tows that attempt to cross at a given radium, the more levels of buildup occur in ways that can’t have axial symmetry. The LLNL tank design has a maximum of six tows crossing near the port radius, and was resized slightly to have 50 tow widths around the average circumference in order to prevent additional idiosyncratic overlaps. The reject (incorrectly manufactured) Thiokol #3 18x48” tank that was cut in half remains as a giant paperweight at LLNL, and its basketwork

confirmed LLNL staff recollections that Thiokol wound the record breaking tanks with four tows in a single band, effectively producing a fourfold larger deviation from the axial symmetry approximation built into its design.

The violation of axial symmetry, departures from ovaloid and geodesic trajectories, and the necessity of winding over surfaces with negative curvature were all apparent. Rough calculations show how easy it is for these effects to cause failure at pressures significantly lower than prediction. Any time a fiber bends, including the locations where it passes over or under other fibers in the basket weave, its local curvature generates large forces inward on the curve. These may balance out when averaged around the circumference, but they can locally load the composite wall in bending. Departures from the ovaloid curve just past the tangent line, where circumferential forces are transferred from hoop wraps to the just-bending-inward trajectories of the helical wraps appear particularly prone to nonaxisymmetric premature failures. Thiokol's (and other vendors') routine ability to 'terminate' a helical at a particular radius (get it to turn around at a chosen height on the dome) also appears likely to sacrifice strength in the dome because it violates geodesic (zero shear) assumptions and can thereby transfer some of the relative huge fiber stresses into the 50-fold weaker matrix.

Figure 7 – Close up of the end dome helical fiber winding pattern (on an SCI 9 ksi tank)

Advanced Container Geometries

When LLNL tank prototype design commenced last year, there was no expectation that better solutions were possible. This began to change when the potential advantages of surfaces with negative curvature were considered. Toroidal metal tanks may seem to be a specialized trick for packing spacecraft efficiently into cylindrical rockets, but other combinations of concave-outward and fluid-on-either-side surfaces also seemed to have tank mass advantages for Water Rocket spacecraft (that must store both compressed hydrogen and oxygen). This richer design space would be available to composite tanks if several unusual conditions could be met. Fiber trajectories should be continuous and uncut, but they need not follow the restricted class of concave-along-one axis that could be wound.

One of the most capable potential winding contractors LLNL expects to solicit composite fabrication from was also capable of a range of manufacturing techniques called fiber placement, in which fiber is molded where it belongs. Closed trajectories, like rings, pancakes, and pretzels can be molded in much more arbitrary paths. Such trajectories can clearly implement an "inverted bulkhead" of the sort found on the bottom of steel laboratory #1 compressed gas cylinders. These bulkhead designs are important for packing efficiency in

launch vehicles, having a concave-outward region that nests into the convex surface of an adjacent tanks. It was obvious that a variety of unconventional tanks designs could be built with closed fiber trajectories that could be mass produced, even if they couldn't be wound. Although molding is potentially far cheaper than winding (due it two or three orders of magnitude lower fabrication time on expensive machines), the first flavors of unconventional structure envision at LLNL had dubious advantages.

Re-entrant Bulkheads Become Foams

Besides being clearly beyond the capabilities of current software to render, identical tanks that fill space by nesting into one another's convex and concave surfaces demand more mass and fiber cost to do the same job as conventional tank shapes. Their advantages would come from the power of "learning curves" to drive costs down in volume production, and from their flexibility to deliver nearly arbitrary, higher storage density shapes from mostly invariant tooling. A standard 4" puffy, dented cube that nested with its neighbors to fill space could be assembled to efficiently address almost all vehicular applications, and could be produced by the millions to build just 10,000 cars. The cost, volume, and mass overhead of connecting a "foam of tanks" were obvious issues that might make small modular tanks produced in huge quantities advantageous or disadvantageous.

LLNL colleagues received early presentations of the "foam of tanks" concept, and came back with substantive questions that further expanded the possibilities. Their curiosity about why sphere were preferable in metal tanks but not composites led to a reconsideration of winding composite spheres. Figure 8 below shows an example of the non-axisymmetric winding pattern that was used inside golf balls to produce isotropic elastic properties (up until ~5 years ago, when the best golf balls got a preferred axis from variable density, solid cores). These same colleagues (Salvador Aceves and Gene Berry) were already investigating mass and volume 'efficiency' separately to compare various forms of thermodynamic and compressed hydrogen storage. The collaboration and critique prompted by these discussions suggested both the new formalism and the re-visitation of nearly-abandoned advanced materials popular in the 1980's.

Figure 8 Non-axisymmetric wound core inside golf ball (rubber band prevents unwinding)

Comparing Hydrogen Storage Subsystems

Mass efficiency hydrogen tanks is the beneficiary of at least 45 years of progress in rocketry. Space and space launch applications were able to afford the high development costs, which has now spun off products ready to adopt in a hydrogen economy. Those products extrapolate to today's advanced compressed hydrogen storage products, some of which DOE is funding to develop for demonstration vehicles. The next generation of products relies on nearly forgotten methods from the best funded days of that development process to save ~30% of the 50% in cost and mass LLNL projects is available from techniques already developed for other applications. Figure 9 below shows a typical design problem from that antique frontier, where

two teams were hired to design multiple failure loci to handle two pressure distributions by two methods:

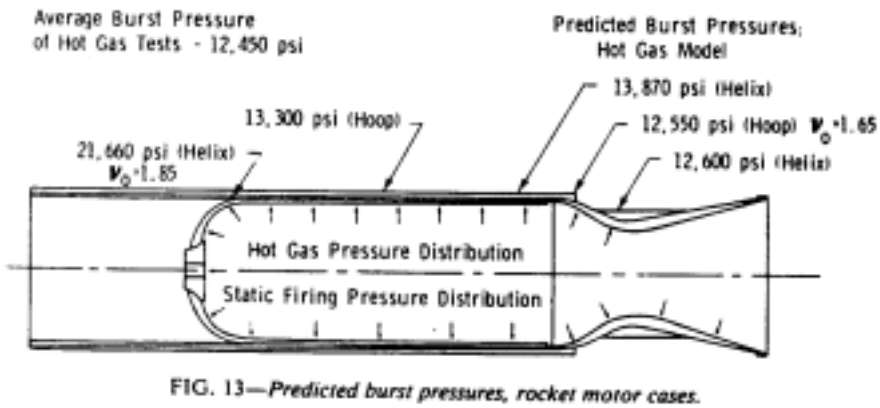

Figure 9 – Aerospace pressure vessel design performed by competing two teams

LLNL colleagues who have been working on vehicular hydrogen storage for road transportation found the aerospace emphasis on mass much less relevant for hydrogen fueled vehicle applications. Perturbations on existing vehicle models show motor vehicle mass increases are only weakly penalized by reduced vehicle range, unlike airborne vehicles which may not be able to fly at all if they get too heavy. The barrier to hydrogen storage adoption aboard many motor vehicles was its large volume requirement. Other applications, especially in the transportation infrastructure, care most about cost per unit mass of hydrogen contained. In an effort to speak a common language, the new formalism converts the range equation for aircraft into equivalent forms that normalize thrust per unit volume or per unit cost as well as per unit mass. Figure 10 below shows a typical aerospace partitioning of vehicle components into a hierarchy:

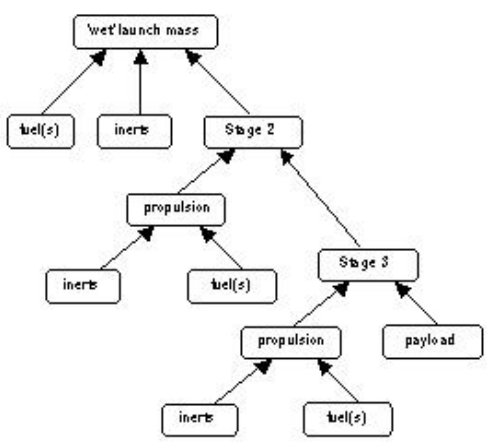

Figure 10 – Multistage aerospace (launch) vehicle component hierarchy

In order to incorporate considerations with such differing dimensions as cost (in $), volume (in cubic meters), and mass (in kg), this formalism borrows from the techniques called Dimensional Analysis and Similarity in Fluid Mechanics. Any quantity with a dimension is normalized by dividing it with a quantity of like dimension, to come up with a dimensionless form which can be

in a valid nonlinear relationship with other dimensionless quantities. Every stage and component in a hierarchy can be characterized by these dimensionless cost, volume, and mass ratios to its parent component. This extended the volumetric overhead that colleagues were exploring for the volumetric efficiency of cryogenic compressed hydrogen storage into a formalism powerful enough to treat and combine all three kinds of dimensionless ratios.

Non-Dimensional Performance Measures

The proposed new formalism considers a vehicle or application model as a black box, with dimensionless inputs and outputs. It can incorporate volume vs. mass vs. cost desirability by forming a cost function to optimize from arbitrary nonlinear functions of its dimensionless outputs. For arbitrary road vehicle black box models, the formalism suggested at the APR used Russian characters for its dimensionless quantities. The obvious dimensionless Inputs were: Ш (cruise Mach Number), Ð (Acceleration in gravities), Д (AR = Aspect Ratio, perhaps best defined for aerodynamic losses as forward cross sectional area over vehicle volume), and Лъ (work ratio $\Delta h/\Delta g$, equivalent to the fraction of work required to put the fuel in its stored state, a monotonic function of pressure). Obvious dimensionless output ratios included : Ъ (mass ratio), Э (volume ratio), Ж (dollars ratio), and Ю (range ratio) compared to a conventional benchmark vehicle. Customer desiderata can be formed into cost functions that combine these dimensionless ratios into strangely dimensioned quantities like dollars-per-mile.

On top of this dimensionless black box model, that could represent anything from a barge-deployed stationary power plant to a cargo dirigible to reformer-powered skateboard, the application designer who wants to serve customer demand with an optimized mixture of performance can employ the Calculus of Variations. This flavor of optimization has long been practiced in aerospace for computing trajectories under various constraints, and can be applied here for constrained optimization. A cost function composed from some arbitrary nonlinear combination of dimensionless outputs (e.g. min J = $/mi) can be minimized using Lagrange Multipliers to constrain other outputs (e.g. for constant demanded range constrain Ю = constant -> min J + λ Ю). This approach can come very close to what the motor vehicle customer wants, given functions of dimensioned variables that can actually be determined by market research.

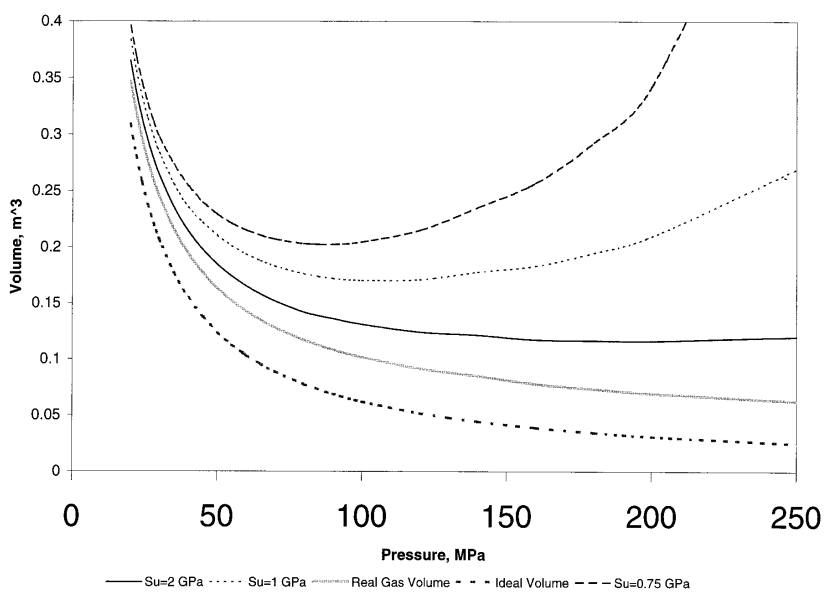

Figure 11 – Tank volume to contain 5 kg of H2 (300K) vs. pressure and wall strength

When this sort of optimization is performed for relatively conventional motor vehicles, their relatively low range sensitivity to additional mass (roughly the –0.3 power of mass perturbations) suggests a very different optima. Figure 11 above was generated by Gene Berry to include the volume overhead of tank walls and the mass overhead of empty tanks for compressed hydrogen. Although it is calculated in dimensional forma s a function of storage pressure, it could routinely be translated into a graph of Э (volume ratio) vs. ЛЪ (Work to ΔG ratio) for Type IV tanks

In this form, or rendered without dimensions, the curves in Figure 11 illustrate a broad optimum pressure that minimizes compressed hydrogen tank volume somewhere beyond 10,000 psi. Diminishing returns from real gas compressibility make pressures above ~15,000 psi unrewarding for all but the highest wall strength. The ratio between the mass of a full tank and the mass of its fluid contents Ъ (the mass ratio) is routinely computable from the corresponding Э (volume ratio), multiplied by the density ratio between fluid and average container density. These curves tell us that advanced structural containment has mass advantages that aren't highly rewarded by customers who want a particular vehicle range, but they can be traded for much more valuable volume advantages by optimizing to much higher pressures (10-15 ksi) than have heretofore been advocated.

Considering trading mass efficiency for more customer-preferable volume efficiency suggests that the utility of mass saving innovations is much greater than previously thought. Presuming constrained vehicle range agrees roughly with a 1/3-power direct relationship between mass ratios and customer economic disiderata like vehicle cost and vehicle cost per mile. But the same constraint agrees roughly with a 2/3-power relationship when mass is traded for volume by increasing storage pressure. All of the structural innovations that may not have been worth their development cost for aerospace must therefore be reconsidered to see if they are worthwhile for new applications in high pressure hydrogen applications. Other innovative structures, that might be in use in Achitecture or microscale Materials Science also merit consideration.

'Lost' Technologies

Among the structural geometries that now make sense for compressed hydrogen storage, nonaxisymmetric spheres wound with novel production equipment are almost certainly worth their development cost for next generation tanks because they save 33% of the mass required to implement infinite cylinders. Literature searching in pursuit of the extremely high strength composite materials that were 'fashionable' in the 1980's found many almost forgotten technologies that are now ripe for 'archaeology' and restoration in compressed hydrogen storage applications. The statistical qualification procedures LLNL had been relying on for ~60% of forecast next generation mass and cost reductions turned out to be on that endangered technologies list, with only one book on the subject published in 1981 whose key finding appears below in Figure 12.

Several classes of ultrastrong composite materials could offer factors of 1.5 –2 mass improvements, and deserve reconsideration. Metal matrix composites, particularly aluminum matrices which should be compatible with SiC coated high strength fibers, whiskers, and flakes offer the attractive prospect of matrix volume fractions below 30%. These and many ceramic matrix materials now in use for strong aerospace refractory applications could make their higher matrix density worthwhile because of their higher tolerance to the shear strains anticipated from non-axisymmetric effects in high pressure end domes. Most attractive among the nearly forgotten exotic materials are composites whose strong component is in the form of thin flakes. Instead of being strong in one dimension (1D) like fibers and whiskers, these 2D-strong components halve the mass of non-axisymmetric spherical tanks walls.

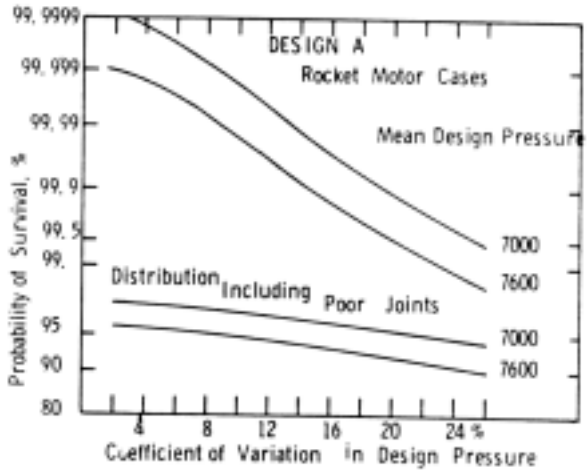

FIG. 12—*Influence of joint quality on structural integrity.*

Figure 12 – Dimensionless statistical performance of rockets similar to tanks, plotted for two choices of tank pressure (that could be normalized to matrix shear strength). Note tanks for motor vehicles need reliability near the top of this graph, and can avoid joints.

The use of stronger matrices than epoxy would do more than reduce non-axisymmetric effects, it would allow shorter coupling lengths to transfer force from one fiber component to another. This makes these materials ideal for building high performance tanks on centimeter size scales, or for filling space with structures even odder than foams of tanks. LLNL researchers can prove that random foams must be at least twice as heavy as structured foams, whether they are built with 1D or 2D strong composites. But open cell ordered foams can fill space with better mass and volume efficiency than nearly closed cell foams, if they can transfer forces from cell to cell. Such structures don't need fluid interconnects, although they do require a surface tiling of structural skin to hold gas in. Architects and Civil Enginers routinely resort to such structures when materials aren't strong enough to carry loads through a hollow outer shell. Figure 13 below shows two of the most advantageous space-filling structures that can be built from identical molded composite parts, if forces can be transferred between those parts in distances short compared to cell size:

Figure 13 – Two space-filling strut geometries ideal for composite mass production

There is also a fabric construction geometry called sprang that appears ideal for filling space with structures. Sprang was a popular craft for several centuries which was largely used to

construct net bags (too stretchy for fishing nets or clothing) and has largely been forgotten (only two book titles in print). Because sprang plaits closed loops of yarn that barely transfer load to one another, its implementation with fiber composites would face few shear transfer, cut end, or bent section strength loss mechanisms. Both struts that fill space and 3D sprang are the dual lattices that computational geometry can construct from closed cells foams (by replacing cells with vertices, faces with edges, edges with faces, and vertices with cells in Voronoi lattices). Figure 14 below suggests a heuristic rationale for implementing structural skins with a different kind of optimal structure than the best structure that fills volume, because Nature found this optima:

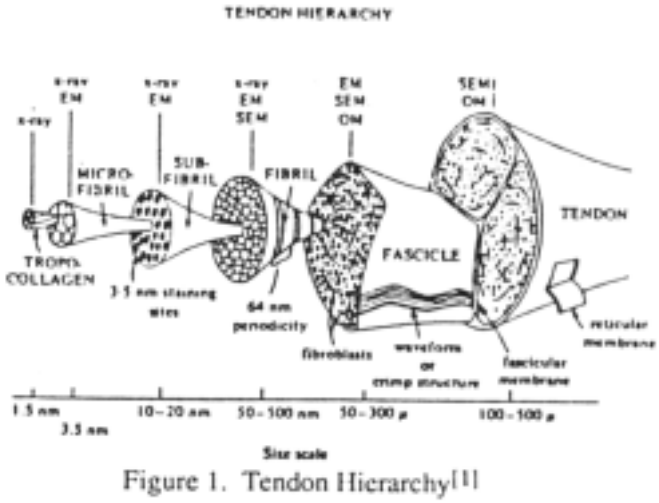

Figure 14 – Illustration of a proven biological structural optima (from the only Conference Proceedings on Hierarchical Structures) suggests surfaces built unlike strong contents.

Two other recoveries from archeology at the Stanford Engineering library (which holds 30 shelf-feet of books on composites, roughly 30% relevant to hydrogen containment structures or materials) deserve mention. The first appears below as Figure 15, and may be the most difficult to realize structural innovation 'recovered' herein. Prestress is routinely used to maximize the stress capability of structural components (e.g. concrete held in compression by pre-tensed rebar and scratch resistant coatings deposited on hot surfaces that remain in compression when thermally equilibrated). Since pressure would load a composite structure in only one direction, while microscopically materials are strong in both directions, this offers the prospect of another doubling in mass performance if structural elements could be prestressed into compression.

The other successful excavation is the only reference found so far to a mechanism related to the abovementioned mechanism than hypothetically results in "turn to dust" failure morphologies. Hypothesized tensor debonding instability waves could be propagating along the strong fibers at perhaps 6 km/s, outrunning the much lower speed of sound in the matrix. If failing the bond between matrix and fiber can liberate strain energy that feeds this solitary, anisotropic wave this hypothesized mechanism could dump the megajoules of elastic energy stored safely in material well below is failure limits, creating a lot of free surface where the solid tank wall used to be. These failure modes occurred at only 45% (down to ~35% at Sandia) of fiber failure stress, and occurred so fast that they must either rely on propagating disturbances in a high speed of sound material or a very uniform nonlocalized mechanism yet to be identified. The reference shown below in Figure 16 used the term "debonding wave" for the explosive disintegration of a particulate (zero-D) composite of polyethylene spheres in phenolic.

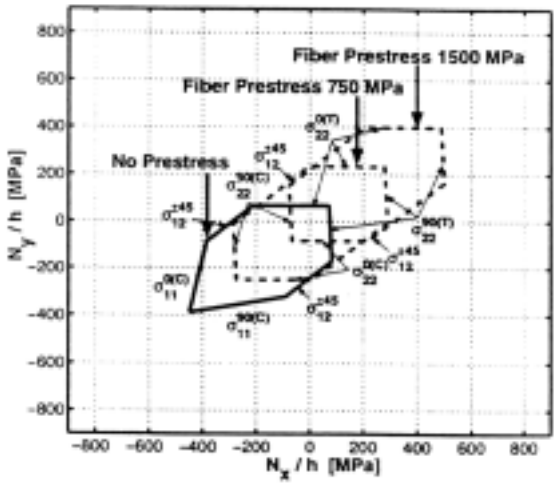

Figure 15 – Prestress shifts the center of safe stress in two axis composites

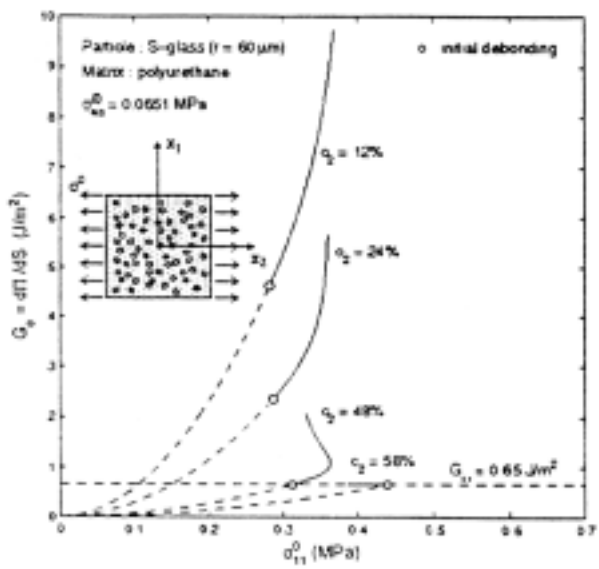

Figure 16 – Scalar debonding wave theory and experiments possibly relevant to Figure 2