Hydrogen Storage
Using Lightweight Tanks

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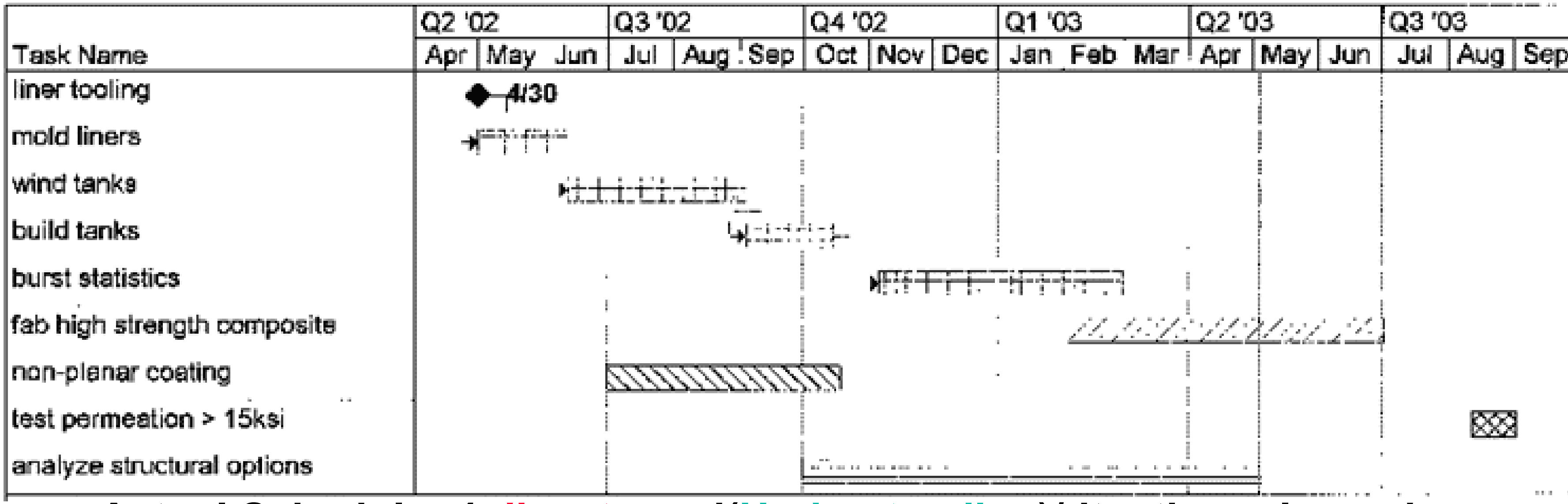
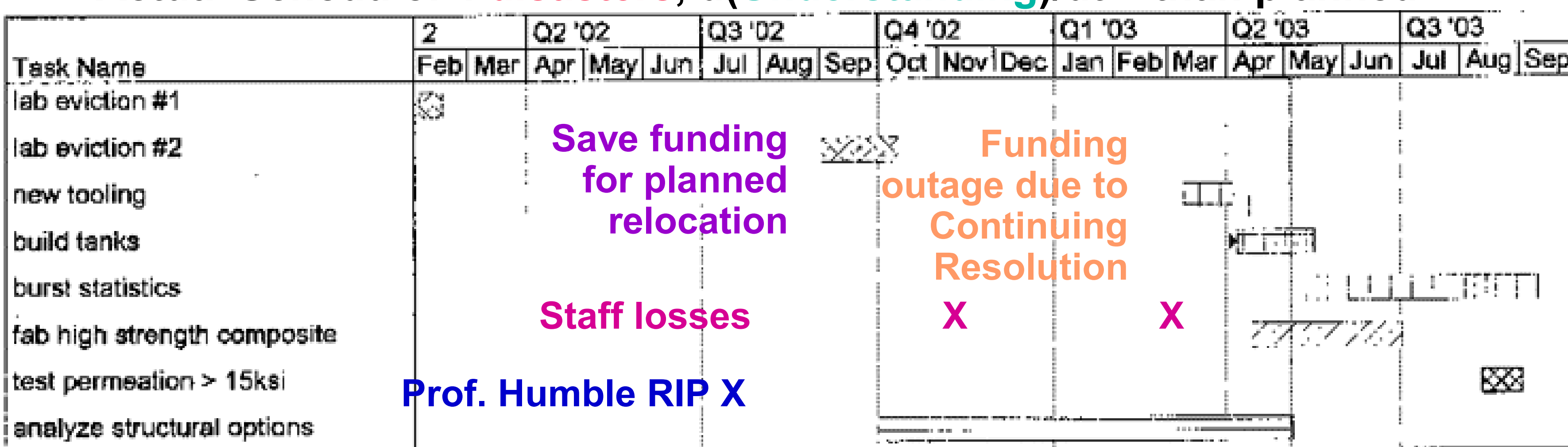
Project Trajectory Through 2002 and 2003

- Tasks predicated on *predictable* funding and facilities occupancy
- Operating Plan for FY02 presumed eviction from 50% of lab space



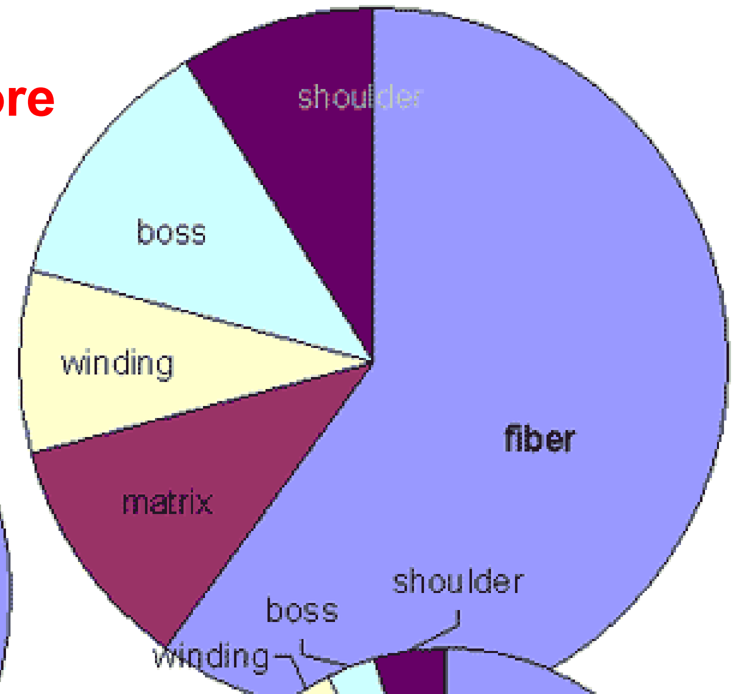
- Actual Schedule: 4 disasters, d(Understanding)/dt > than planned



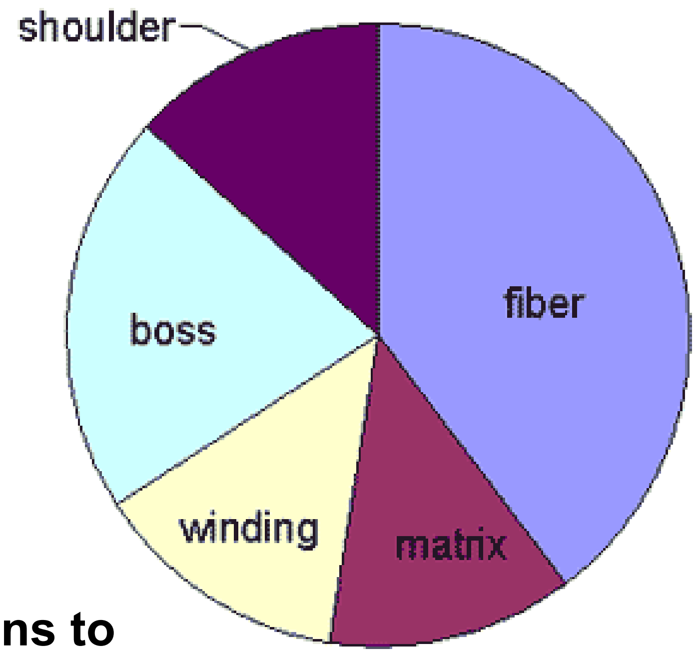
Cost Reduction Strategy (Advanced Type IV Tanks)

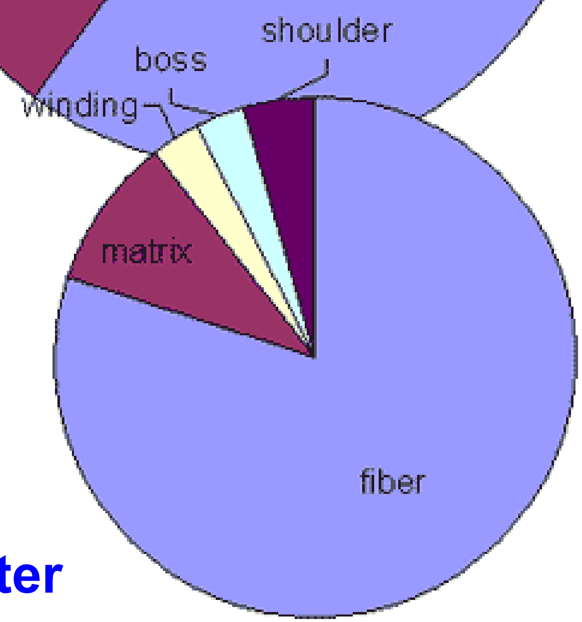
Promised approach to cutting costs of advanced compressed hydrogen tanks by factor of two

Before



Savings

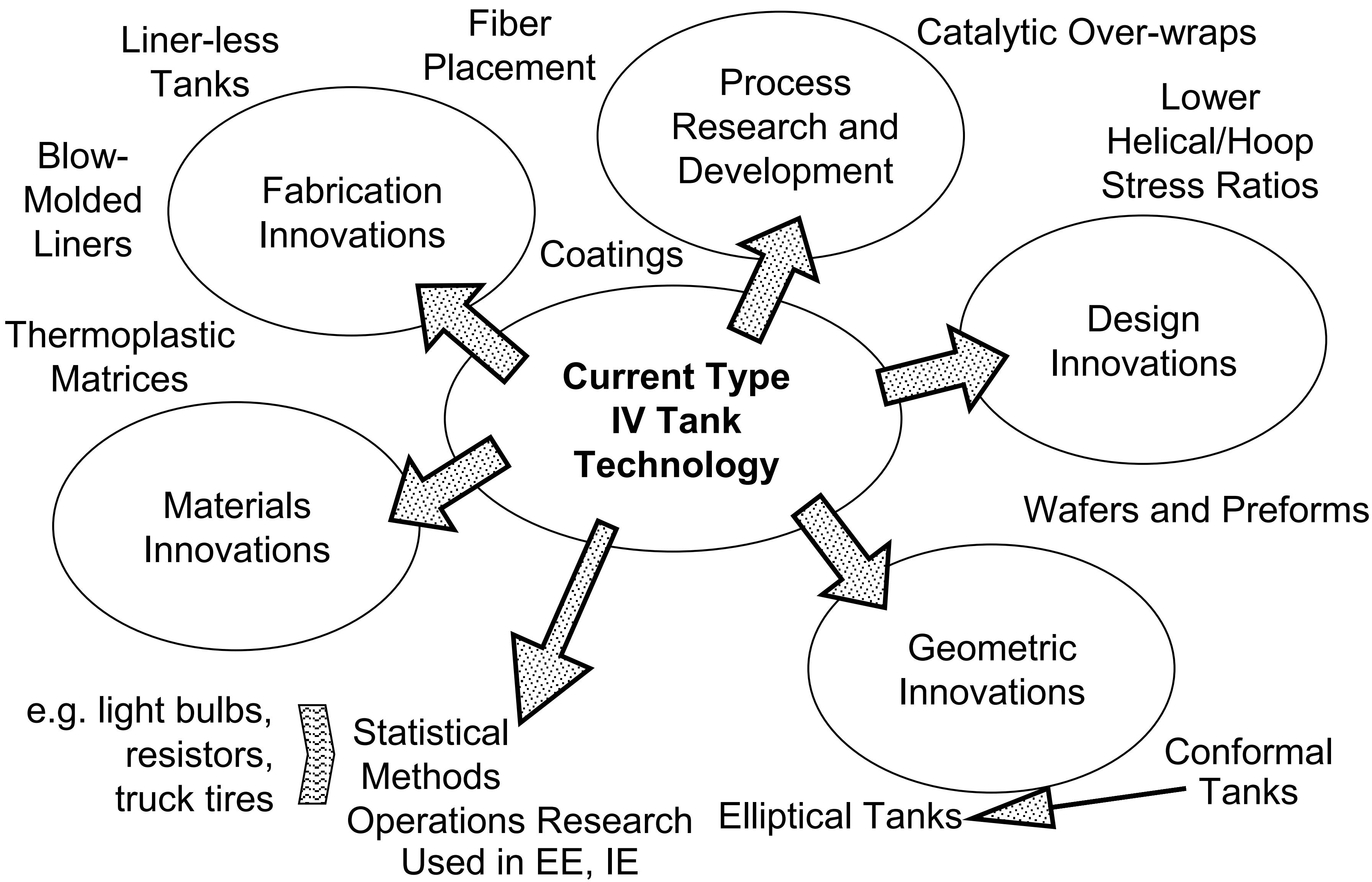




After

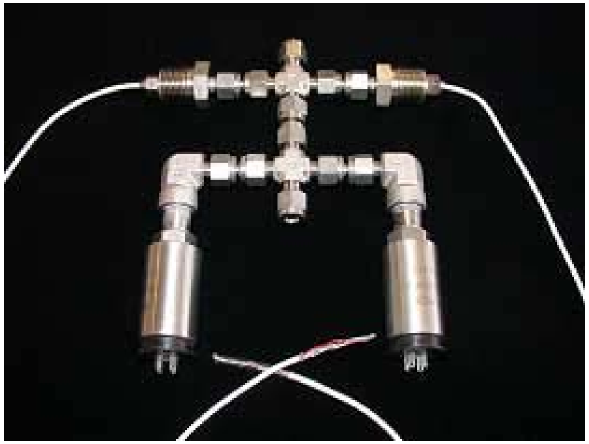
Comparisons to FY01 cost projections (confirmed in discussions with Quantum and Alliant) with updated fiber cost

Avenues for Improvement [Projected in FY01]



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…]

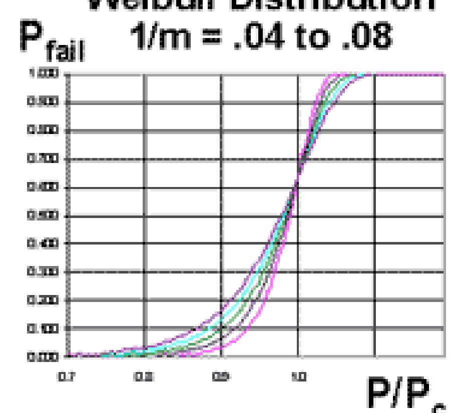


Sensors measure Pburst

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



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 Disribution**

Weibull distribution

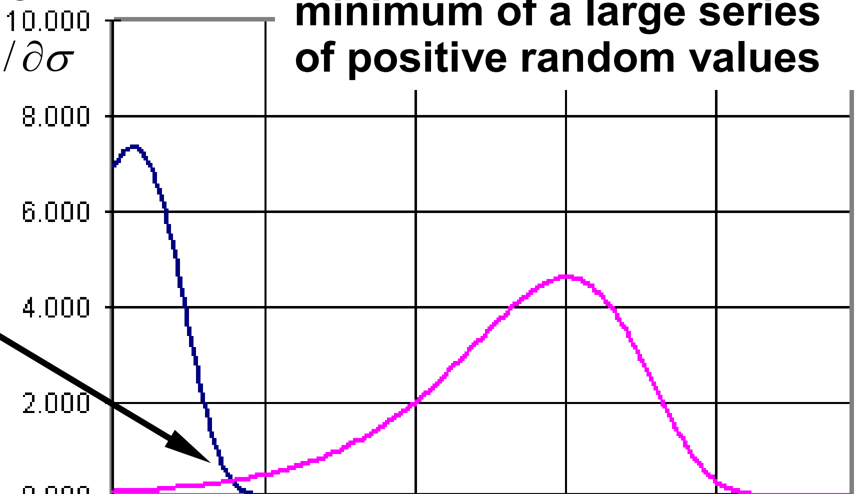
$$P(\sigma) = 1 - e^{-(\sigma/\sigma_c)^m}$$

$$p(\sigma) = \partial P / \partial \sigma$$

The other "extreme value" distribution (vs. Gaussian) correct in the limit of the minimum of a large series of positive random values

- **Risk of 'suppressed' failure modes with higher variance is neglected in current safety standards – not good enough for thousands in service!**

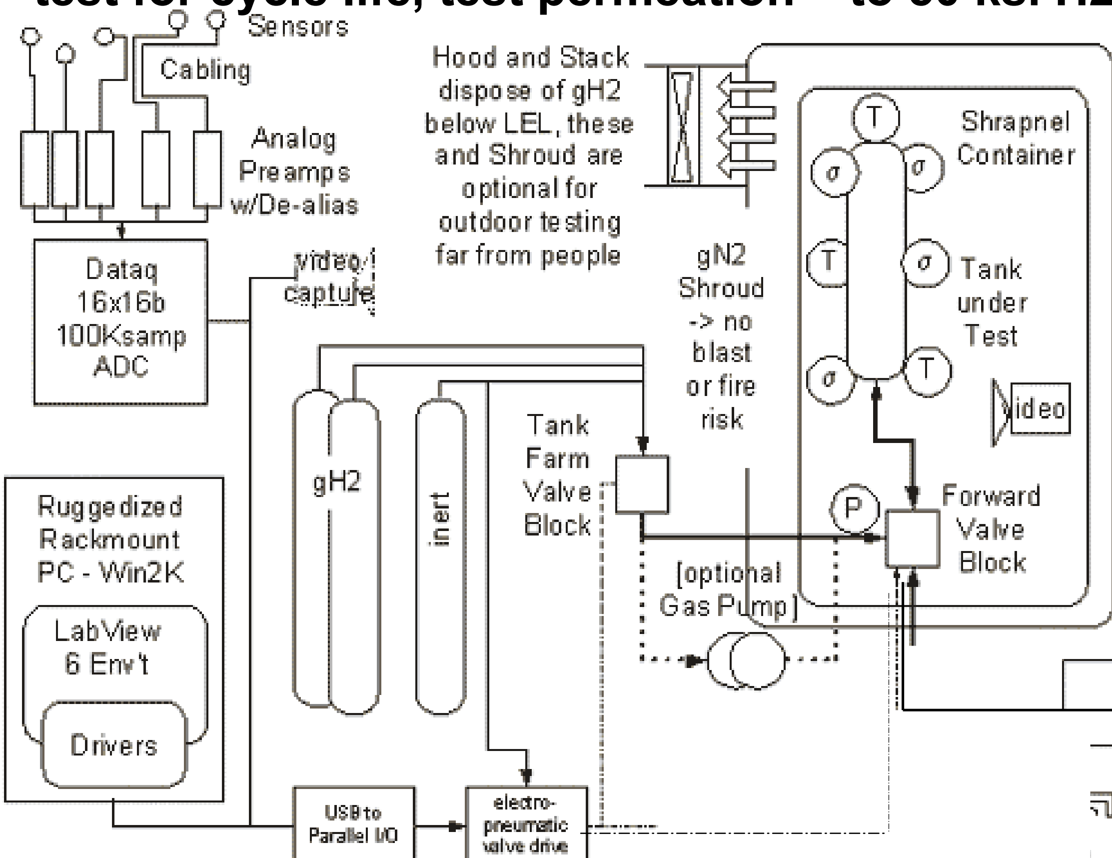
Overlap of 1/m=.05 and 1/m=.08 with "safety factor" of 1.3

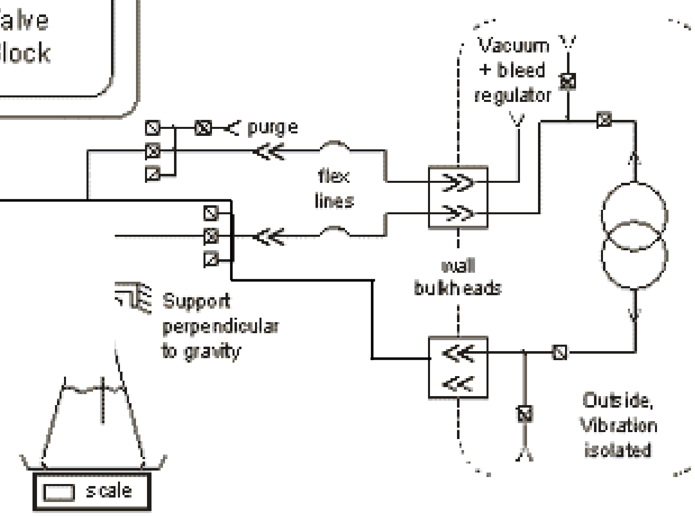


- **Recommend insurance requirements, European-required batch testing**

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**

Deferred Advanced Tankage Research Topics

- **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-metalics, densified xerogels?
  - **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 cycling above yield stress

    few plastics remain elastic beyond 10,000 psi, defects build up
- **Safety Innovations – several attractive possibilities**
  - **Strain energy in compressed storage could be advantageous**

    Megajoules stored in elasticity and PdV work are released by failure

    Compares to Gigajoules of chemical energy in stored hydrogen
  - **Sonic Disposer 'Nozzles' (hydrogen is very difficult to ignite)**

    Flame speed ~60 m/s easily exceeded by sonic jets from cracks

    Controlling how a container breaks can eliminate ~5% risk of fire
  - **Dust instead of shrapnel observed in > 3 different test programs**
- **'New' Physical Instability –> basic research + safe disassembly**
  - **Tensor 'debonding' waves presumed to dissipate strain energy**
  - **Faster than 4,000 frame/sec cameras -> arduous instrumentation**

“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

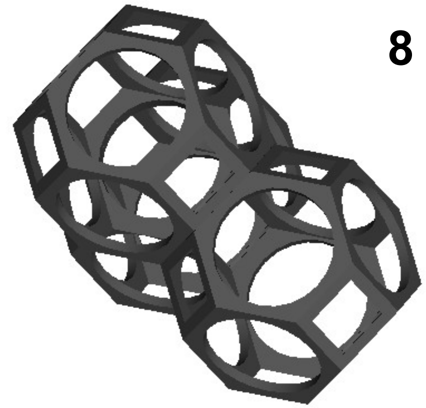
- Stress ratio (helical / hoop) “too high”
- Dome failure activated – high dispersion
- Real manufacturing problems on dome

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

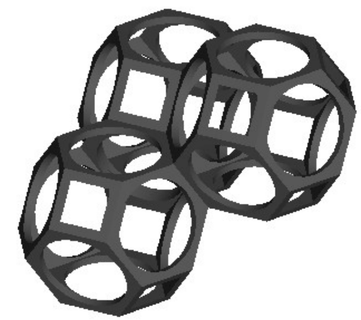
This is a repeatable class of failure modes with the potential for new Science and Engineering (designer failure modes)!

The Ultra-Conformable Zoo

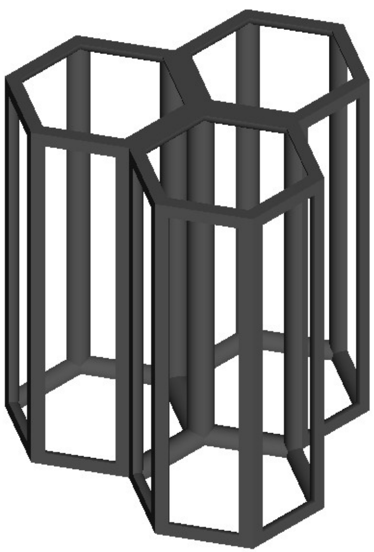
- **Initially believed fabrication easiest for hexagonal facets of truncated octahedral cells**
- **Discovered that curvature at corners of closed-trajectory faces implied excessive shear stresses that would fail matrix**

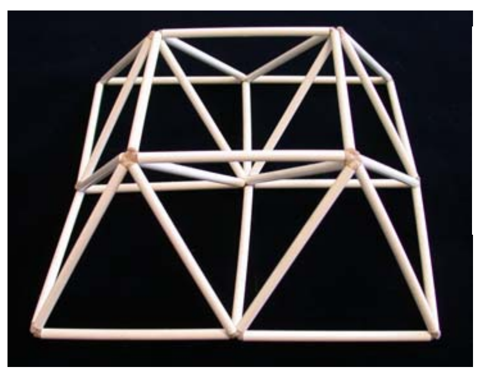


8 ‘wound’ faces (nearly rings) can assemble to fill space

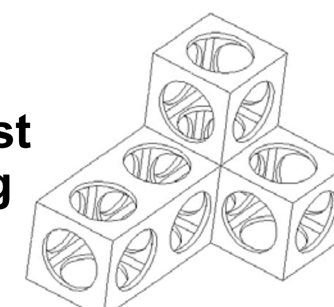


- **Problems with radii of curvature are fixed by trusses whose replicated fiber struts don’t cross**





- **Fuller’s “Octet Truss” is strong in shear, which may or may not be a feature, compared to cubic**



- **Cubic best for strong biaxial materials**

- **Solid modeling of replicates non-trivial, hexagonal-closed-packed cell was easiest to render, builds slabs with skins**

Macrolattice Replicates

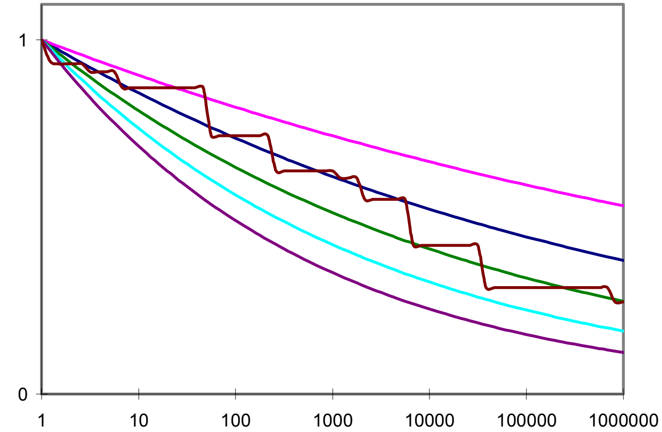
- **Mass produce identical parts**

  - **Speed down the "Learning Curve"**

    Millions of parts for just

    hundreds of vehicles !

Learning Curves



- **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

  - **A 'vocabulary' of geometries from a fixed lexicon of parts (more is richer)**

Advanced Materials = Worthwhile Frontiers

- **Metal Matrix Composites**
  - **Modification of max-strength continuous fiber = 10 Gpa failure graphite**
    - Only ~30% worse mass performance than epoxy matrix with same fiber
    - But ~3X higher shear strength reduces minimum cell size of macrolattices
  - **Whisker composites – diamond whiskers at 5 Gpa**
    - Dissolve in molten Al, but SiC coating found to allow *castable* mixtures
    - Mass performance ~50% worse than 10 GPa graphite in epoxy
      - Compares favorably to most economic 5 Gpa graphite-epoxy, lower cost!
  - **Nanocrystaline structures**
    - Some CVD and xerogel deposition methods produce spirals 20-300 nm
- **Nanolaminates – an LLNL innovation sputtered 2m meters wide**
  - **Soon to be deposited by sputtering with roll-coater (DOE funding)**
  - **Only 500 MPa failure, but strong in two axes and no matrix**
    - Comparable volume to most economic graphite-epoxy, but ~2.5X mass
    - Extremely flexible and tough -> tanks that bounce, ideal macrolattice skins
- **Nanolaminate 'Adhesives' – chemical energy fuses thin films**
  - **Likely can bond metallic thin films with >250 MPa shear strength**
- **Amorphous Metals – 2002 MRS 500 MPa, cheapest two-axes-strong**
- **Deep Compression – if prestress can be induced, $Al_2 0_3$ at –13.5 GPa**

Mass-Performance Horizons

- **Potential to exceed incremental progress in physical containment**
- **No manufacturers will be harmed by funding basic research**
  - **Test articles capable of hydrogen storage are *not beyond 2012 horizon***
  - **Materials Scientists have yet to work on relevant structural performance**

    Considerable work on wear resistance, hardness, toughness, refractories
- **Factor of ~14 mass reduction (applicable at any T) is conceivable:**
  - **First factor of 1.5X comes from empirical statistics sought in this project**

    Might be pushed as high as ~1.8X for millions of units tested (macrolattices)
  - **Another factor of ~1.05X comes from several liner innovation prospects:**

    Thin liners = prestress Elgiloy –0.3%, POSS Oligomers, spin glasses and

    Linerless (e.g. DCPD matrix) and/or coatings << combined high probability
  - **Another factor of ~1.15X is available from packaging innovations:**

    Regulatory relief from incompetent installers = no shoulder pads (3 ways)

    Miniaturize bosses, pre-fab center of end-dome, smaller in-tank fluidics
  - **Process innovations that push fiber fractions above 70% -> factor 1.3X**
  - **Next factor of 1.5X comes from geometric innovations, with decrements:**

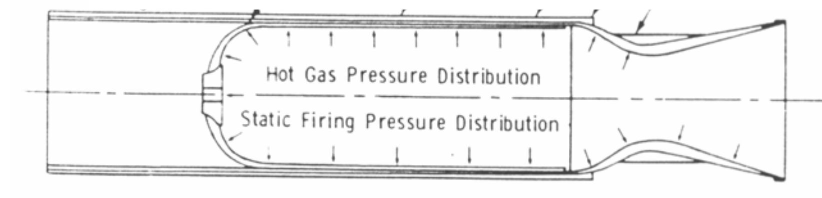
    Non-axisymmetric winding of spheres saves 1.5X but wastes > 12% volume

    Macrolattices and Hierarchical Structures tradeoff in mass overhead ~10%
  - **Factor as high as 1.9X (most fibers) available if pre-stress can be built in**
  - **Factor of Two available from materials with strength in two axes, not one**

Why Storage Mass Matters

- Range at cruise limited by drag
  - Power from fuel enthalpy ζc^2
  - Energy-per-unit-volume wins
  - Volume fraction of vehicle
- Appears to make mass irrelevant !
- Hard to reconcile with Aerospace

$$\text{Range} = \frac{2\rho_E \eta \zeta \Lambda \sqrt[3]{\text{Volume}}\,\text{Á}}{\rho_{Air} \Gamma M^2}$$



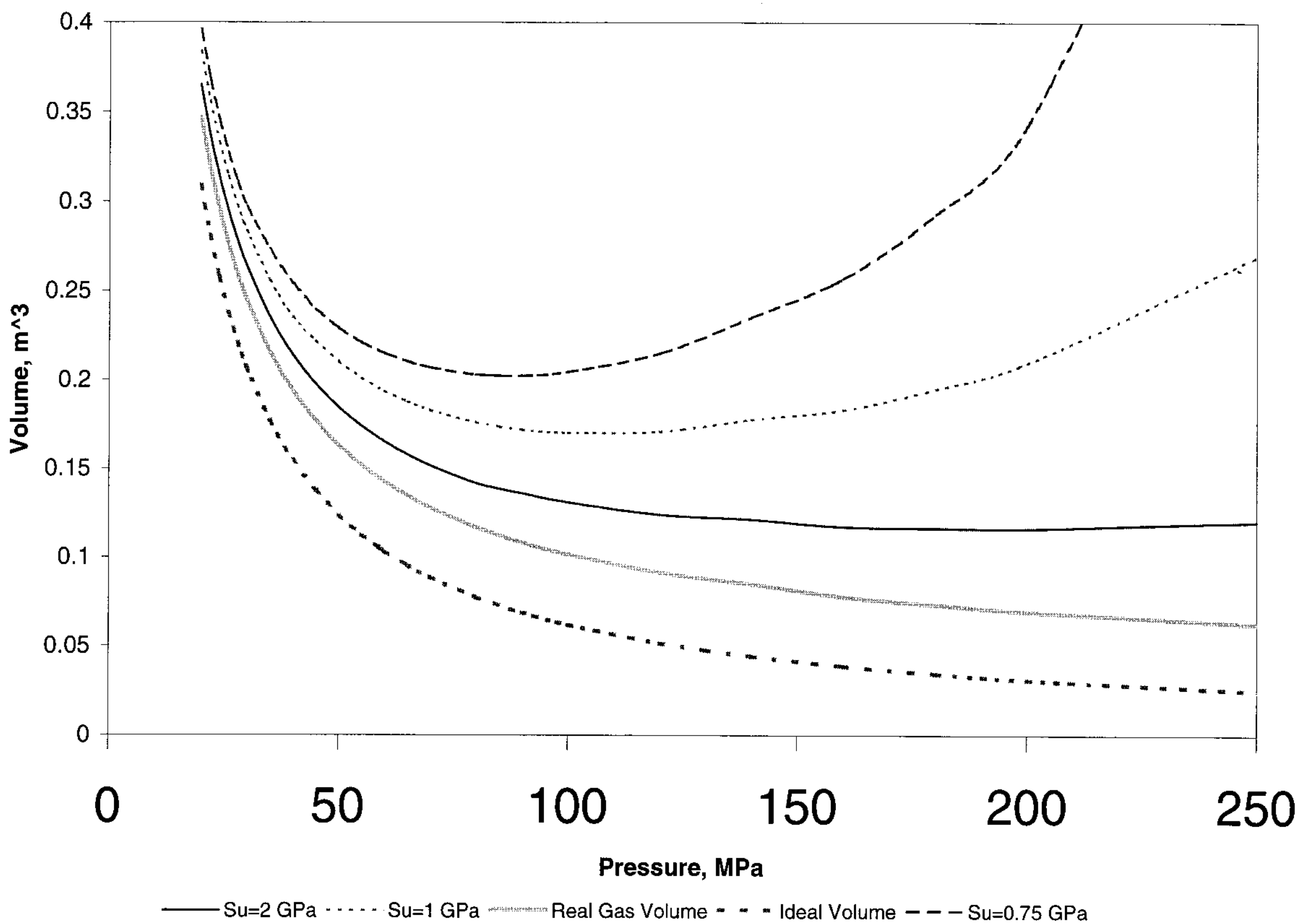
$$\text{Range} = \frac{2\eta\zeta\Lambda m_{total}\,\text{qF}}{\rho_{Air}\,\text{Volume}^{2/3}\,\Gamma M^2}$$

- drag limited range in mass fractions
  - Same role for enthalpy $h = \zeta c^2$
  - Energy-per-unit-fuel-mass here
  - Mass fraction of vehicle in fuel
- Still depends on vehicle volume but 2X stronger dependence

- Note dependence on total mass
- "Clean sheet of paper" analyses, but
  - Assumed total mass and volume were specified independent of ζ and ρ
  - Either form is only true as a perturbation that doesn't change totals
- Perturbation theories break down when mass or volume fractions -> 0.1
  - This is the case for 300 mile range with current physical and chemical hydrogen storage, but not for < 150 mile range – a "dirty sheet of paper"
  - Hydrides don't directly falsify volumetric range equation, physical does

Widely-Applicable Conclusions

Graph t (volume ratio) vs. ζ (Work to ΔG ratio) for Type IV tanks



F (mass ratio) computable from t (volume ratio) X density ratio

Dimensionless Notation

- **Symbology facilitates comprehension**
  - **Too easy to confuse volume and velocity**
  - **Subscripts don't immediately decode**
    - Volume vs. mass vs. power fractions
    - Which quantities are bounded < 1
  - **Show by inspection what has dimensions**
- **Use of Greek characters** →
  - **For dimensionless quantities, usually > 0**
- **Only exception is ρ, used for density**
  - **Others non-dimensionalized via c and g**
- **Use of Kannada characters**
  - **Table below shows fractions of total:**

	mass	volume	cost	power
Energy storage	gÀ	Á	o	D
fuel available	F	t	<- energy fractions	
Power Train	vÀ	9	«	P
Structure	Ui	Q	M	
Payload	£À	zÀ	—	ò

Μ = Mach Number = velocity/sound-speed (c ~ 300 m/s)

Λ = Aspect Ratio = AR = frontal-area/spherical-surface-area

Γ = Drag Coefficient = Cd = drag-force/kinetic-pressure*front-area

Ψ = Lift-to-Drag Ratio = L/D = lift-force/drag-force

μ = Coeffiecient of Friction = friction-drag-force/normal-force

Ξ = Avogadro's Number = particles/mole

ϖ = Average Molecular Weight = grams/mole

γ = Ratio of Specific Heats = Cp/Cv

η = Efficeincy (power application) = power-delivered/power-consumed

ϕ = dimensionless acceleration = Thrust/mass*g (g = 9.8 m/s2)

φ = Mass Overhead = added-mass /functional-mass

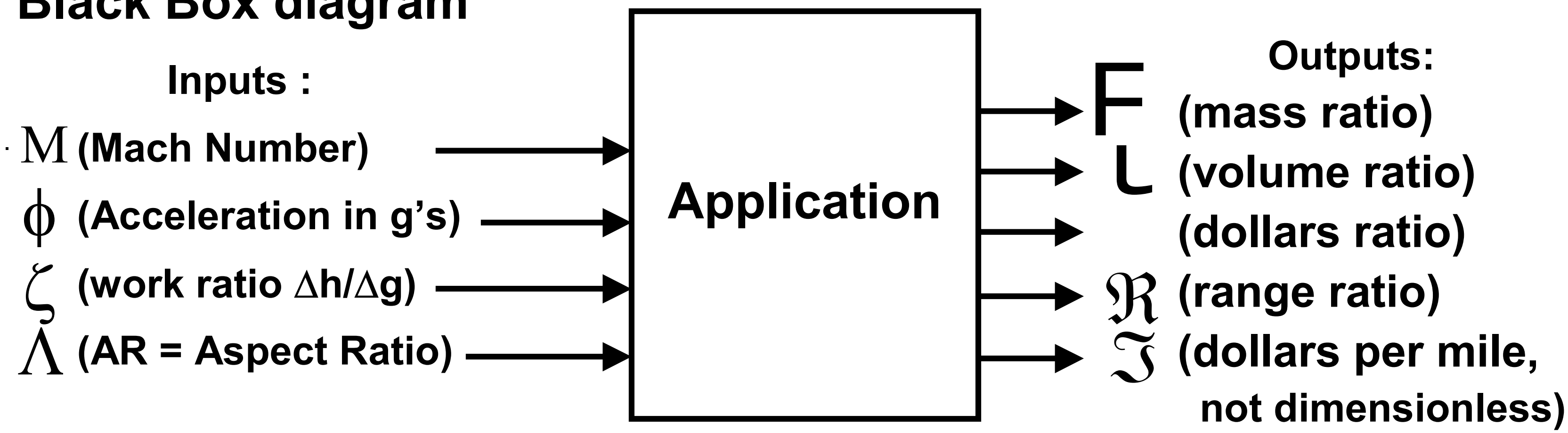
ϑ = Stress Coupling Ratio {at Ncycles} = shear-stress/fiber-tensile-stress

ζ = dimensionless specific strength = Joules/kilogram*(speed-of-sound)2

ξ = dimensionless specific power

Mixed Dimensionality Theory

Black Box diagram



Calculus of Variations for constrained optimization (e.g. min J = $/mi)

Use Lagrange Multipliers to constrain (e.g. = constant -> min J + $\lambda \Re$)

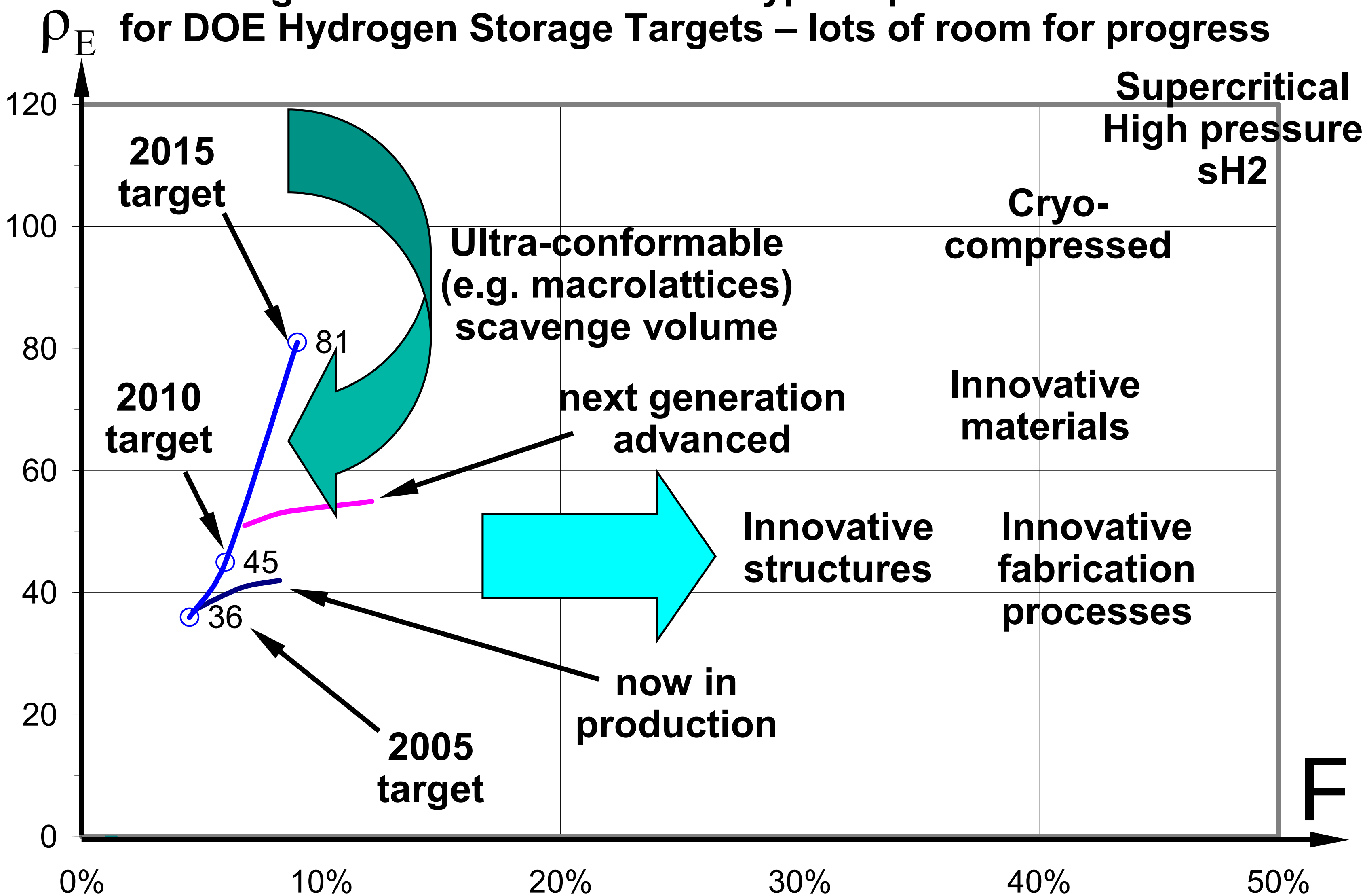
- **Mass partitioning derived from rocketry** $\pounds = 1 - q - V - U$
  - **The "Rocket Equation" non-dimensionalized:** $q = \exp\left(\left|M_{final} - M_{initial}\right| / M_{exhaust}\right) / F$
- **Extended to the Aircraft Range Equation:** $\Re = \mathrm{Range} * g/c^2 = \Psi\, \eta\, \zeta \ln\left(1/1 - qF\right)$

  where ζ refers to fuel enthalpy $/c^2$ and η is thrust efficiency
- **Applies directly to vehicles whose power goes into friction** $\Psi \rightarrow \mu$
- **Solve for and eliminate Lagrange Multiplier with:**

$$\partial(J + \lambda \Re) / \partial V = 0 \quad \lambda = -V m_{total}\, g(\partial J / \partial[V m_{total}])\xi / \zeta\eta M \quad \Re = \frac{q}{V}\left(\frac{\zeta}{\xi}\right)\eta M$$

Strategy for Exceeding DOE Targets

- Current generations of advanced Type IV pressure vessels on track for DOE Hydrogen Storage Targets – lots of room for progress



More Economic Correlates, Collaborations

Miles-per-dollar delivered by truck in a Mobile Infrastructure = same issues

Optimal pipelines will not just re-use (add liners in) existing CNG pipelines

Using Costlier Materials makes sense for enabling applications, small scale

Laptops > Remote Power > Prostheses (cleanliness) > Small Vehicles

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.

Three other DARPA projects have started over the past year with contributions from the PI, including the popular launch-on-demand vehicle RASCAL and 3 versions of the Eyeglass Space telescope.

Long term collaborations with academics have been underway with Stanford, Berkeley, and Purdue. The small tankage prototyping and test capability LLNL is developing is intended to re-ignite academic research into containment structures. Private sector vendors have learned to furnish liners, and entire test rigs, allowing ~one-PhD-per-$100K funding levels. These vendors have been prepared to contribute to the ONRL-managed academic outreach program, so that DOE can sponsor the most cost-efficient research into hydrogen tankage. Other sponsoring agencies besides DOE have mandates to fund advances in Mechanical Engineering, Material Sciences, and Computer Science at PhD levels.