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Enhanced Materials and Design Parameters for Reducing the Cost of Hydrogen Storage Tanks

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Project ID # **ST101**

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Overview

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Timeline

- Start date: Jan 2012
- End date: September 2016
- Percent complete: *90%*

Budget

- FY16 DOE Funding: $387K
- Total project funding: $2,625K
  - DOE share: $2,100K
  - Contractor share: $525K (20%)

Barriers

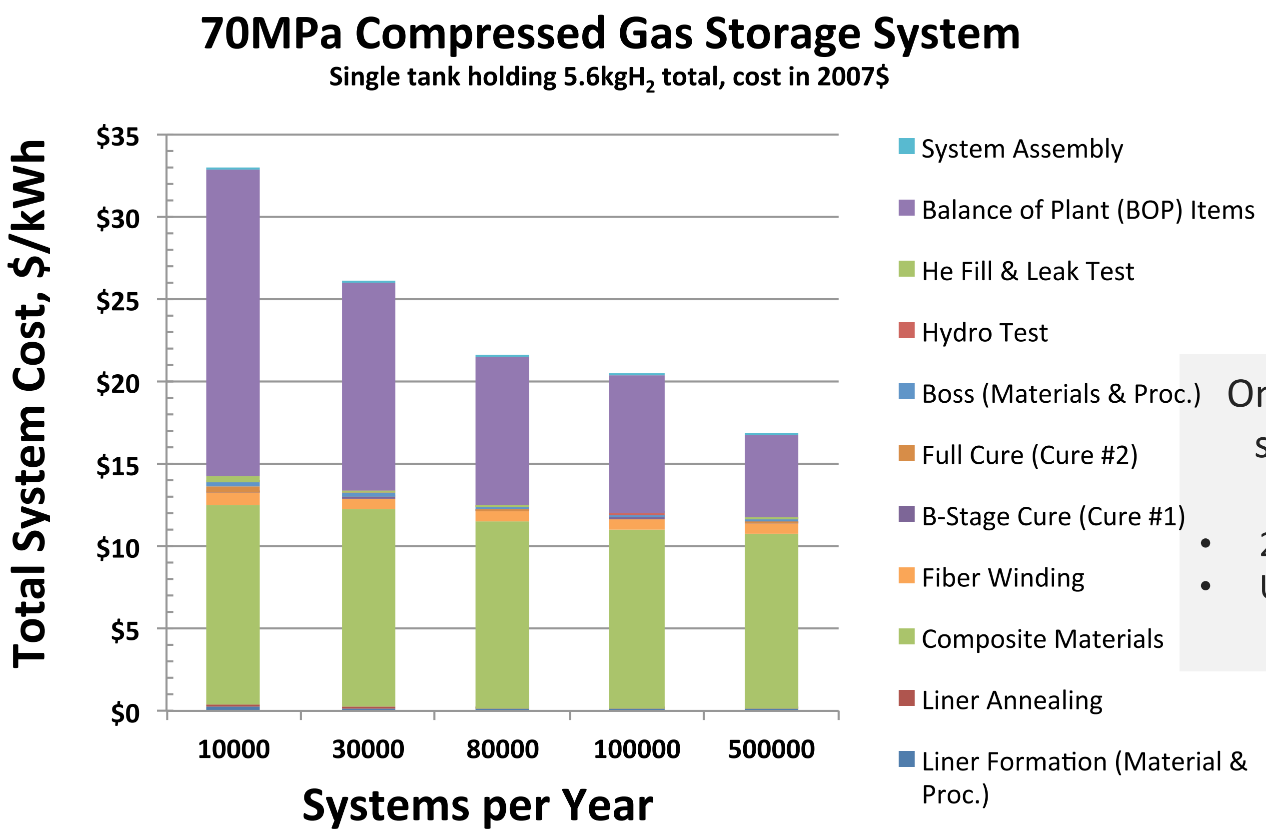
- E: System Cost
  - Alternate low cost resin
  - Improved winding efficiency
  - Cold gas storage
- G: Materials of Construction
  - Alternate resin and fibers
- J: Thermal management
  - Low cost insulation for cold gas

Partners

- Hexagon Lincoln
- Toray CFA
- AOC, LLC
- Ford Motor Company

Relevance

System Cost Analysis Study
2013 DOE Hydrogen Storage Record



500k System per Year
System Cost: $3,134
$600/kgH$_2$
$17/kWh

Onboard automotive hydrogen storage system cost targets:

- 2020 - $10/kWh of useable H$_2$
- Ultimate - $8/kWh of useable H$_2$

Project Approach and Accomplishments

Approach: Improve individual constituents of **materials**, **design** and **operating conditions** to synergistically enhance tank performance and reduce cost.

700 bar compressed tanks can meet the DOE targets except:
cost, volumetric capacity, and weight

OPTIONS

Material Selection

Reduce material cost

Increase performance

Tank Design and Manufacturing

Better material use

Improve efficiency

Operating Conditions

Reduce pressure

Increase density

PROJECT SCOPE

Alternative low cost resin
Resin with nano-particles

Optimize fiber pattern
Mix different fiber types

Cold gas storage concept

FY15 Milestones

Milestone Name/Description	End Date	Type	Status
Impact and burst testing of Hexagon Lincoln reference tanks with new resin system	12/31/15	Quarterly Milestone (Stretch)	Complete
Demonstrate low cost insulation performance for cold gas storage and demonstrate feasibility of modified fibers and resins at enhanced operating conditions	3/30/16	Quarterly Progress Measure (Regular)	Complete
Burst testing of demonstration tanks at 200 K and build of an insulated tank to demonstrate thermal characteristics.	6/30/16	Quarterly Milestone (Stretch)	In progress

- <u>FY16 Major Accomplishments:</u>
- Low cost resin alternative tested for fatigue and impact performance
- Nanoparticle reinforced resin tanks tested
- Low temperature testing of all key materials for tank and system
- Burst testing of low temperature tanks
- Enhanced operating condition insulation tested

Vacuum Vessel Insulation Cost, Volume, and Mass

- TIAX performed cost analysis of the vacuum vessel insulation for the LLNL Gen-3 cryo-compressed tank (Lasher, 2010).
- Aceves et al (2010) lists the Gen-3 tank dimensions and the added mass and volume of the vacuum insulation system.
- This information used to estimate the multi-layer insulation cost as $135/m^2 of the pressure vessel surface area.
- The cost estimate includes insulation wrapping plus initial evacuation.
- Vacuum vessel cost estimated as $26.6/m^2 of the vacuum vessel surface area.
- Added mass and volume scaled based on the insulation volume.
- Cost analysis by PNNL (HSECoE) and SA showed similar insulation costs with slight differences in material and processing cost.

Aceves, S., F. Espinosa-Loza, E. Ledesma-Orozco, T. Ross, A. Weisberg, T. Brunner, O. Kircher. 2010. *High-density automotive hydrogen storage with cryogenic capable pressure vessels.* International Journal of Hydrogen Energy, Elsevier, Vol. 35, Issue 3, pp. 1219-1226.
Lasher S, et al. 2010. Analyses of Hydrogen Storage Materials and On-Board Systems. Project ID #ST002. 2010 Annual Merit Review, Hydrogen Storage, Arlington, VA, June 7-11, 2010. TIAX LLC, Lexington, MA.

Technical Accomplishment - Cost Analysis Reduction Opportunities

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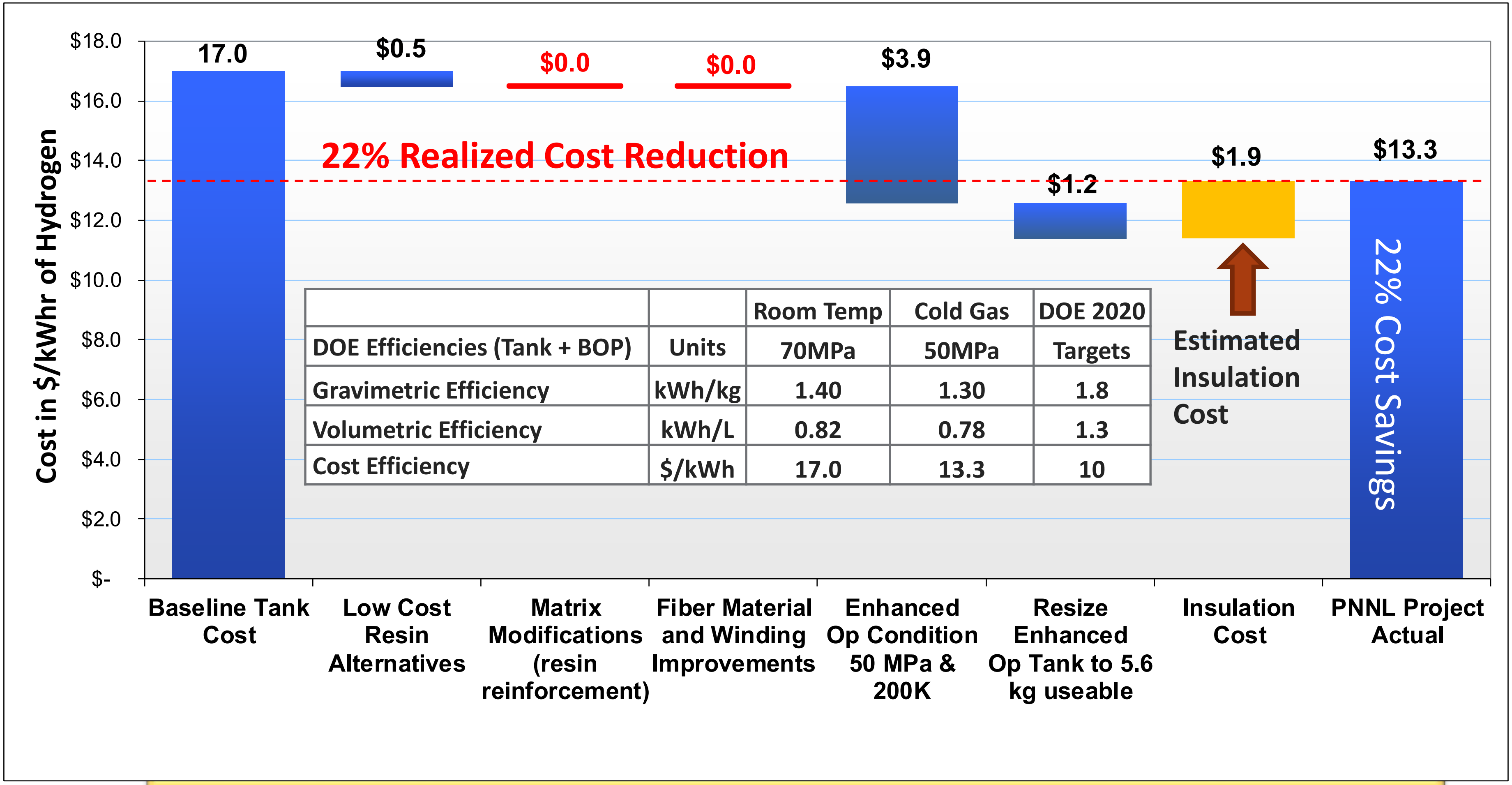
70 MPa H2 Type 4 Tank Cost Analysis Projections

5.6 kg useable H2 (baseline system cost based on DOE's 2013 700 bar storage system cost record)

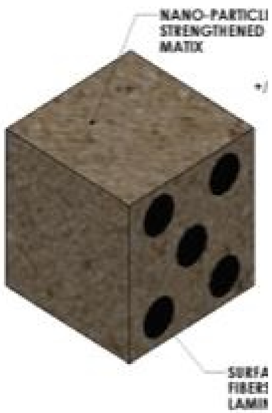


		Room Temp	Cold Gas	DOE 2020
DOE Efficiencies (Tank + BOP)	Units	70MPa	50MPa	Targets
Gravimetric Efficiency	kWh/kg	1.40	1.30	1.8
Volumetric Efficiency	kWh/L	0.82	0.78	1.3
Cost Efficiency	$/kWh	17.0	13.3	10

Reinforced Resins Have Not Improved Burst Strength to Date.
Fiber Type and Winding Pattern Near Optimum.

Technical Accomplishment - Resin Improvements and Modifications

- Develop vinyl ester resin
  - Lower cost alternative to epoxy
  - Viscosity and gel time to match Hexagon Lincoln's winding process
  - T700 standard sizing and tow
  - Smaller tow (12k) with sizing selected for VE resin
- Modify resins with nanomaterials
  - Tested two materials in full tanks
    - Carbon – Ashbury Nano 307
    - Silica Nano Fibers (SNF)
  - No improvement observed, but large increase in burst variation
  - Continuing to evaluate other commercial resin additives



Material Selection

Reduce material cost

Increase performance

↓

Alternative low cost resin
Resin with nano-particles

	Target Savings	Demonstrated
Low Cost Resin	$0.5/kWh	$0.5/kWh
Resin Modifications	$0.7/kWh	$0/kWh

Alternative VE Resin Shows Excellent Results

- Polyvinyl ester resins are considered for use to save cost ~ 60% the cost of epoxy and are commonly used in bath fixtures, ships, wind blades, etc.
- Multiple resins have been explored for compatibility
- Final resin system is the XR-4079 vinyl ester resin based on T015 and modified to have reduced tackiness
- **Burst pressure of XR-4079 tanks equal to or higher than epoxy tanks with identical wind pattern and fiber content**

ACCOMPLISHMENTS

TANK BURSTS – BASELINE VS XR-4079

	Baseline		VE with standard T700		VE with 12K fiber FOE sizing	
Tank #	Burst relative to baseline avg	Weight (lbs)	Burst relative to baseline avg	Weight (lbs)	Burst relative to baseline avg	Weight (lbs)
1	98.6%	74.5	103.0%	71.1	103.0%	67.8
2	97.6%	75.2	92.8%	69.3	104.0%	68.2
3	101.7%	71.9	102.7%	69.8	95.7%	67.8
4	99.7%	72.0	101.4%	68.5	96.9%	67.1
5	100.0%	72.2	96.0%	70.2	108.6%	69.4
6	102.3%	73.0	101.1%	68.3	99.1%	68.7
avg	**100.0%**	**73.1**	**99.5%**	**69.5**	**101.2%**	**68.2**

5-7% reduction in mass and indication that proper fiber sizing is advantageous

Vinyl Ester Resin: Fatigue and Impact Testing

		Epoxy	Vinyl Ester
	Test Type	**Relative Burst**	**Relative Burst**
No Impact	Burst	105%	111%
	Cycle A	100%	103%
	Cycle B	99%	95%
Impact test round 1	Burst	57%	55%
	Cycle A	67%	DNF
	Cycle B	58%	63%
Impact test round 2	Burst	70%	82%
	Cycle A	55%	74%
	Cycle B	62%	67%

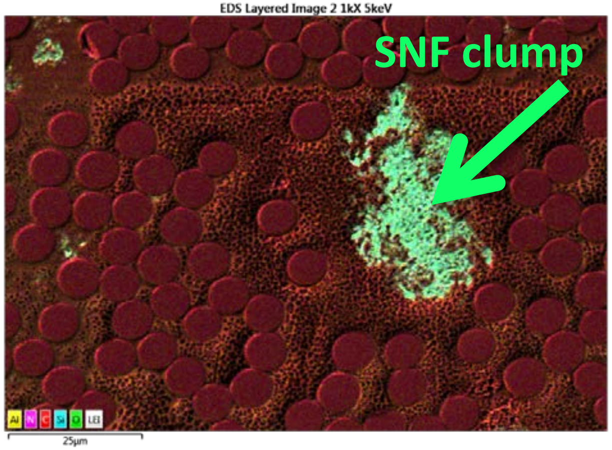
- Additional testing needed for production validation:
  - Environmental testing, extreme temperature cycling, flaw tolerance, multiple sizes and aspect ratios, gunfire
- Facility changes would be needed to handle styrene vapors
  - Increased venting, exhaust treatment, additional automation

Nanoparticle Reinforced Resins

	Carbon Nanoparticles		Nanosilica	
Tank #	Burst relative to baseline	Weight (lbs)	Burst relative to baseline	Weight (lbs)
1	70.7%	71.4	80.7%	69.8
2	97.0%	70.5	92.9%	70.1
3	87.1%	71.1	81.4%	69.8
4	93.8%	70.0	92.5%	70.7
5	76.8%	70.4	96.9%	70.1
6	98.7%	68.3	95.1%	69.8
Avg	**87.4%**	**70.3**	**89.9%**	**70.1**

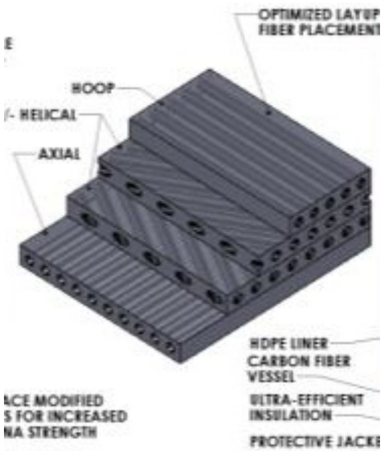
- Average burst pressure is reduced significantly with a large spread in tank performance
- May be due to clumping of particles
- Continuing to evaluate commercial alternatives

EDX of cross-section



Technical Accomplishment - Alternate Fiber Placement and Multiple Fiber Types

- Investigate alternate carbon fibers
  - Evaluate performance/price
  - Looked at T720 and T800 fibers
- Look at hybrid fiber reinforcement
  - Some materials give strength
  - Some materials address durability
- Look at layering options
  - Higher modulus materials on outside to improve load share with inner layers
  - One material for helical layers, one for hoop layers



Tank Design and Manufacturing

Better material use

Improve efficiency

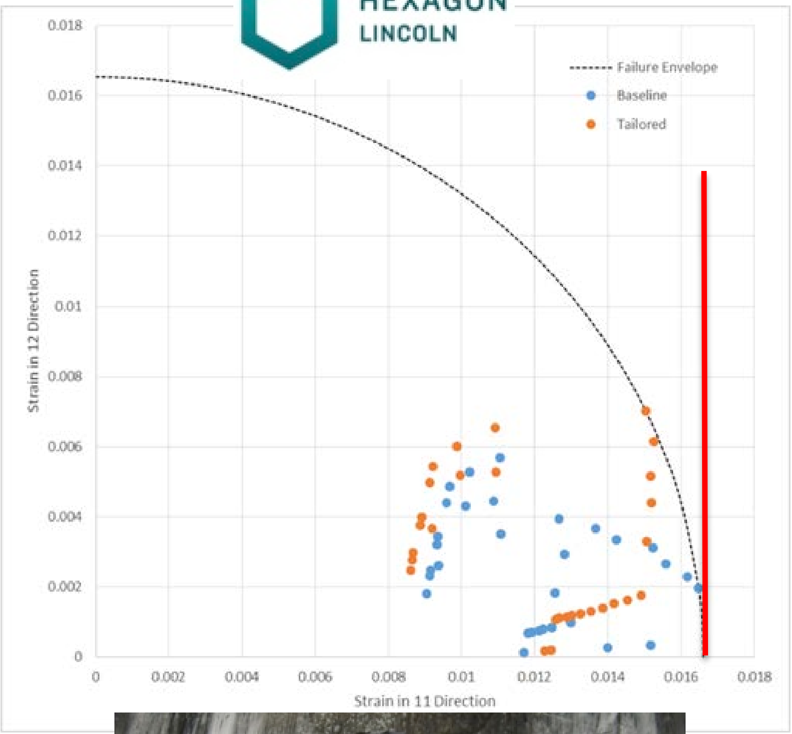
Optimize fiber pattern
Mix different fiber types

	Target Savings	Demonstrated
Alternate Fiber Placement	\$0.4/kWh	\$0
Multiple Fiber Types	\$0.4/kWh	\$0

Alternate Fiber Placement and Multiple Fiber Types

- A range of different layups were tested, but all failed at lower pressures than anticipated
- New failure model identified that explains failure when there is a high shear component
- Current tank design is likely near a local optimum and further improvements will require substantial new efforts in modeling with limited chance of success
- Multiple fiber types can be integrated, but currently, cost/performance is balanced.
  - Lighter tanks, but increased price outweighs mass savings
  - T720 and T800 tanks showed 6.7% and 10.1% mass reduction, but overall cost increase

HEXAGON
LINCOLN



Technical Accomplishments: Enhanced Operating Conditions

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- Assess the operating condition alternatives
  - Target temperature is 200K (-73°C) based on HDPE Tg.
- Pros
  - Allows equivalent density at lower pressure which reduces the carbon fiber and cost
  - Lower pressure allows for a thinner, lighter, efficient pressure vessel
- Cons
  - Insulation is required to maintain temperature and extend dormancy, which reduces the cost and volume benefits
  - Requires alignment with gas delivery infrastructure

Operating Conditions

Reduce pressure

Increase density

↓

Cold gas storage concept

	Current H_2 Tank	Enhanced H_2 Tank
Operating Conditions	700 bar at 15° C	500 bar at -73° C
H_2 Density	40 g/l	42 g/l
Tank Mass	93.6 kg	48.2 kg

Technical Accomplishment - Enhanced Operating Conditions: Composites

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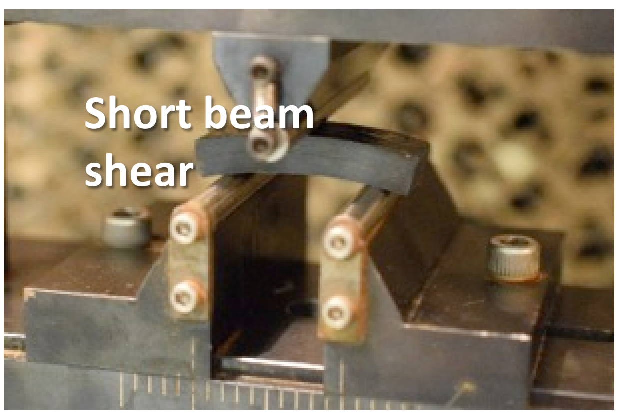
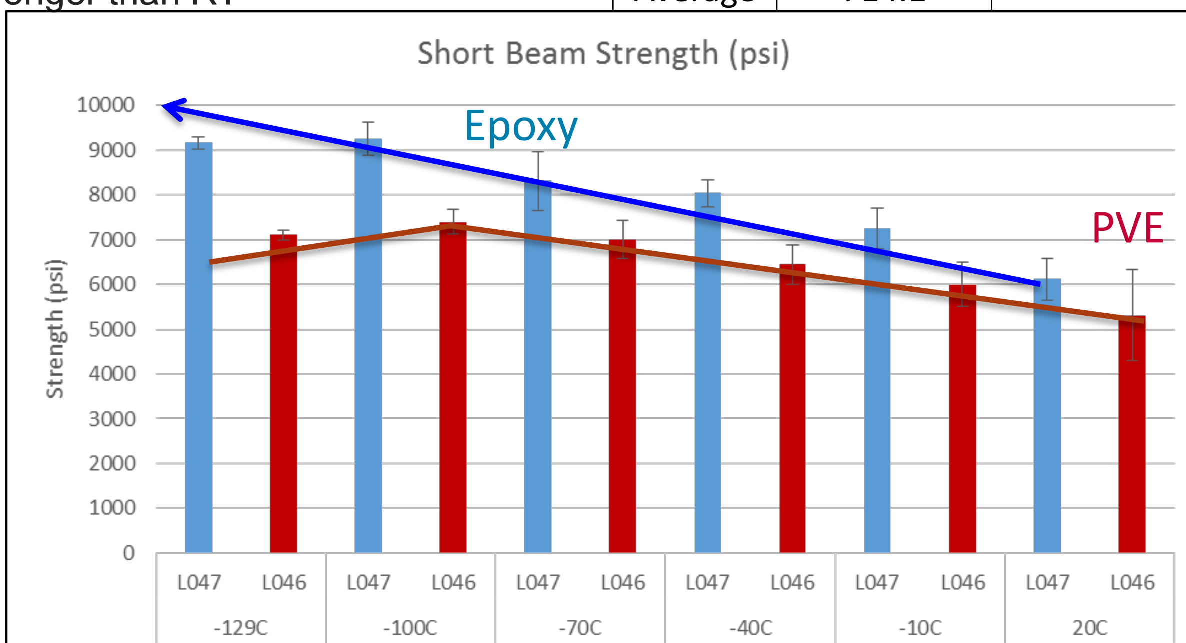
- Short beam shear measurements were carried out on HL PVE resin (L046) ASTM ring sections as compared to epoxy baseline (L047)
  - All SBS composite samples showed a general increase in strength as temperature decreased over this range
  - The baseline epoxy outperforms the PVE at all temperatures, but more strongly at cold temperatures
  - PVE appears to peak in strength at -100 C, near the EOC, but even -129C is stronger than RT

250bar VE tanks burst tested at 200K by Cimarron Composites. Good average pressure, slightly high variation

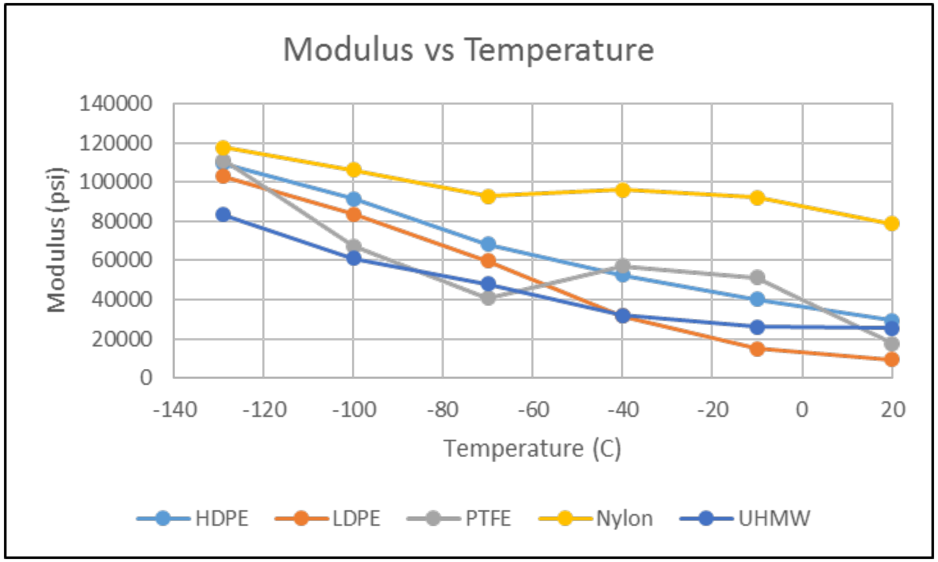
Tank	Burst (bar)
1	731.6
2	704.6
3	759.7
4	753.7
5	674.5
6	660.5
Average	714.1

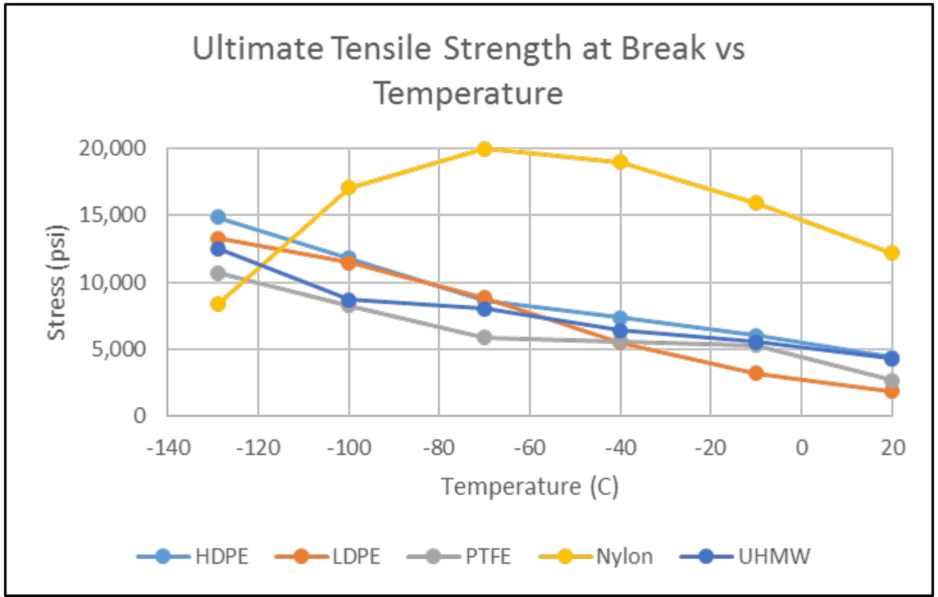


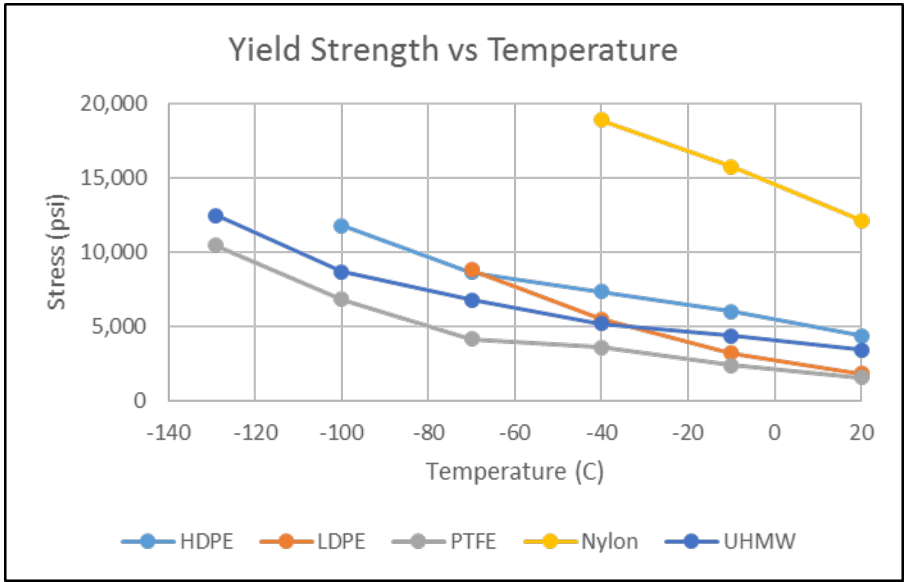


Technical Accomplishment - Enhanced Operating Conditions: thermoplastics

- Modulus generally increases with decreasing temperature.
- Most materials show a ductile-brittle transition based on their glass transition temperature(s)
- Some materials (nylon) are not suitable for EOC at 200K







Insulation for cold operation

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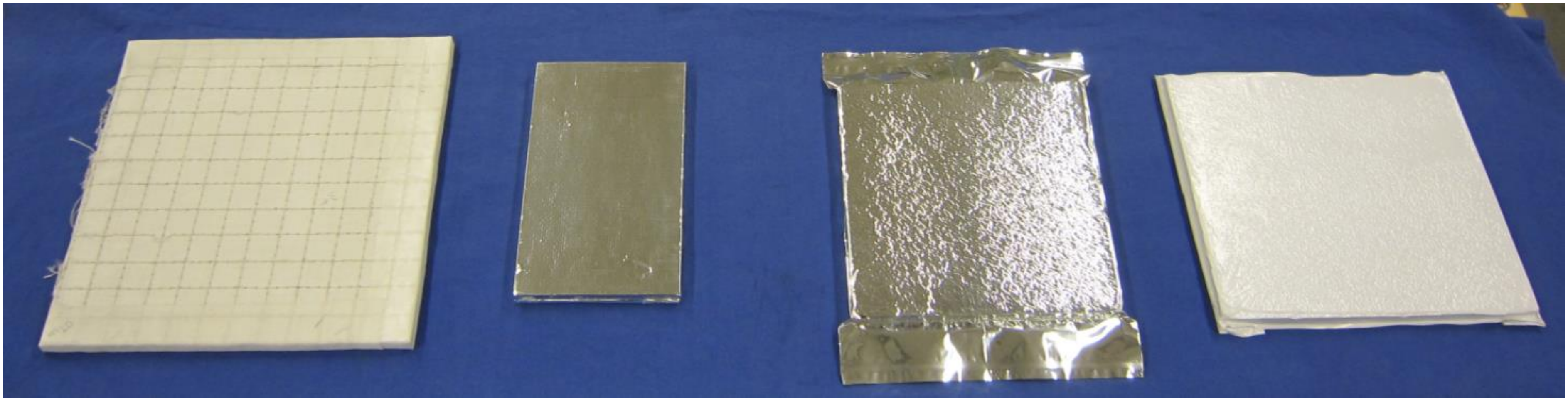
- Advanced physical insulation such as vacuum insulation panels (VIP) will likely be the only physical insulation capable of achieving required dormancy
- VIP material typically vacuum packaged fumed silica (FS) in stiff board-like configuration – most aluminized mylar packaging
- Quilted (non vacuum packaged, VP) material also available – would need to vacuum package after tank wrap

Quilted FS (not VP) | VIP-AM (vendor 1) | VIP-AM (vendor 2) | VIP (vendor 2)



Tank Dormancy Tests

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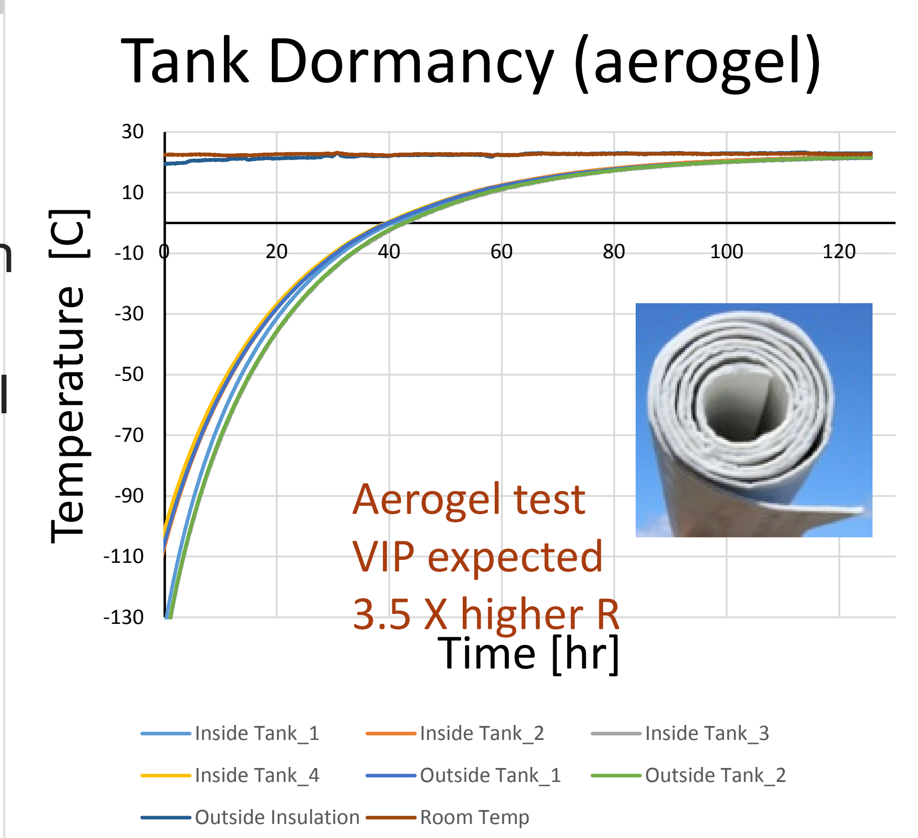
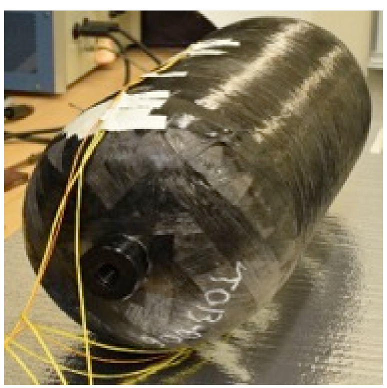
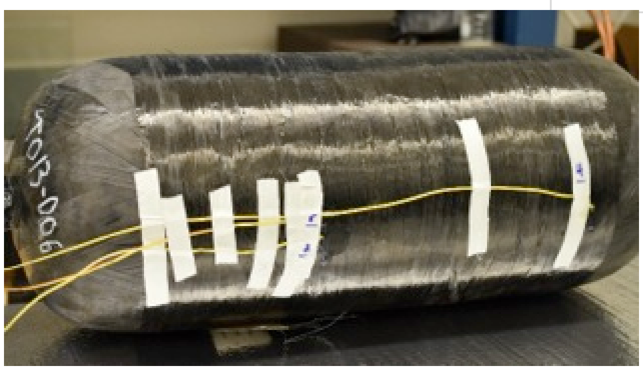
- We are in the process of carrying out tank dormancy tests of advanced physical insulation.
- Test is with advance aerogel insulation blanket 3” thick
- 12.5 kg sand approximates H_2 thermal mass
- VIP panels on order expected to have ~3.5 x thermal resistance
- Tank recovers to room temperature within approximately 60-80 hr – 2.5-3 days, empty tank is 2 days







Program Results

- >80 tanks built and tested
- Low cost resin alternative developed with $0.5/kWh savings
  - Improved burst strength compared to standard epoxy resin
  - Nano-particulates tested, but show increased burst variation
- Alternate winding patterns tested
  - Identified improved failure criteria that must be used to accurately predict failure where there is a high shear component
  - Current design is likely near optimum
- Material testing at cold gas operating condition in progress
  - VE and epoxy resins both show improved strength at 200K
  - VE tanks burst at 200K, show good average burst (714bar) but slightly higher variation than reference tanks, 6% vs. 2-3% for standard tanks
  - Multiple insulations in test
- Along with ANL, supported Strategic Analysis' work to update the standard cost model

Reviewers Comments

- FY15 Comment: However, the relationship of fiber, resin and process beyond only burst strength is a key element that is not being addressed by the approach. The absence of this understanding (impact, cycle, etc.) may lead to a retraction of the learning to date and may force a new look into the winding process and/or fiber reinforcement.
  - Testing the VE tanks for fatigue and impact was added to the project for this year and showed positive results. Additional testing has been identified that would be needed to continue to move this new resin into production, including more testing of different tank sizes and diameters, rapid impact (gunfire), extreme temperatures, and drop testing
- FY15 Comment: While the development of a 200K storage vessel will potentially reduce system mass and volume as well as potentially cost, issues relating to mechanical behavior over the desired operating conditions and identification of suitable effective insulation materials have not yet been clarified.
  - This has been a focus of this year, with work on evaluating material and full tank properties at low temperatures as well a insulation validation.

Collaborations

- Pacific Northwest National Laboratory: David Gotthold (PI), Ken Johnson, Kyle Alvine, Matt Westman, Tim Roosendaal, Mike Dahl
  - Project management, material and cost models, resin modifications
- Hexagon Lincoln: Norm Newhouse, Alex Vaipan
  - Tank modeling, tank fabrication, tank and materials testing
- Ford Motor Company: Mike Veenstra, Dan Houston
  - Enhanced operating conditions, cost modeling, materials testing
- AOC Resins: Thomas Steinhausler, Mike Dettre
  - Resin system design and materials testing
- Toray Carbon America: Anand Rau*
  - Carbon fiber surface modification and testing
  - *currently Crosslink Technologies

Proposed Future Work

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Remainder of FY16

- Complete low temperature materials testing for cold gas operation
- Complete advanced physical insulation testing for cold gas operation
- Complete dormancy tests for cold gas operation with full tanks
- Burst tests on tanks using commercial nano-resin

Suggestions for future research areas

- Continue to identify low cost, high performance alternative insulation useful for both cold gas and cryo-compressed tank systems
- Compact and low power active cooling to enable longer dormancy
- The cost/benefit analysis of mixing different fibers will likely continue to evolve as new products and manufacturers mature.
- Commercial resin additives may yet demonstrate improved performance for 500/700bar tanks

Project Summary

Relevance: Reducing pressure vessel cost, mass, and volume

Approach: Establish baseline cost and reduce tank costs and mass through engineered material properties through efficient use of carbon fiber

Technical Accomplishments: Built >80 tanks to evaluate actual performance of previously modeled performance improvements. Evaluated nanoparticle reinforced resin. Extended testing of VE resin tanks to include impact and fatigue. Low temperature materials testing

Technology Collaborations: Active collaborations with Hexagon Lincoln, Ford Motor Company, Toray CFA, and AOC, LLC

Proposed Future Research: Improved insulation for low-temp operation. Evaluation of commercial resin additives

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Technical Backup

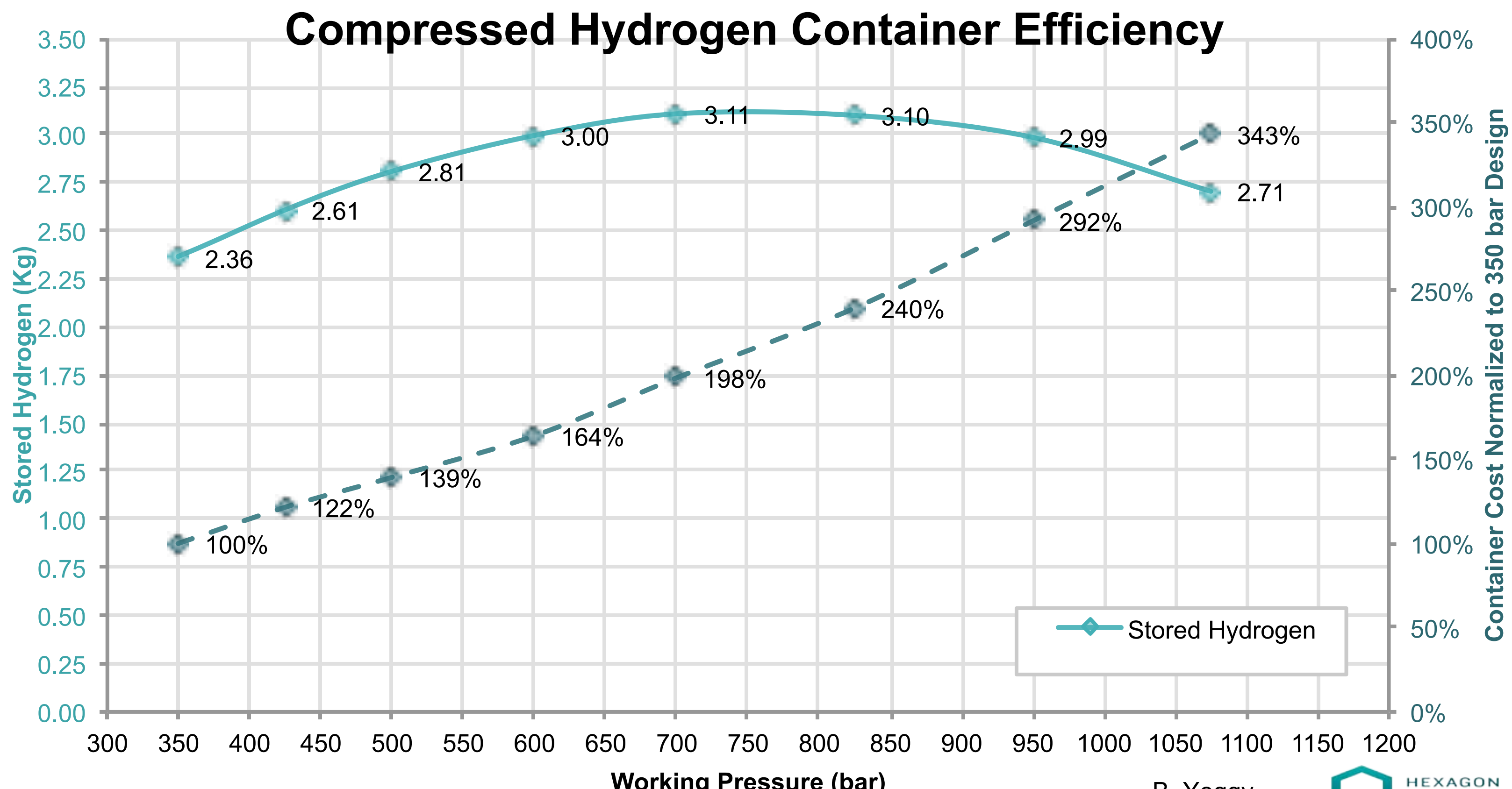
Technical Accomplishment – Prototype Tank Fabrication and Testing

	Actual		Estimated Values Based on Mass Scaling with Pressure 100% Burst					
	Relative to Baseline		Relative	Carbon	Resin	Liner	Bosses	Mass
Description	Mass	Burst	Mass	Fiber, kg	kg	kg	kg	kg
Baseline	100.0%	100.0%	100.0%	18.0	8.4	2.8	4	33.2
Low Cost Resins								
Baseline + Resin 1 Substitution	95.3%	100.0%	95.3%	18.0	6.9	2.8	4	31.6
Baseline+Resin1+12kT700+Alt. Sizing	93.2%	101.2%	92.3%	17.7	6.1	2.8	4	30.7
Modified Resins								
Baseline + Resin 1 + Nano Mod 1	Tanks Wound, awaiting Burst Testing							
Baseline + Resin 1 + Nano Mod 2	Tanks to be Wound and Burst					2.8	4	6.8
Fiber Winding Patterns								
Sorted HAHs, Interspersed with LAH	95.0%	91.0%	102.4%	18.5	8.7	2.8	4	34.0
Sorted HAHs, No Interspersion	88.0%	83.0%	101.8%	18.4	8.6	2.8	4	33.8
Baseline with 1 Adj Removed	96.0%	95.0%	100.0%	17.9	8.4	2.8	4	33.2
Baseline with 2 Adj Removed	91.0%	88.0%	100.6%	18.1	8.5	2.8	4	33.4
Alternative Fibers								
Baseline with T720 Substitution	96.2%	104.0%	93.3%	17.3	6.9	2.8	4	31.0
Baseline with T800 Substitution	98.7%	112.6%	89.9%	15.9	7.1	2.8	4	29.9
Baseline with fiber hybrid structure	Not Manufactured, Modeling indicated minimal improvement							

- Tank masses reported for input to standard cost and tank models by SA & ANL
- Data reported as tank testing progressed
- Tank mass and burst pressure reported relative to baseline tank design
- Carbon fiber and resin scaled to estimate tank mass and cost to achieve 100% of the target burst pressure

COMPRESSED H2 CONTAINER EFFICIENCY

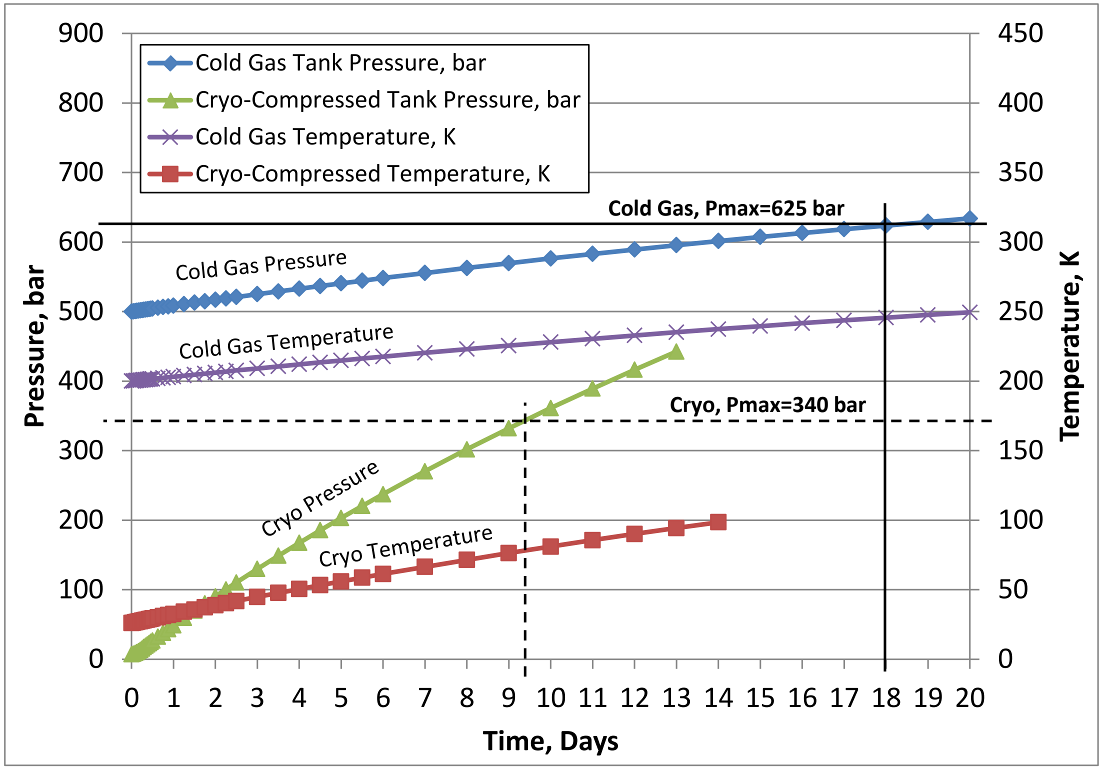
Storage for constant outside envelope as a constraint from the automotive industry



1) Calculations based on maintaining an unpressurized container envelop of Ø 410 mm x 1016 mm

B. Yeggy
April 16

Gen-3 Cryo-Compressed Tank at Cryo and Cold Gas Conditions



- Materials Challenges:
- Insulation
  - Cost must be less than carbon fiber reduction
  - Thickness should match tank diameter reduction
- Liner
  - Thermal expansion limits filling when cold
  - Tg may limit lower temp

Enhanced Operating Conditions – polymer test plan

Use	Material	Reported Useful Temp Range, °C	T_g , °C	T_m , °C	Linear CTE, 10^{-5}/C
Valve Seals	Viton	-23 / +204	-20	260	8.3 – 10.5
	Nitrile Rubber (Buna-N)	-34 / +250		---------	11.2
	Teflon (PTFE)	-100 / +260	115	335	10
	EPR (ethylene-propylene-rubber)	-62 / +160	-60	---------	
	Fluorosilicone	-59 / +232	-50	---------	81 (low Temp)
	Silicone	-62 / +216	-50	---------	18 – 25.5
	Neoprene	-40 / +121	-43	---------	61 - 72
Valve Pistons	PEEK	/ +250	143	343-374	
Valve Seats	Nylatron	/ +105		260	6.3 – 10.6
	Vespel	-100 / +500	none observable	none observable	2.7 – 5.4
	PCTFE		45	215	7
Tanks: Resin	Epoxy				
	Vinylester				
Fibers	Carbon Fiber				
	Glass Fiber				
	Kevlar Fiber				
Liner	HDPE		-110	130	12
	PPS (polyphenylene Sulphide)	/ +220		282	5
	Nylons		50	255	8-10

New Failure Criteria Accurately Predicts Failure Conditions

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HEXAGON LINCOLN

$$\left[\frac{\varepsilon_1}{X_1}\right]^2 + \left[\frac{\varepsilon_{12}}{S_{12}}\right]^2 = 1$$

- Hexagon Lincoln correlating observed burst performance with Yamada-Sun combined strain failure criteria.
  - ε_1 = Uniaxial strain
  - ε_{12} = Shear Strain
  - X_1 = Uniaxial failure strain
  - S_{12} = Shear failure strain
- Fitting shows baseline and tailored wind patterns have failure strains on the circular arc where X and S are nearly the same.