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

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Pacific Northwest National Laboratory

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Project ID # **ST101**

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

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Timeline

- Start date: Jan 2012
- End date: March 2016
- Percent complete: *75%*

Budget

- FY14 DOE Funding: $600K
- Planned FY15 DOE Funding: $518K
- Total project funding: $2,625K
  - DOE share: $2,100K
  - Contractor share: $525K (20%)

Barriers

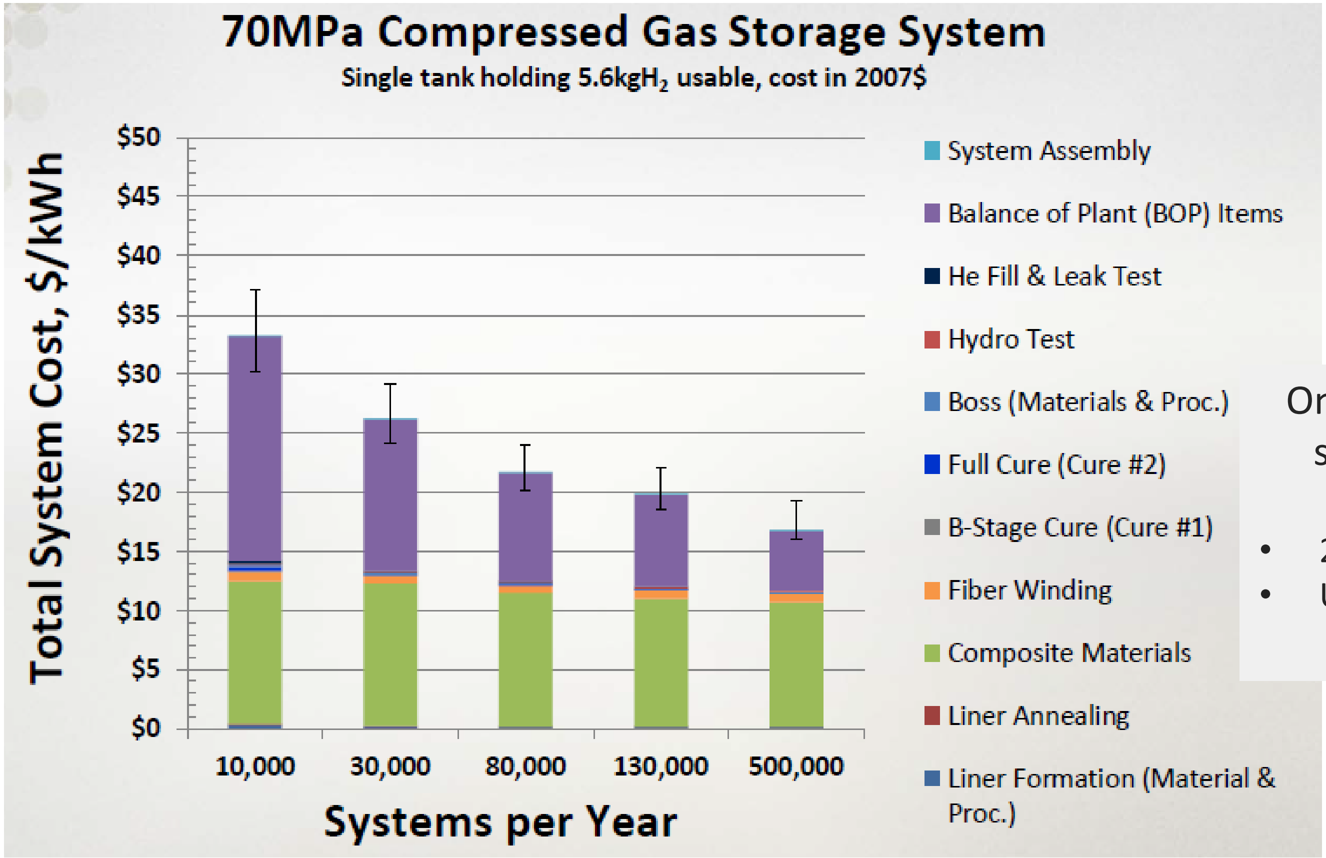
- E: System Cost
  - Alternate low cost resin
  - Improved winding efficiency
  - Cold gas storage
- G: Materials of Construction
  - Alternate resin and fibers
- J: Thermal management
  - Low cost insulation for cold gas

Partners

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

System Cost Analysis Study

2013 AMR Presentation - Strategic Analysis



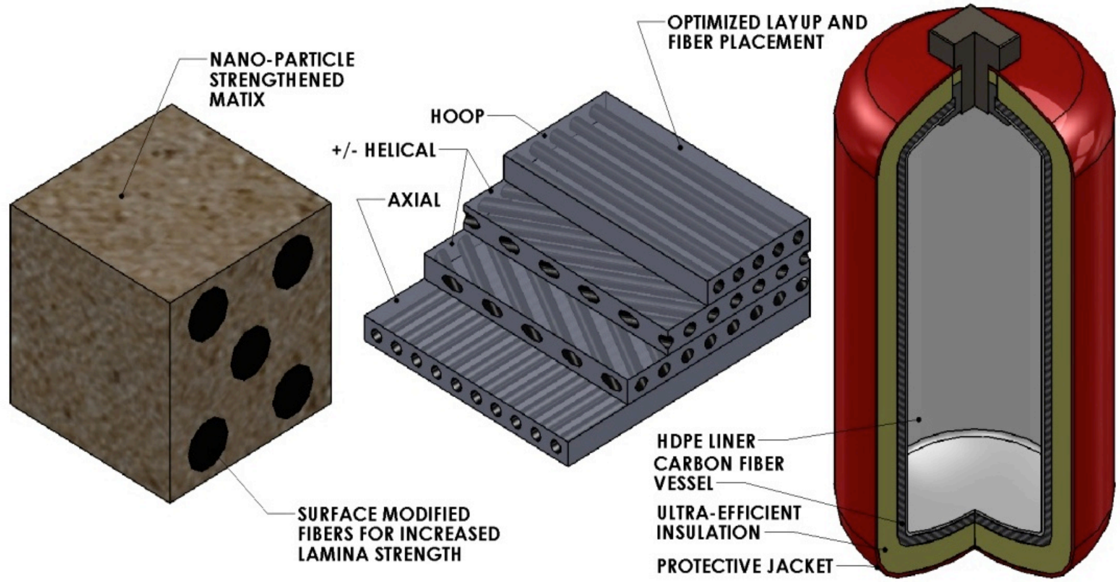
500k System per Year
System Cost: $3,134
$600/kg$H_2$
$17/kWh

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

Materials | Design | Cold Gas



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

- Materials: Use alternative low cost resin enhanced with nano-particle modifications to reduce both direct resin cost and improve carbon fiber efficiency.
- Design: Optimize fiber layup pattern to minimize CF usage. Mix different fibers to maximize strength at minimal cost.
- Cold Gas Operation: Reduce temperature to enable equivalent H_2 storage at lower pressure while maintaining the same system volume.

FY15 Milestones

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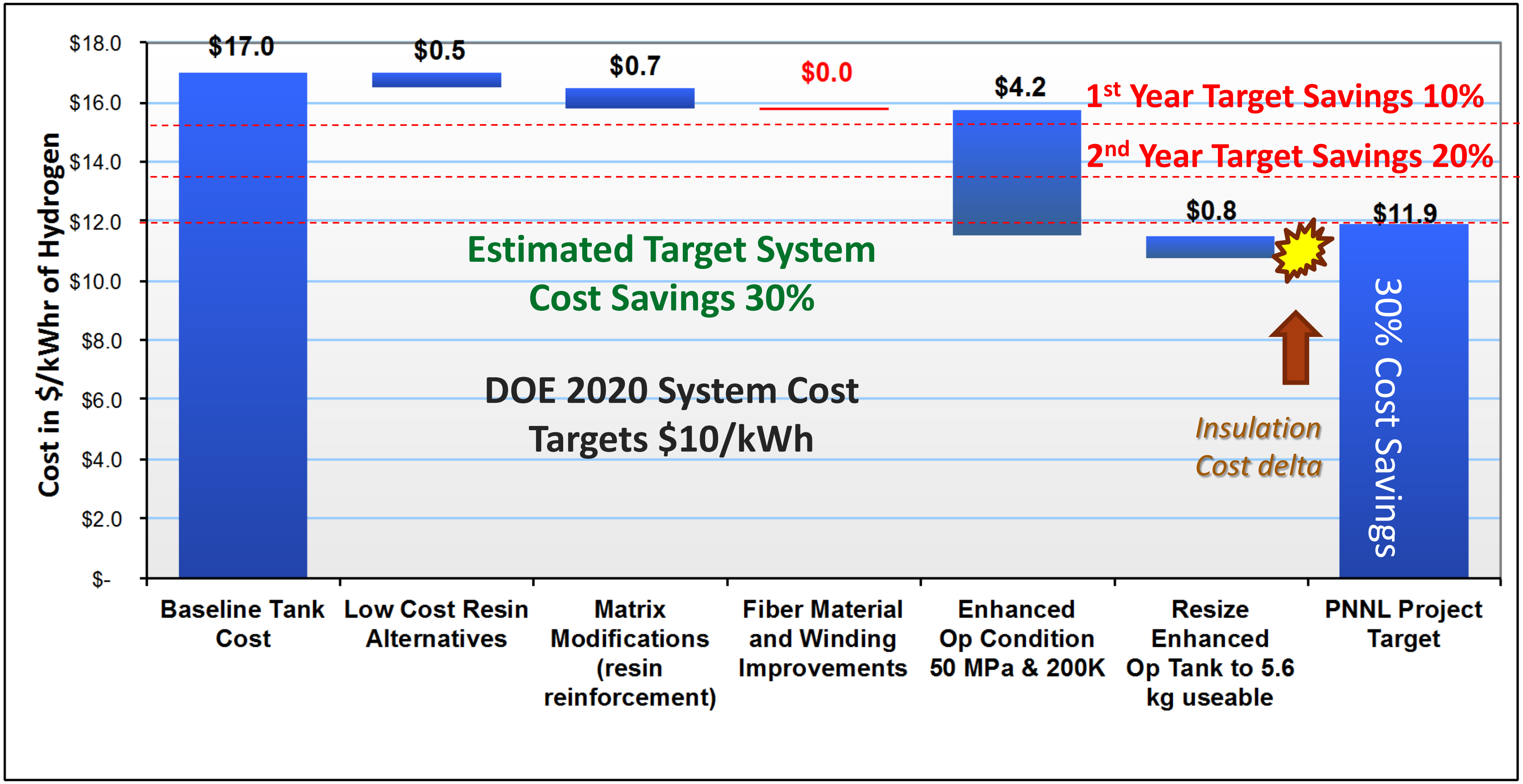
Milestone Name/Description	End Date	Status
Complete high volume resin mixing system for production of filled resins for tank winding	12/31/14	Complete
Optimize final resin/CF modification systems with Optimize final tank design models	3/31/15	Complete
Demonstrate low cost insulation performance for cold gas storage and demonstrate feasibility of modified fibers and resins at enhanced operating conditions	6/30/15	At risk, Low temp upgrade now late June delivery
Demonstrate optimized prototype tank with 5.6 kg useable H2 with a 30% reduction in cost compared to the 700 bar baseline and burst test.	9/30/15	On target

- FY15 Major Accomplishments:
- Low cost resin alternative developed and tested with equivalent or better performance than existing epoxy
- Optimized nanoparticulate materials and processing selected and scaled.
- Alternate winding patterns tested, improved high shear failure model developed
- 60 tanks built and tested, nanoparticle results still pending

Technical Accomplishment - Cost Analysis Reduction Opportunities

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)



Fiber Material and Winding Improvement Cost Improvement at Risk. Full cost analysis still in progress

Technical Accomplishment – Prototype Tank Fabrication and Testing

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FY15 Focus = Fabricate and Burst Tanks to Validate Optimization Strategies

	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

Mass Reduction Summary Data

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	Measured Data Relative to Baseline		Estimated Mass at 100% Burst
Description	Mass	Burst	
Baseline = T700 with Epoxy Resin	**100.0%**	**100.0%**	**100.0%**
Low Cost Resins			
Baseline + Resin 1 Substitution	95.3%	100.0%	95.3%
Baseline+Resin1+12kT700+Alt. Sizing	93.2%	101.2%	92.3%
Modified Resins			
Baseline + Resin 1 + Nano Mod 1	Tanks wound, awaiting burst testing		
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Baseline with 2 Adjacent Layers Removed	91.0%	88.0%	100.6%
Alternative Fibers			
Baseline with T720 Substitution	96.2%	104.0%	93.3%
Baseline with T800 Substitution	98.7%	112.6%	89.9%
Baseline with fiber hybrid structure	Skipped due to limited pure fiber improvement		

All values relative to baseline tank
Design burst pressure of 1575bar (2.25x 700bar)

Technical Accomplishment - Resin Improvements and Modifications

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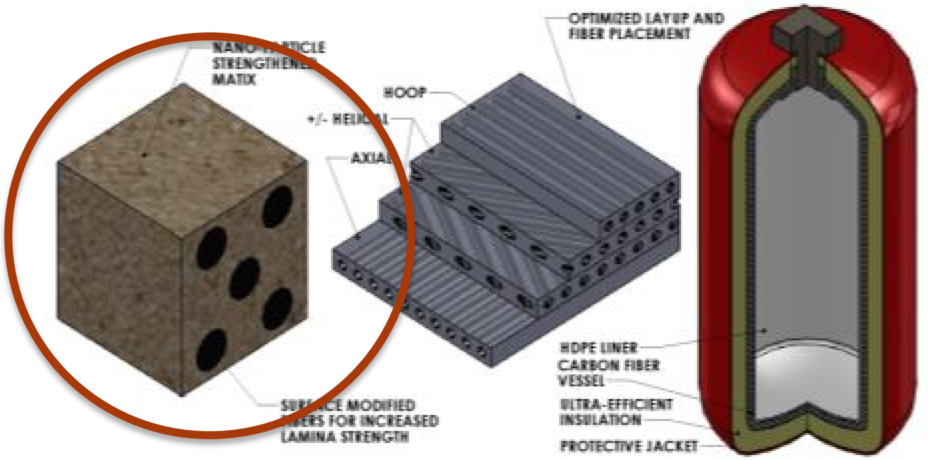
- Develop vinyl ester resin
  - Lower cost alternative to epoxy
  - Viscosity and gel time to match Hexagon Lincoln's winding process
  - T700 standard sizing and tow
  - Smaller tow (12k) with sizing selected for VE resin



- Modify resins with nanomaterials
  - Down-selected to two materials based on viscosity and mechanical performance
    - Carbon – Ashbury Nano 307
    - Silica Nano Fibers (SNF)
  - Tested surface modifications and improved particle-resin bonding
  - Improved dispersion using sonication and high shear mixing

	Target Savings	Demonstrated
Low Cost Resin	\$0.5/kwhr	\$0.5/kwhr
Resin Modifications	\$0.7/kwhr	TBD

Low Cost Resin Alternatives

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AOC® World Leader in Resin Technology

- Polyvinyl ester resins are considered for use to save cost ~ 60% the cost of epoxy
- 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**

Test	Units	ASTM	015 RT	015 (-73C)	017 RT	017 (-73C)	XV-3175 RT	XV-3175 (-73C)	Epoxy RT	Epoxy (-73C)
Flexural Strength	MPa	D-790	137.9	157.2	129.6	134.4	128.2	124.1	157.9	144.8
Flexural Modulus	GPa	D-790	4.1	4.96	3.4	4.7	4.1	5.0	3.6	4.3
Tensile Strength	MPa	D-638	89.6	75.8	75.8	89.6	72.4	51.7	91.7	82.7
Tensile Modulus	GPa	D-638	3.7	5.5	3.2	4.4	4.1	5.1	3.7	5.5
Elongation	(%)	D-638	4.0	1.8	4.8(Y) 7.0(B)	1.85	2.4	1.15	5.1(Y) 5.9(B)	1.9

Technical Accomplishment - Full Tanks Made with XR-4079 Resin

HEXAGON LINCOLN

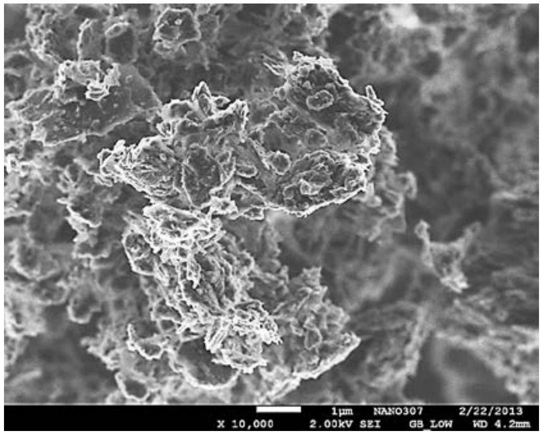
Lower viscosity resin increased the amount squeezed out during winding – lower final tank mass.

Tanks burst in cylinder with a more shredded appearance compared to epoxy tanks

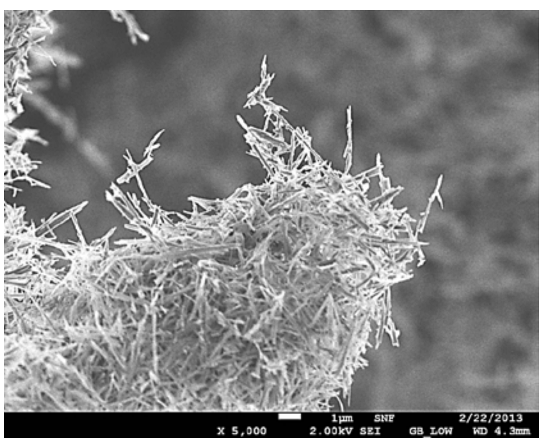
Burst pressure of XR-4079 tanks equal to or higher than epoxy resin tanks with identical wind pattern and fiber content.

Technical Accomplishment – Selection of Nanoadditive Powders

Carbon - Asbury Nano 307

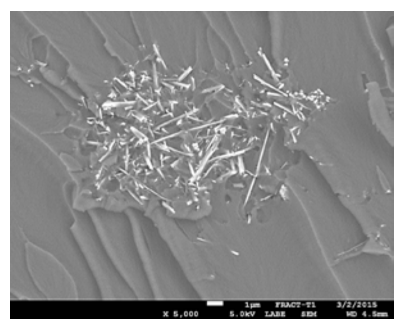


Silica Nanofibers (SNF)

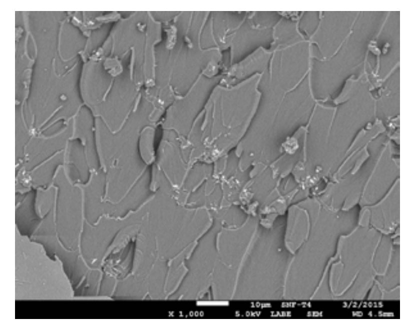


- Other additives tested but eliminated
  - Carbon nanotubes – high cost
  - Nanoclays – interactions with catalyst
- Carbon used as delivered
- Silica Nanofibers (SNF) need surface modification to improve adhesion
  - Silane (3-(Trimethoxysilyl) propyl methacrylate) (MPS)

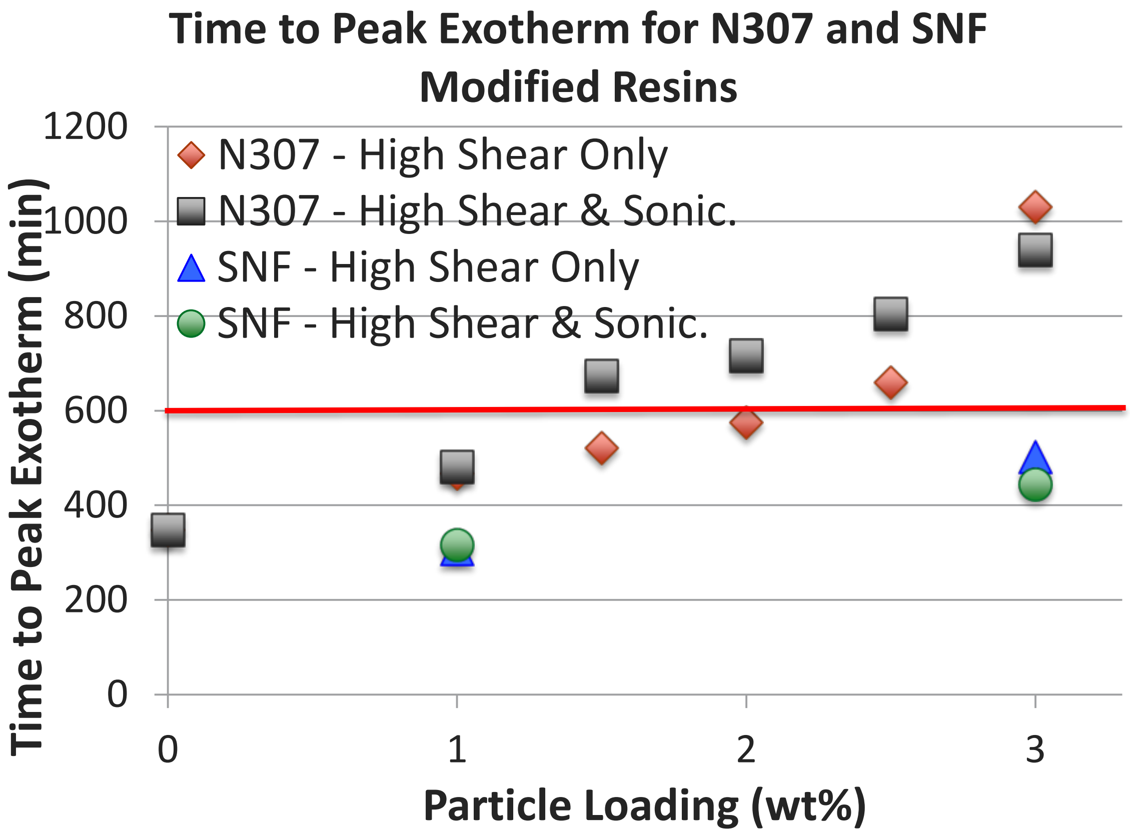
Unmodified SNF clump and show poor adhesion

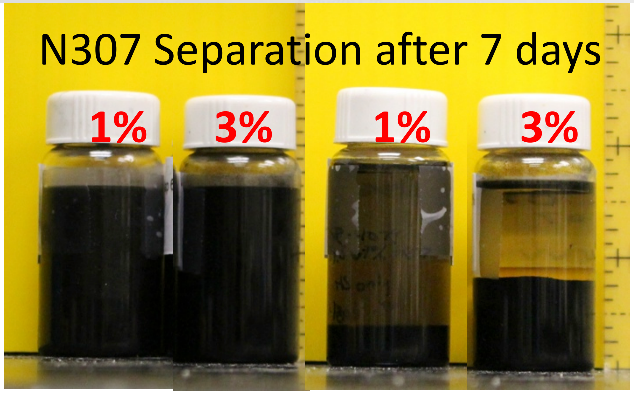


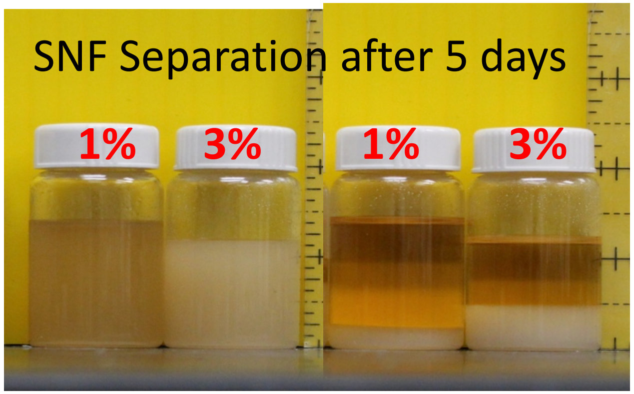
With MPS surface modification



Technical Accomplishment - Effect of Nanoparticle Loading on Resin Properties





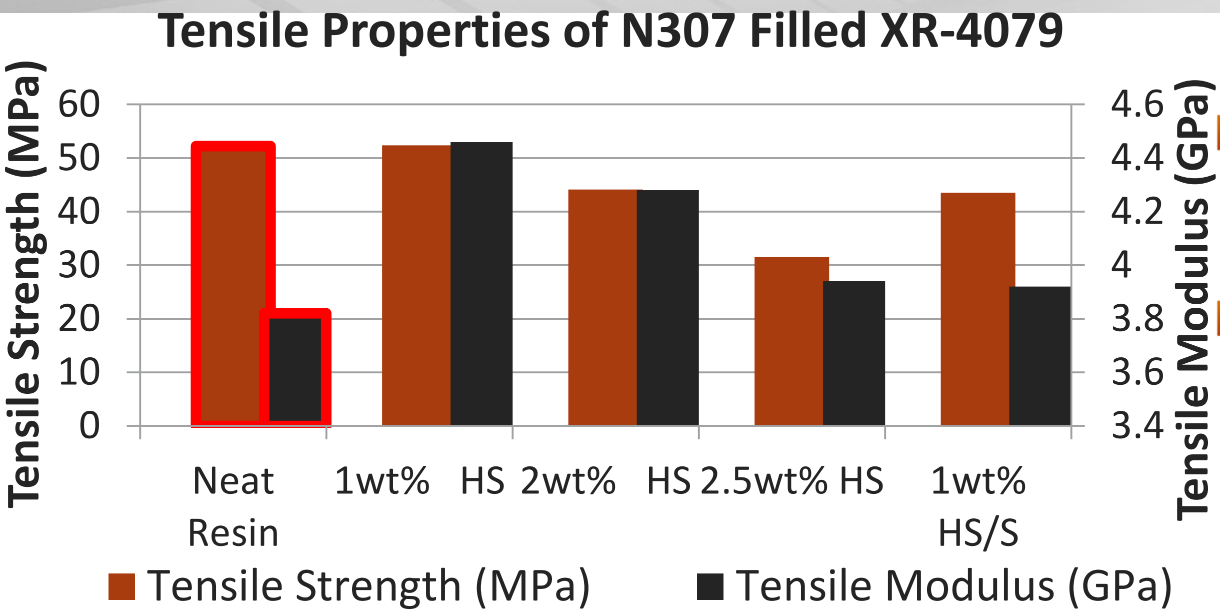


Formulation	Neat Resin	1wt% N307 HS	1wt% SNF HS	1wt% SNF HS+S	3wt% SNF HS	3wt% SNF HS+S
Viscosity (cP)	422.3	688.3	658.9	1016.9	791.1	1097.2

Stability doubled over FY14 accomplishments

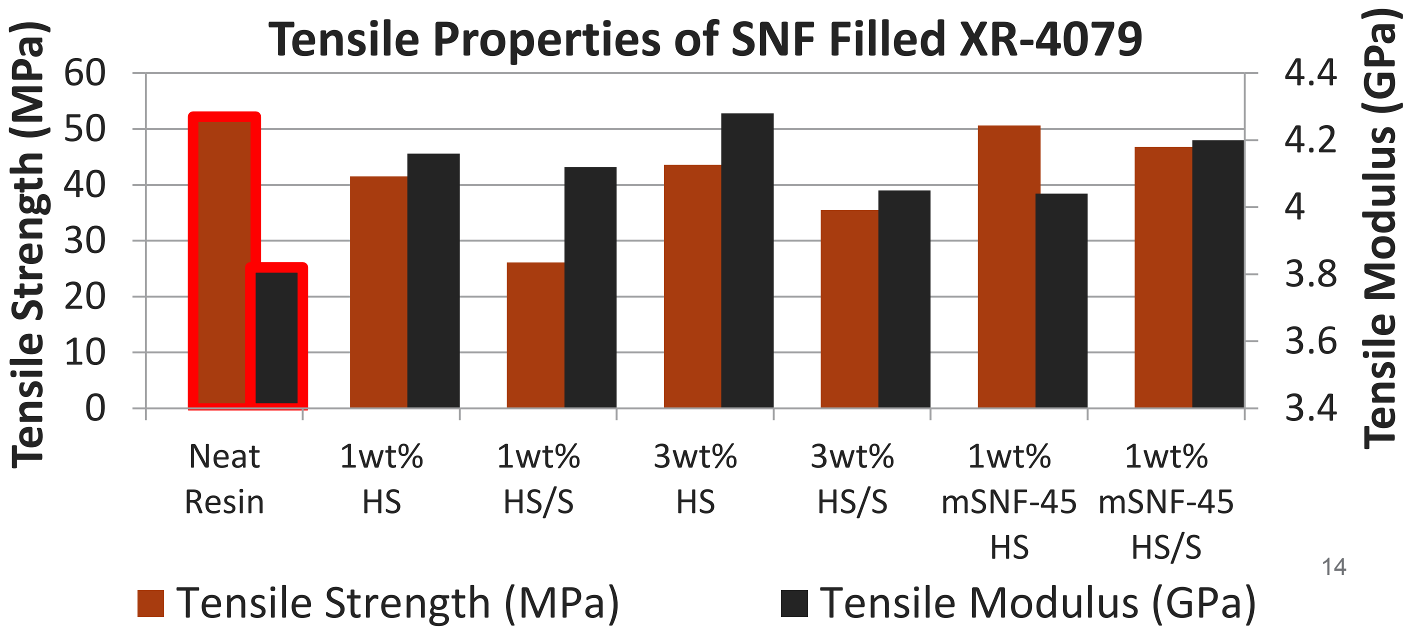
Ideal cure kinetics with 1wt% N307 with high shear only and all SNF formulations. Stability enhanced with optimized process conditions.

Tensile Test Data XR-4079 Nano-composites



- 1wt% N307 high sheer (HS) mixing **only** is top performer
- Combination of high sheer and sonication (HS/S) has shown a net loss of mechanical properties with N307 filler

- 1wt% silane modified SNF (mSNF-45) is top performer
- Surface modification of SNF improves tensile strength



Technical Accomplishment – High volume resin modification for production

- Semi-Automated mixing process for batch filled resin production of up to 5 gallons
  - In-line open loop mixing system combining high shear particle size reduction with high energy ultra-sonic particle dispersion.
  - Optimized process conditions have lead to increased material stability with samples exceeding 30 days with minimal phase separation (N307)

1L sample of the 1wt% N307 HS sent to HL 45days after processing, **no separation visible**

Delivered 2, 18 gallons batches of nano filled modified resin to Hexagon Lincoln

Low Cost Resin: Summary and Next Steps

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Description	Measured Data Relative to Baseline: Mass	Measured Data Relative to Baseline: Burst	Estimated Mass at 100% Burst
Baseline	100.0%	100.0%	100.0%
Low Cost Resins			
Baseline + Resin 1 Substitution	95.3%	100.0%	95.3%
Baseline+Resin1+12kT700+Alt. Sizing	93.2%	101.2%	92.3%
Modified Resins			
Baseline + Resin 1 + Nano Mod 1	Tanks wound, awaiting burst testing		
Baseline + Resin 1 + Nano Mod 2	Tanks to be wound		
Fiber Winding Pattern			
Sorted HAHs, Interspersed with LAH	95.0%	91.0%	102.4%
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Baseline with 1 Adjacent Layer Removed	96.0%	95.0%	100.0%
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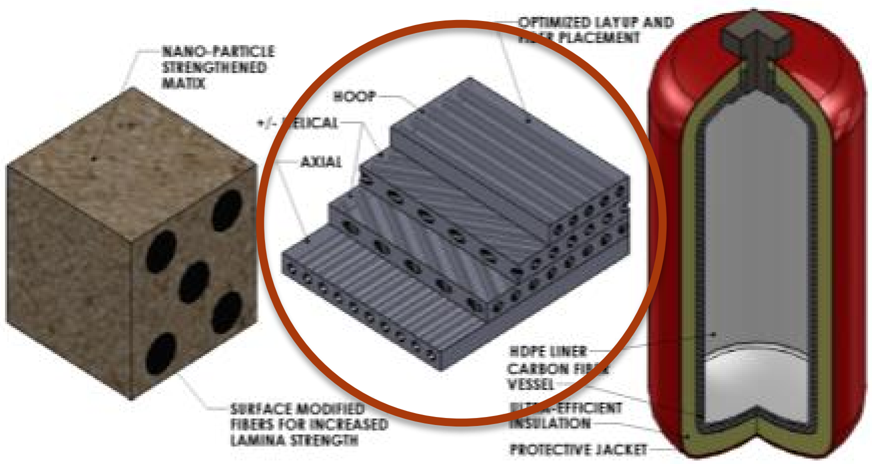
Alternative Fibers			
Baseline with T720 Substitution	96.2%	104.0%	93.3%
Baseline with T800 Substitution	98.7%	112.6%	89.9%
Baseline with fiber hybrid structure	Skipped due to limited pure fiber improvement		

- Optimized XR-4079 resin gave burst strength equal to or better than epoxy
- Total tank mass reduced compared to baseline due to lower viscosity resin being forced out during the winding process
- High volume resin mixing system used to make 18gal of N307 modified resin and tanks are wound (awaiting burst data)

Technical Accomplishment - Alternate Fiber Placement and Multiple Fiber Types

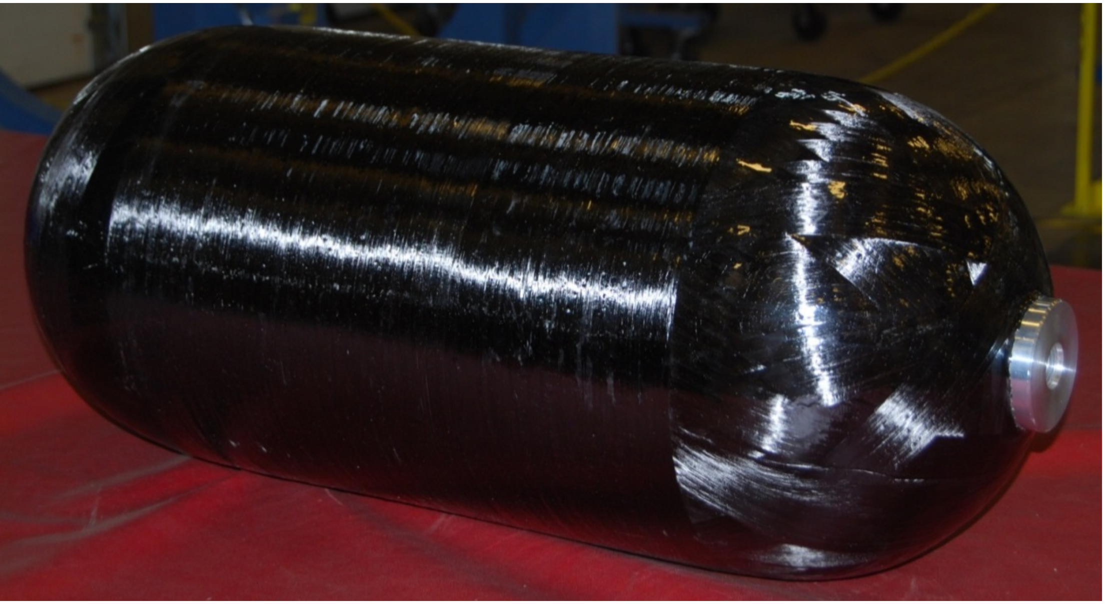
- Investigate alternate carbon fibers
  - Evaluate performance/price
  - Looked at T720 and T800 fibers
- Look at hybrid fiber reinforcement
  - Some materials give strength
  - Some materials address durability
- Look at layering options
  - Higher modulus materials on outside to improve load share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



	Target Savings	Demonstrated
Alternate Fiber Placement	$0.4/kwhr	$0
Multiple Fiber Types	$0.4/kwhr	$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 correctly predicts failure when there is a high shear component
- Currently feel that tank design is likely near a local optimum and further improvements will require substantial new efforts in modeling with limited chance of success

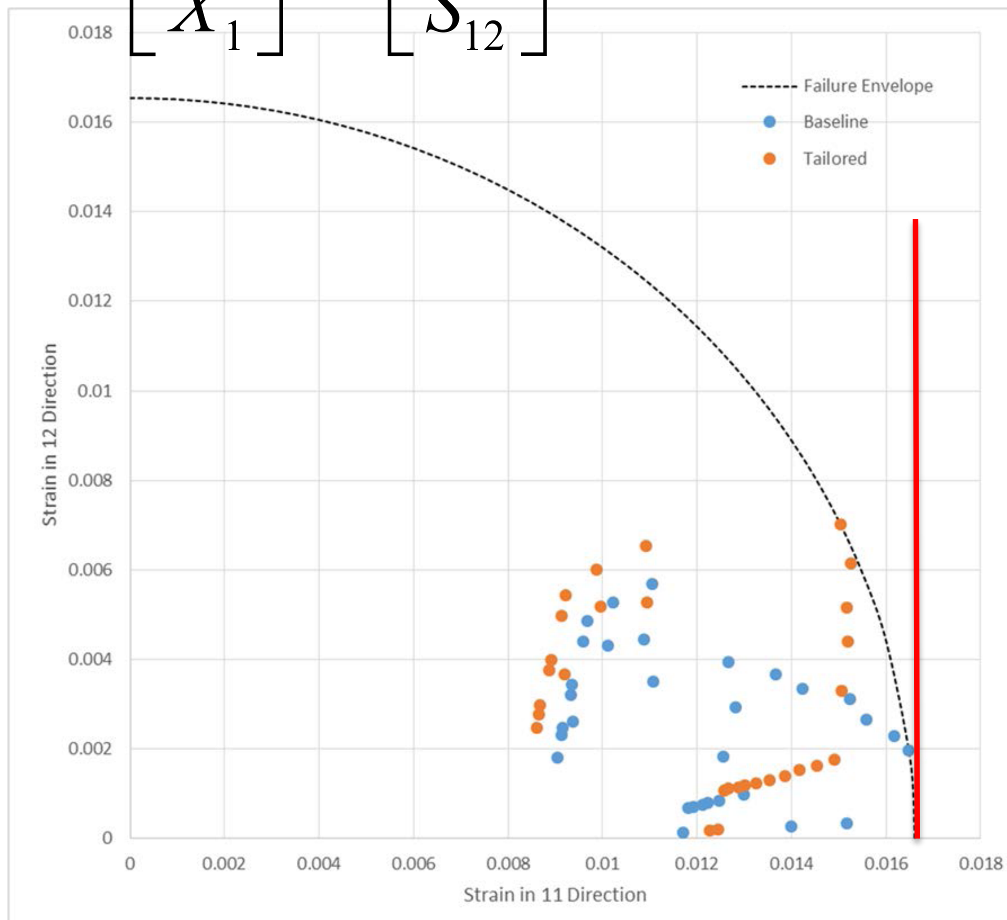


New Failure Criteria Accurately Predicts Failure Conditions

- 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.

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



New Failure Criteria Accurately Predicts Failure Conditions

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HEXAGON LINCOLN

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

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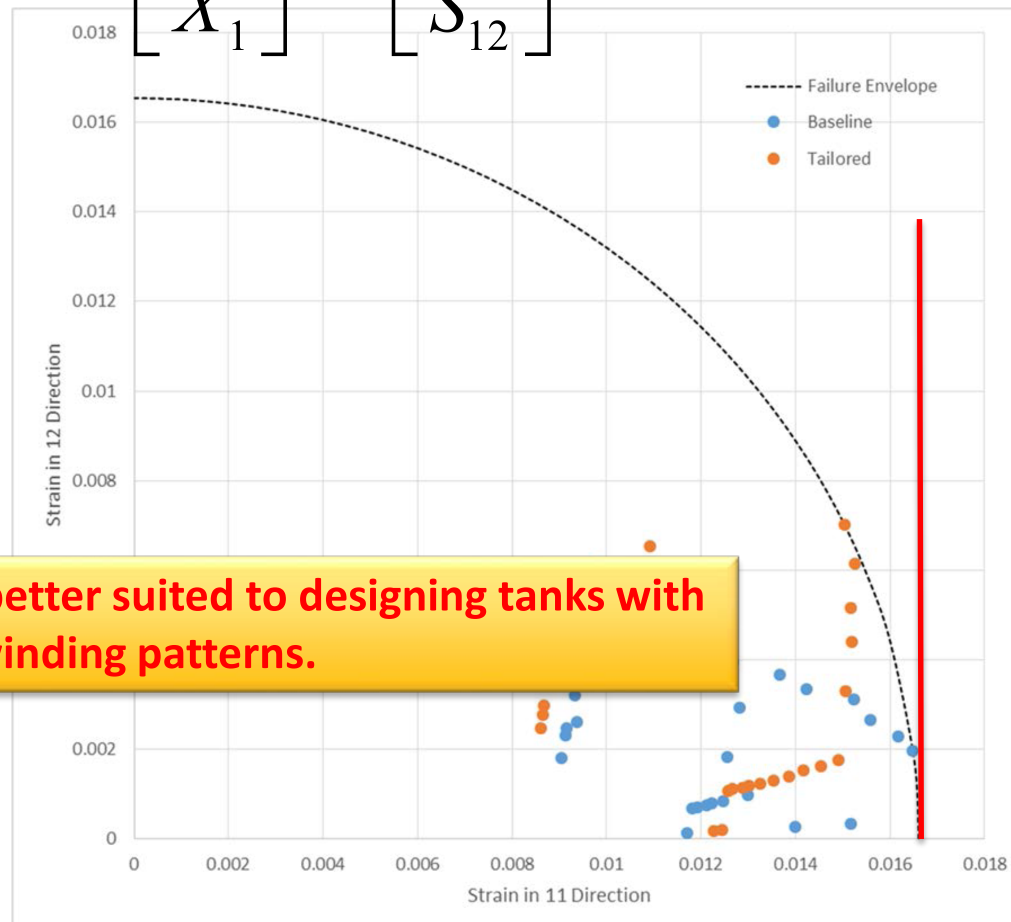

Improved failure model is better suited to designing tanks with novel winding patterns.

Alternate Fiber Placement Results

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Description	Measured Data Relative to Baseline: Mass	Measured Data Relative to Baseline: Burst	Estimated Mass at 100% Burst
Baseline	100.0%	100.0%	100.0%
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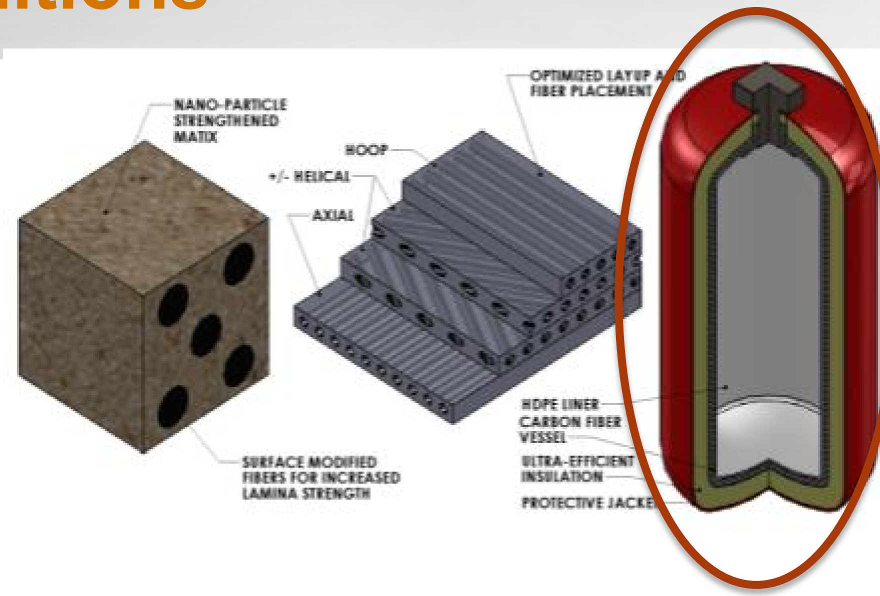
Baseline with T800 Substitution	98.7%	112.6%	89.9%
Baseline with fiber hybrid structure	Skipped due to limited pure fiber improvement		

- Multiple alternative winding patterns tested, but all showed lower burst
- New failure model identified that more accurately represents designs with higher shear components

Technical Accomplishment - Enhanced Operating Conditions

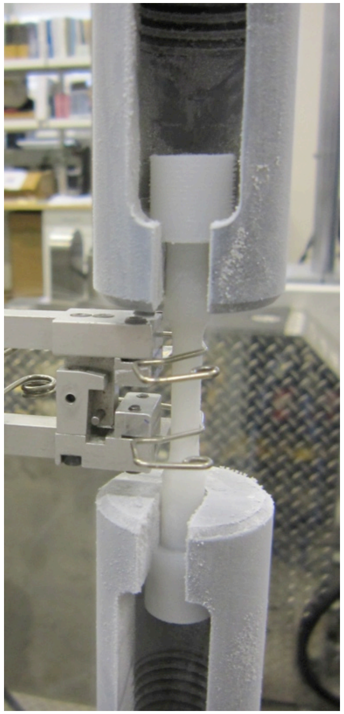
- Assess the operating condition alternatives
  - Target temperature is 200K (-73° C) based on HDPE Tg.
  - At 200K and 500bar, system volume is equivalent to a 700bar ambient system
- Pros
  - 1. Allows equivalent density at lower pressure which reduces the carbon fiber and cost
  - 2. Lower pressure allows for a thinner, lighter, efficient pressure vessel
- Cons
  - 1. Insulation is required to maintain temperature and extend dormancy
  - 2. Insulation reduces the cost and volume benefits of the lower pressure

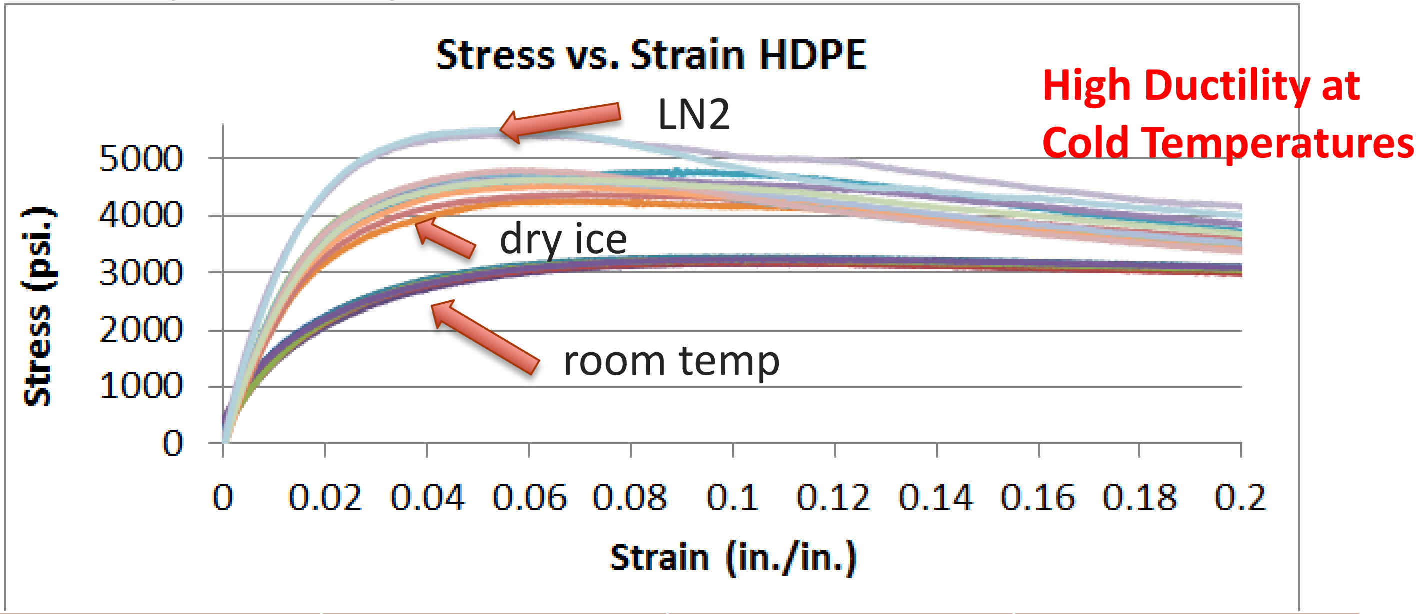


	Current H_2 Tank	Enhanced H_2 Tank
Operating Conditions	700 bar at 15° C	500 bar at -73° C
H_2 Density	40 g/l	42 g/l
Tank Mass	93.6 kg	48.2 kg

Technical Accomplishment - Cold Gas Materials Testing

- Preliminary testing was done with HDPE tensile samples at dry ice (~195 K)
  - Samples & grips cooled down for several hours in dry ice
  - Testing done immediately
  - Some variability due to change in temperature of grips – will be addressed in future testing with an environmental chamber
  - Baseline RT and LN2 temperature comparisons were also done





Temperature	300 K	195 K	77 K
Modulus [Gpa]	1.2 ± 0.1	1.9 ± 0.1	2.7 ± 0.3
UTS [Mpa]	22.2 ± 0.2	32.3 ± 1.6	37.9 ± 0.3

Cold gas appears to enhance some material properties

Enhanced Operating Conditions Work Plan

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Material Compatibility

- Evaluate performance of vinyl ester resin at 200K
- Evaluate effect of nano-particle modifications at 200K
- Variable temperature testing to understand effect of thermal cycling in operation
- Schedule: Q3, FY15 (Pending equipment delivery)

Insulation

- Obtain samples of high R-value physical insulations
- Test R-value performance at cold gas operating temperature (200K).
- Compare:
  - Insulation performance vs. cost (current & high volume $$)
  - Formability
  - Insulation volume and cost vs. operating temperature and pressure range
- Schedule: Q4, FY15

Program Results

- 60 tanks built and tested
- Low cost resin alternative developed and tested
  - Improved burst strength compared to standard epoxy resin
  - Nanoparticulate materials and processing that improve on neat resin properties selected and scaled up.
- Alternate winding patterns tested
  - Identified improved failure criteria that must be used to accurately predict failure where there is a high shear component
  - Likely near local minimum in tank design with variable winding.
- Material testing at cold gas operating condition in progress
  - HDPE at 200K shows improved modulus and tensile strength while retaining high ductility

Reviewers Comments

- FY14 Reviewer Comment: It would be great if the Project can complete all of the tasks outlined in Slide #28. However, it doesn't seem probable that prototype and full-scale tanks will be fabricated and tested given the current status shown in Slide #19. There appear to be both unresolved materials and test facilities issues to be dealt with.
  - FY15 Response: The focus in FY15 has been to address both the material and test facility issues in order to complete the tank builds and testing. 60 test tanks have been built and tested so far.
- FY14 Reviewer Comment: They have performed some testing of material properties and behavior of resins with nanophase additives but apparently are just starting to build and evaluate prototype vessels for validation of their models and predictions. It is also unclear what are the properties of these resins at cryogenic temperature and I saw no plans to evaluate them.
  - FY15 Response: Full tanks are now built and tested. Additional low temperature material evaluations are now planned and variable temperature test capability has been expanded to enable both more low temperature testing and improved understanding of material response to thermal cycling.

Collaborations

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

Proposed Future Work

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Remainder of FY15

- Complete burst testing of full scale tank designs based on performance data from FY14 small scale tank builds
- Correlate full scale tank build material masses into cost savings
- Complete testing on insulating materials cost and performance

FY2016 (No-cost extension effort)

- Fatigue and impact testing of new resin and fiber combinations using industry standard test tanks
- Additional low temperature testing

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 60 tanks to evaluate actual performance of previously modeled performance improvements. Demonstrated low cost resin with equivalent performance to standard epoxy. Developed improved failure model that accurately predicts observed failures with high shear component layers

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

Proposed Future Research: Evaluate burst, fatigue and impact strength of new resin tanks. Low temperature insulation

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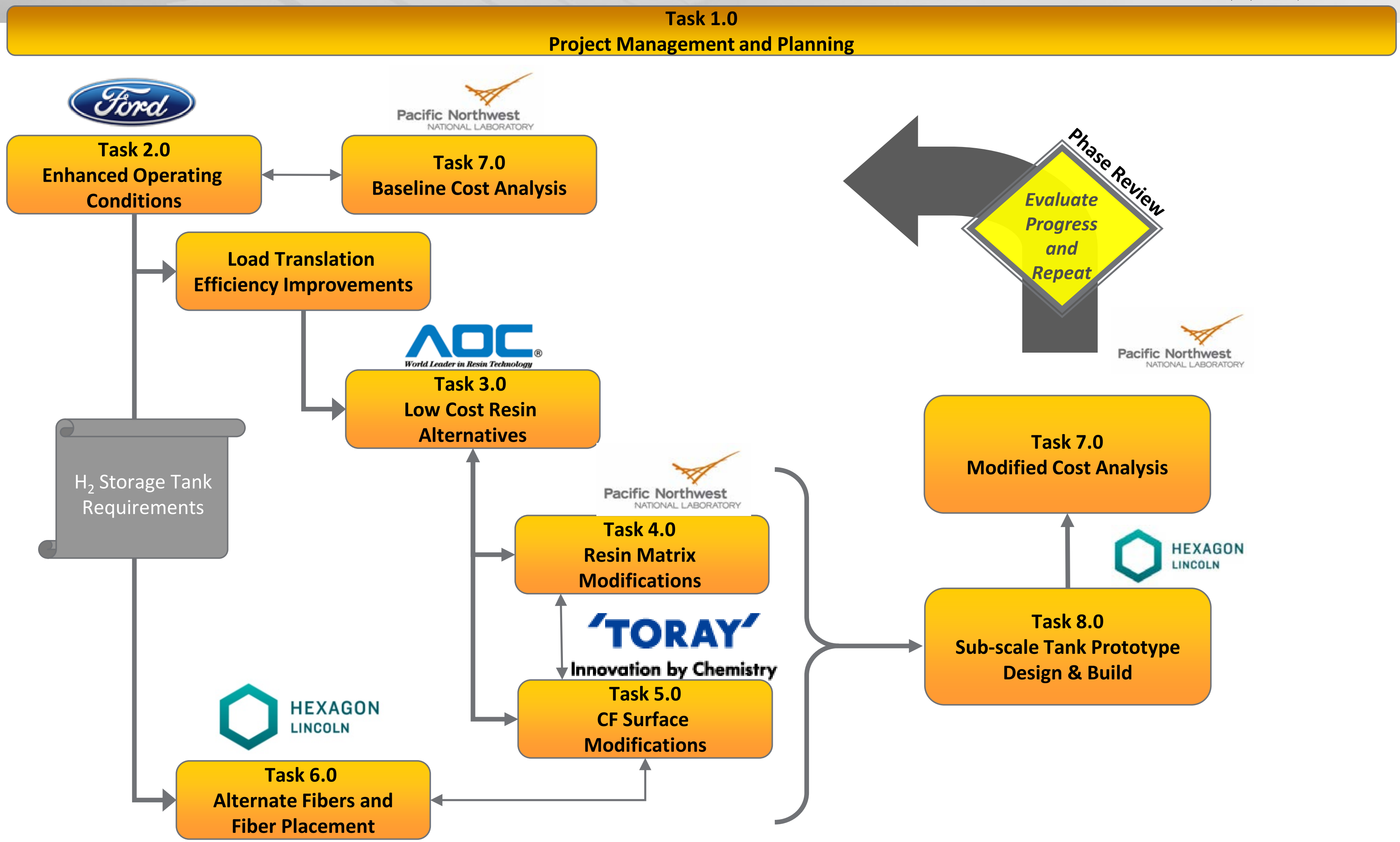
Technical Backup

Project Approach



Flow chart illustrates the approach of the project and inner relationship of each task (task leads are indicated)

Low Cost Resin Alternatives: Cup Tests

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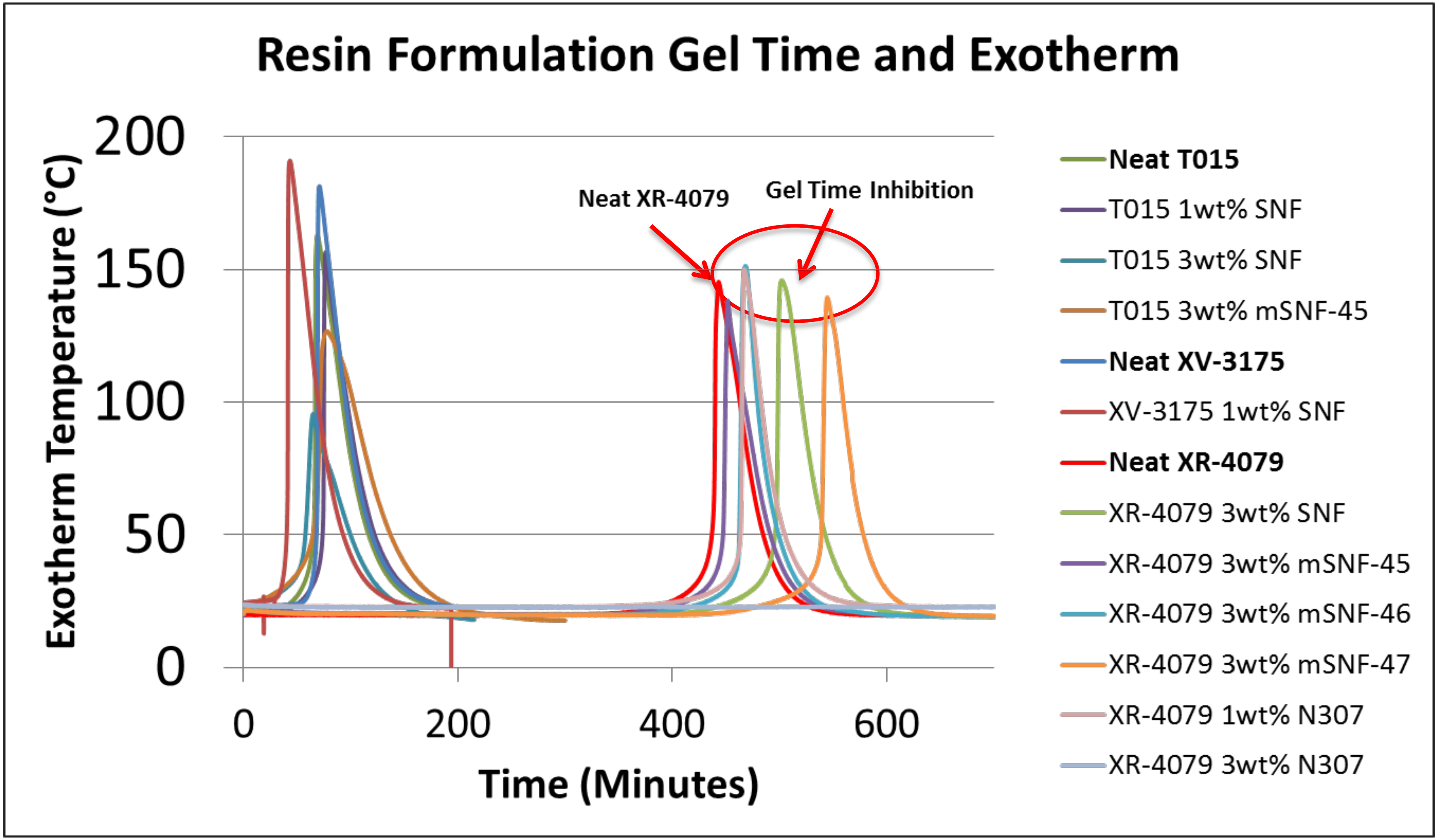

Technical Accomplishment – Alternate Fiber Placement and Multiple Fiber Types

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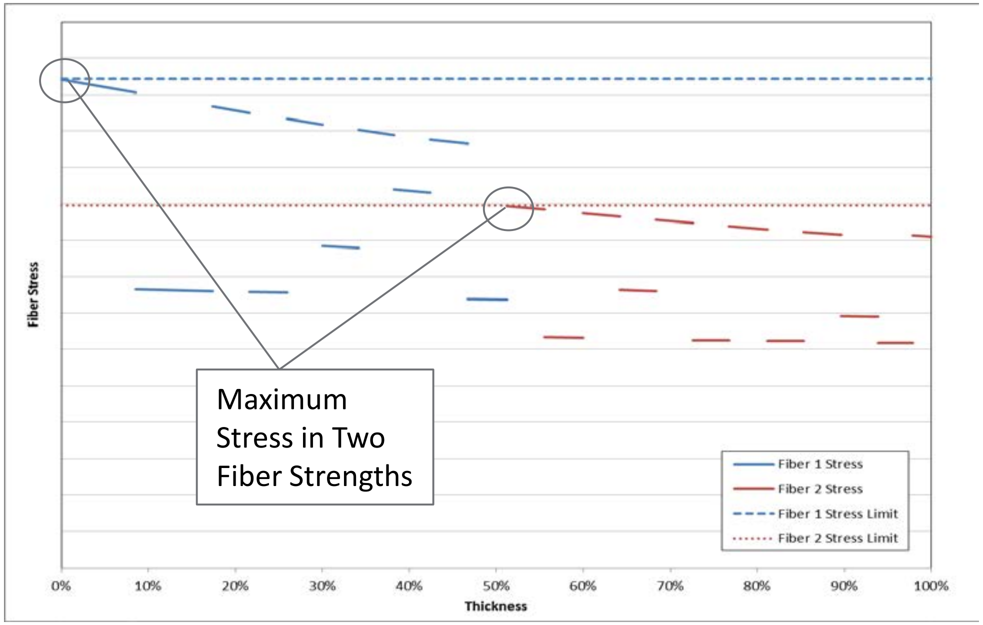

Single Fiber Designs

Evaluation Criteria	T300	T720	T800
Percent Change in Cost	+19%	+9%	+63%
Percent Change in Mass	+59%	-30%	-30%

Combinations of Modulus and Strength Fiber Designs

Evaluation Criteria	Hybrid Modulus Design	Hybrid Strength Design
Percent Change in Cost	+38%	-1%
Percent Change in Mass	-34%	-23%

Low (LAH) and High Angled Helical (HAH) Combinations

Evaluation Criteria	Mild Tailoring	Aggressive Tailoring
HAH Percent Change in Cost	-3%	-14%
HAH Percent Change in Mass	-3%	-14%
LAH Percent Change in Cost	-7%	-16%
LAH Percent Change in Mass	-7%	-16%

Fiber Properties

Material Property	E-Glass	T300	T700	T720	T800
Tensile Strength [ksi]	350	512	711	850	850
Tensile Modulus [Msi]	12.0	33.4	33.4	38.7	42.7
Fiber Count [x1000]	2	12	24	24	24
Yield [ft/lb]	1341	1862	903	1367	1446
Density [lb/in3]	0.093	0.064	0.065	0.065	0.065

HEXAGON LINCOLN

Gen-3 Cryo-Compressed Tank at Cryo and Cold Gas Conditions (from FY14 AMR)

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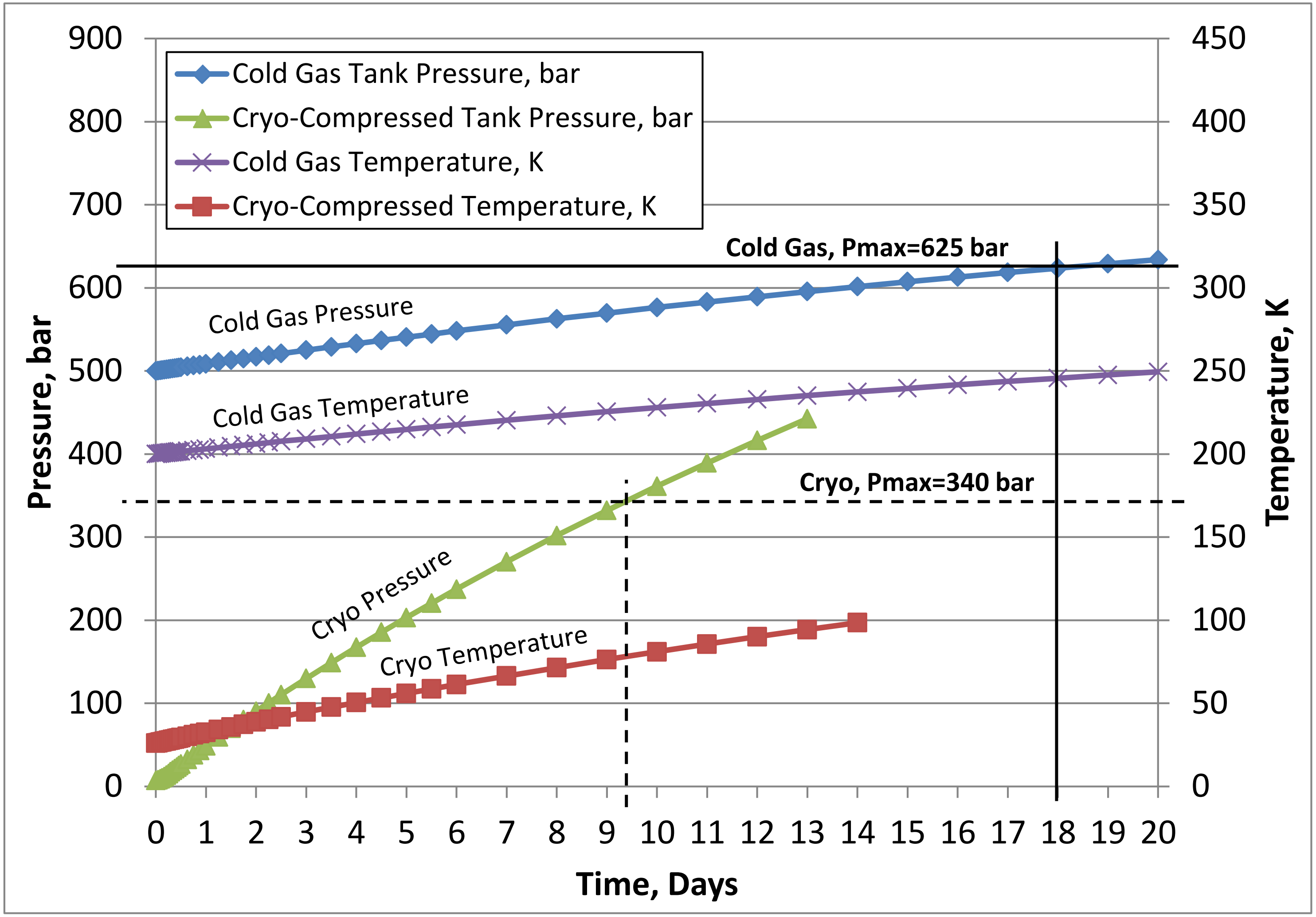

Gen-3 Vacuum Jacket Insulation vs. Vacuum Insulated Panel (VIP), R39, t=60mm