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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

May 15, 2013

Project ID # **ST101**

Overview

Timeline

- Start date: Jan 2012
- End date: Jan 2015
- Percent complete: *33%*

Budget

- Total project funding
  - DOE share: $2,100K
  - Contractor share: $525K
- Funding for FY12: $600K
- Funding received in FY13: $180K
- Funding expected in FY13: $382K

Barriers

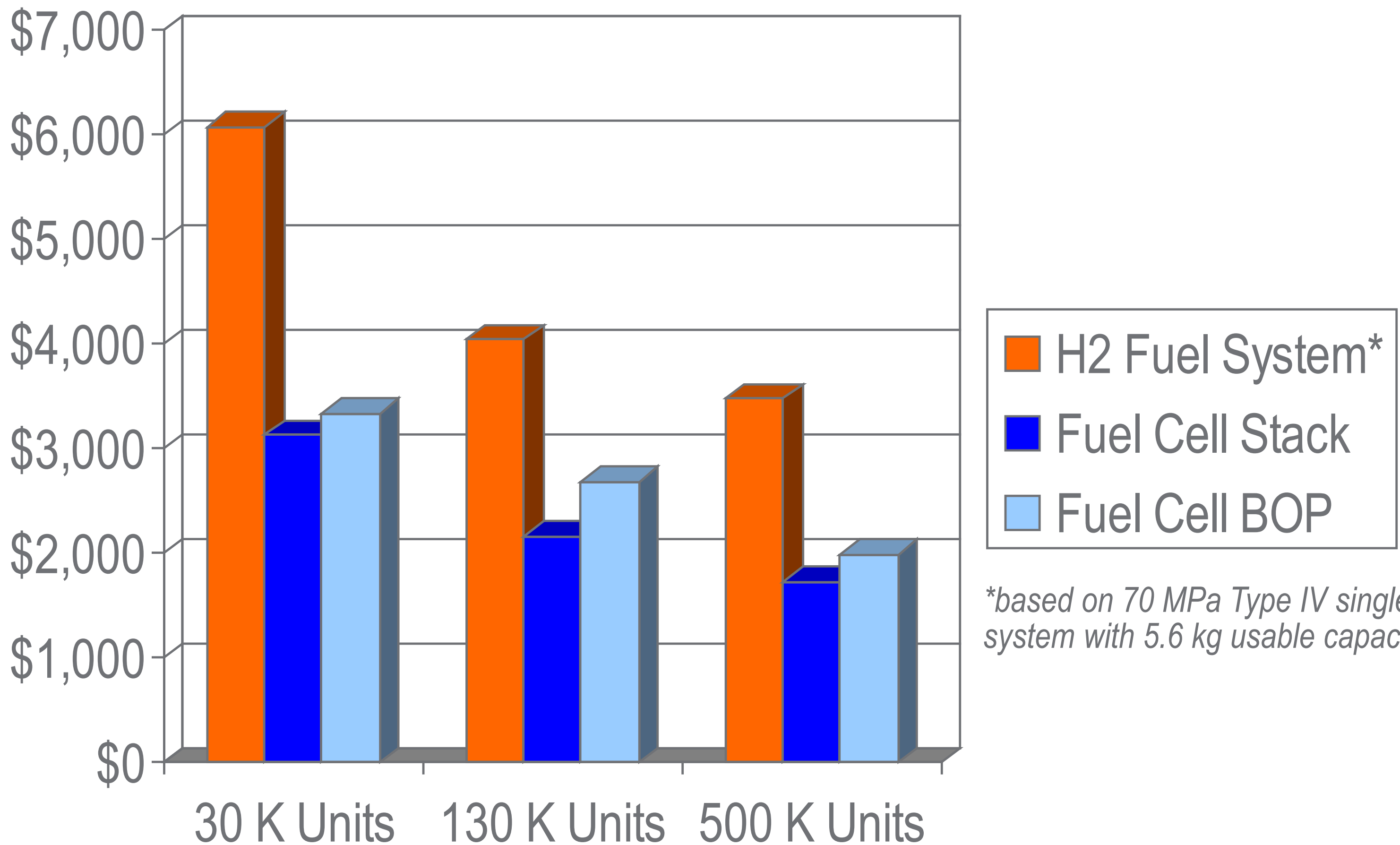
- Barriers addressed
  - Reduce the cost of manufacturing high-pressure hydrogen storage tanks
  - Improved material properties to reduce carbon fiber use
  - Alternative tank operating parameters provides wider operating envelope of pressure and volume
  - Strategic alternative fiber types and fiber placement for cost reduction

Partners

- Project Lead - PNNL
- Collaborating Team Members
  - Hexagon Lincoln
  - Toray CFA
  - AOC, LLC
  - Ford Motor Company

Fuel Cell Vehicle Cost Analysis Study – Highest Cost Systems

based on the 2011 AMR reference projections (DTI and TIAX)



**based on 70 MPa Type IV single tank system with 5.6 kg usable capacity*

The hydrogen fuel system is one of the most expensive systems on a fuel cell vehicle.

Relevance

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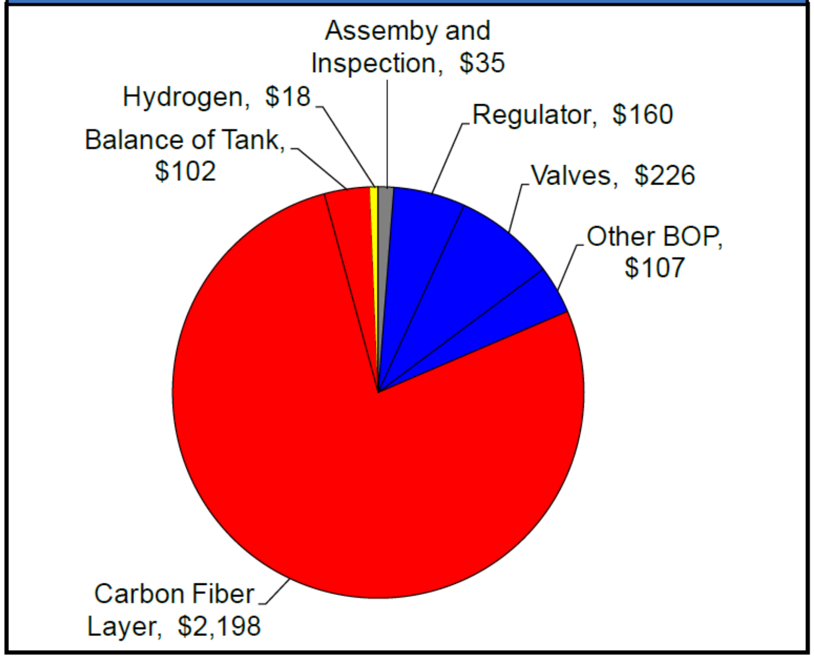
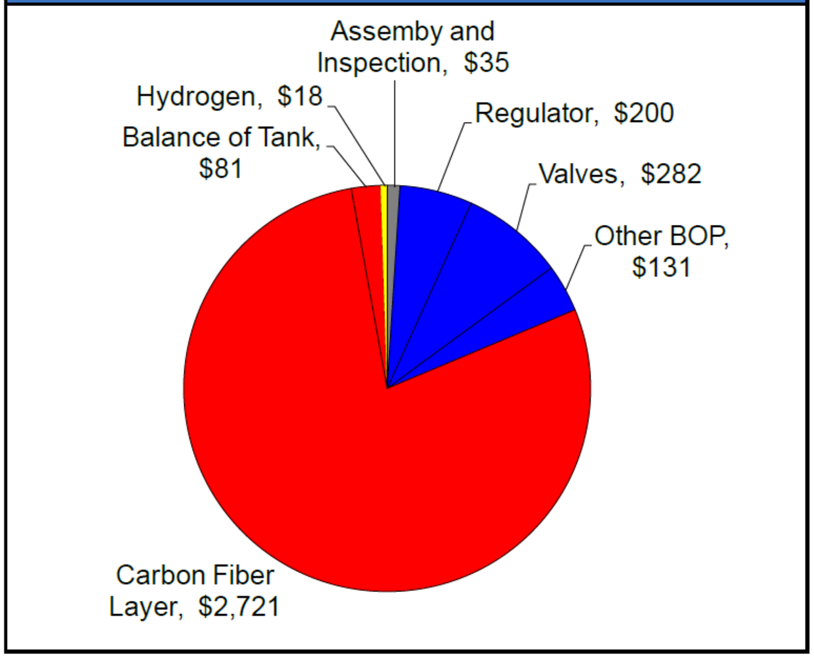
TIAX Cost Analysis Study – High Volume -based on the 2011 AMR reference projections

Type IV 350-bar 500,000/yr
Factory Cost[1] = $2,850
\$15.3/kWh based on 5.6 kg usable H_2 (5.8 kg stored H_2)



[1] Cost estimate in 2005 USD. Includes processing costs.

Type IV 700-bar 500,000/yr
Factory Cost[1] = $3,480
\$18.6/kWh based on 5.6 kg usable H_2 (5.8 kg stored H_2)

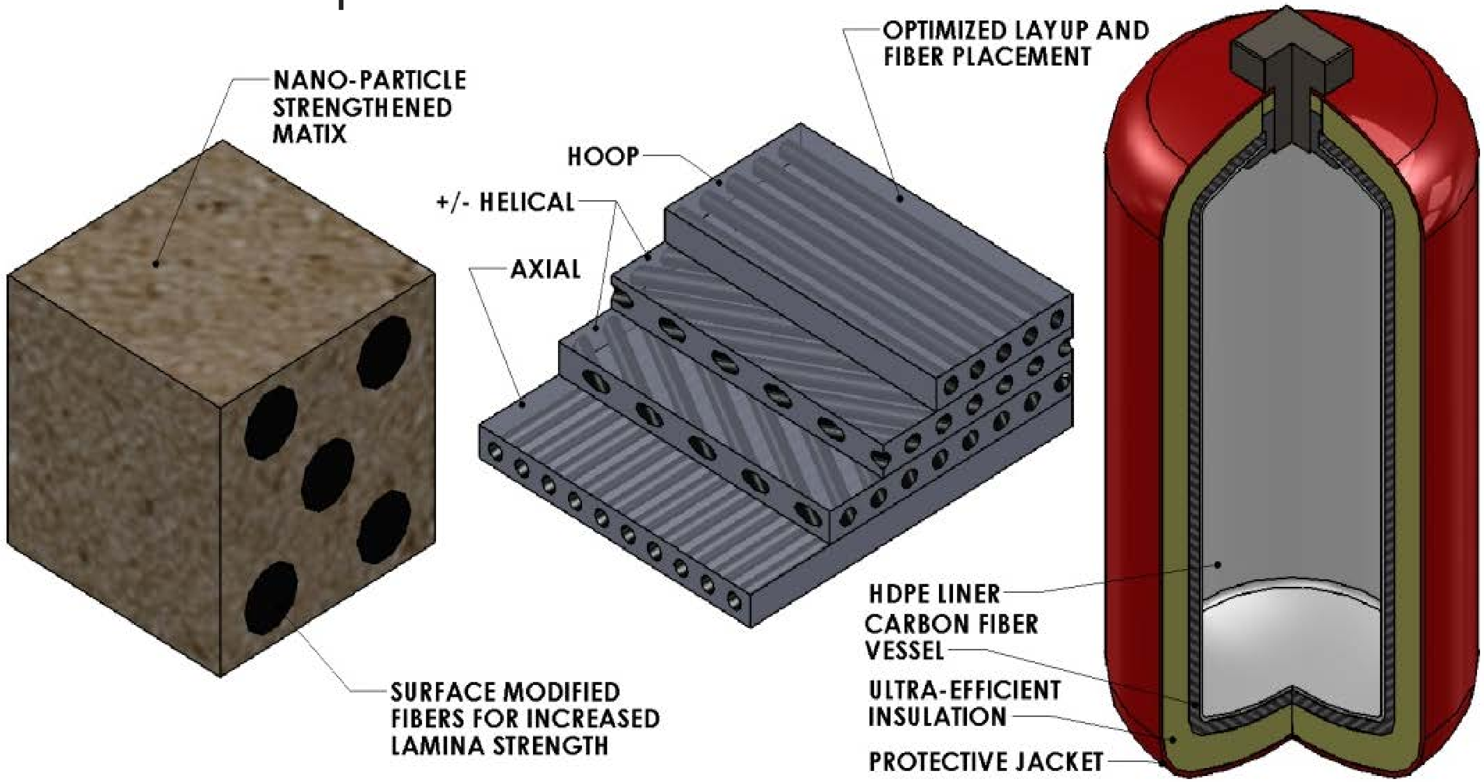


[1] Cost estimate in 2005 USD. Includes processing costs.

The carbon fiber layer (fiber and resin) is the dominant cost of the hydrogen fuel system which is the focus of this project.

Project Approach

- Improvement of the individual constituents for synergistically enhanced tank performance and cost reduction



Reduced tank costs and mass through engineered material properties for efficient use of carbon fiber

Updated Milestones

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Date	Milestone or Go/No-Go Decision	Status
8/30/2012	Milestone: Develop a baseline cost model for an on-board vehicle capacity tank with resin, fiber, liner, bosses, and processing and compare cost against prior DOE studies with TIAX and ANL	**Completed**
2/28/2013	Milestone: Design and model new tank design with enhanced operating parameters of pressure and temperature for an equivalent tank with alternate fibers and/or new fiber placement technique and develop cost model for the new improved tank and compare against DOE target of 50% cost reduction	**Completed**
3/31/2013	**Go/No-Go: "PNNL, with partners Toray Carbon Fibers America, AOC Inc., Lincoln Composites, and Ford Motor Company, will develop a feasible pathway to achieve at least a 10% ($1.5/kWh) cost reduction, compared to a 2010 projected high-volume baseline cost of $15/kWh for compressed H_2 storage tank through detailed cost modeling and specific individual technical approaches."**	**Completed**
8/30/2013	Milestone: Demonstrate integration of modified CF fibers and alternate/modified resins	**In progress**
9/30/2013	Milestone: Baseline sub-scale prototype tank and burst test	In progress
1/30/2014	Milestone: Demonstrate feasibility of modified CF fibers and resins at operating conditions called out by enhanced operating conditions design	Not started
3/31/2014	**Go/No-Go: "PNNL, with partners Toray Carbon Fibers America, AOC Inc., Lincoln Composites, and Ford Motor Company, will develop a feasible pathway to achieve at least a 20% ($3.0/kWh) cost reduction, compared to a 2010 projected high-volume baseline cost of $15/kWh for compressed H2 storage tank through detailed cost modeling and specific individual technical approaches."**	In progress

Project Approach
Tasks and Assignments

- **Task 1.0** – Project management and planning (Lead Org. – PNNL)
- **Task 2.0** – Enhanced operating conditions (Task Lead – Ford)
- **Task 3.0** – Low cost resin alternatives (Task Lead – AOC)
- **Task 4.0** – Resin matrix modifications (Task Lead – PNNL)
- **Task 5.0** –CF Surface modifications (Task Lead – Toray)
- **Task 6.0** – Alternative fibers & fiber placement (Task Lead – Lincoln)
- **Task 7.0** – Cost analysis (Task Lead – PNNL)
- **Task 8.0** – Sub-scale tank prototype (Task Lead – Lincoln)

Project Approach

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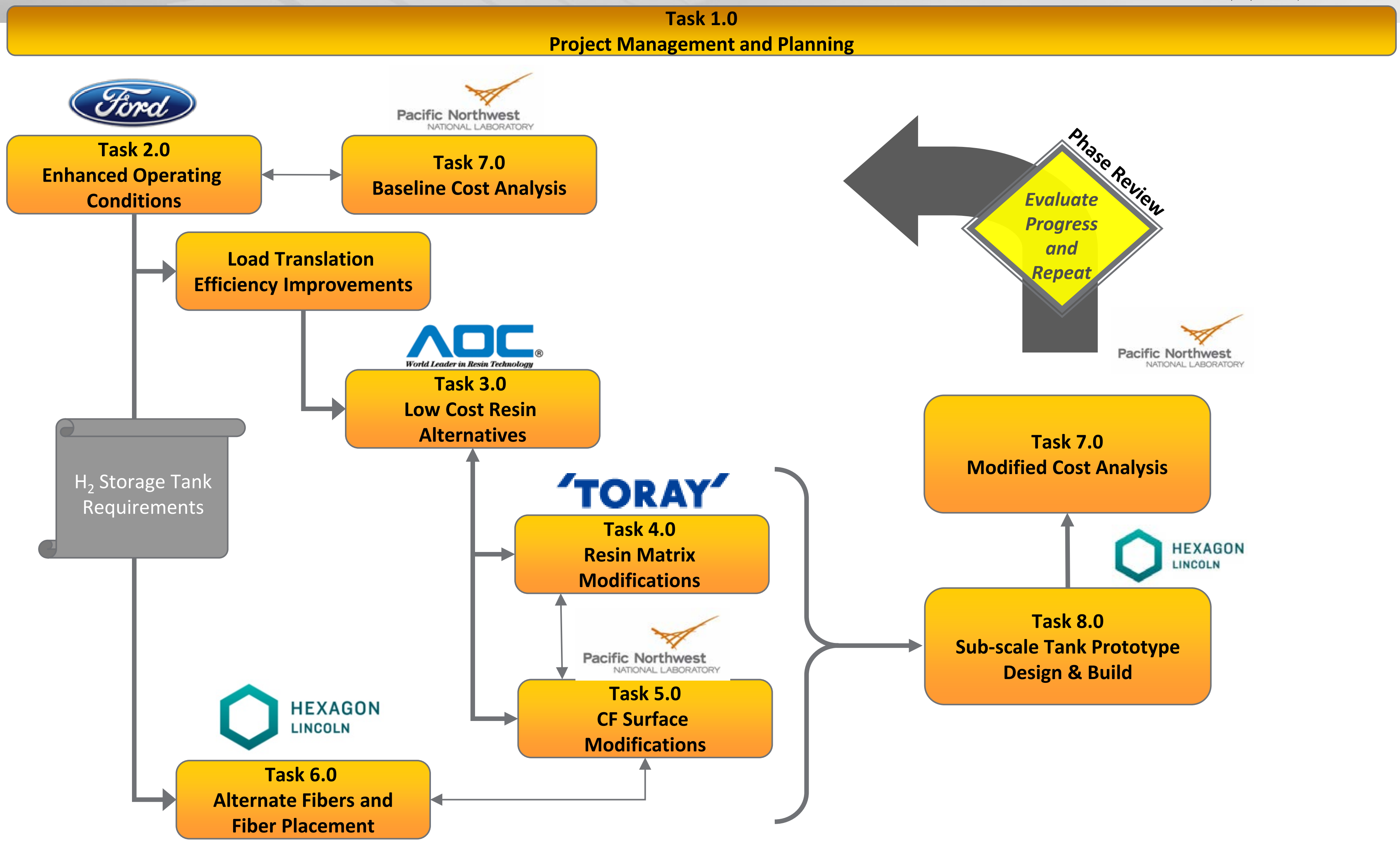

Flow chart illustrates the approach of the project and inner relationship of each task (task leads are indicated)

Project Approach
Baseline Cost analysis

- Baseline cost model for an on-board vehicle tank was considered a critical element for the project in order to evaluate the starting point and progress.
- Cost factors:
  - Carbon Fiber Options: material and usage
  - Insulation Concepts: vacuum, ultra-insulations
  - Design Alternatives: resin, fibers, liner, processing
- Compare with prior DOE cost studies by TIAX and Strategic Analysis (SA).
- Cost model will allow for trade-off studies to be performed in order for the team to focus on the most promising concepts.
- Desire to use a simplified estimator tool for predicting storage system parameters and cost without extensive CAE modeling.

Project Approach - Cost Analysis Estimator Model

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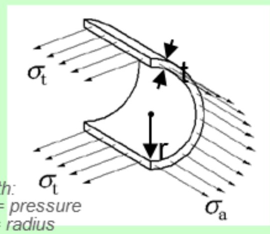
Cylinder Performance Model Setup:

- based on "thin walled pressure vessel equation"
- cylinder divided into three main regions:
  - cylindrical region
  - dome region
  - neck/boss



with:
p = pressure
r = radius
t = wall thickness

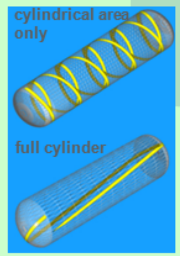
hoop layer

$$\sigma_t = \frac{p \cdot r}{t}$$

reinforce

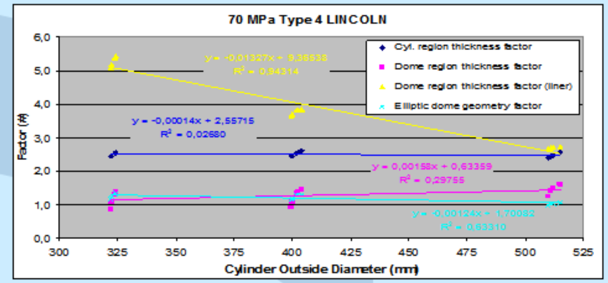
helical layer

$$\sigma_a = \frac{p \cdot r}{2 \cdot t}$$

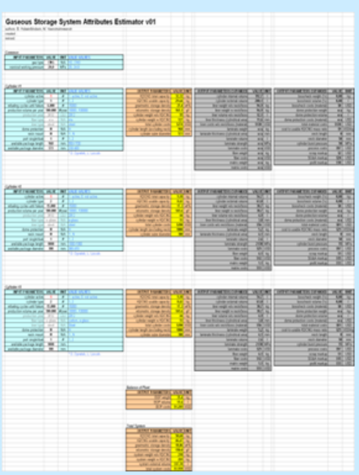


Establish Functions for different Types & NWPs:

- Laminate thicknes in cyl. area
- Laminate thickness in dome region
- Eliptic dome radius
- Liner thickness in dome region



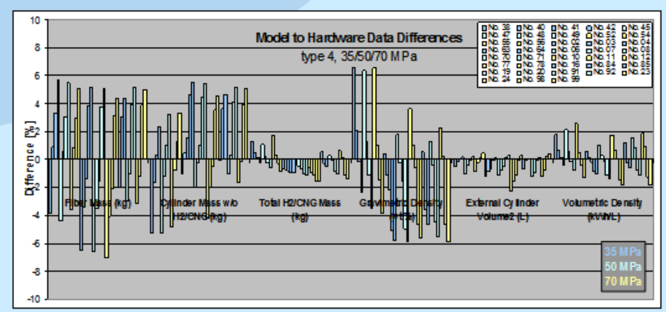
Generate/include into GUI:



- Include calculation into GUI
- Check data consistency
- Release as next version
- Document under Change Log

Validate Model Results to Hardware/Design Data:

- Confirm model deviation to hardware/design data
- Optimize calculation where required
- Release calculation approach to model/GUI



Developed simplified estimator model for predicting tank parameters within +/- 5% of existing tank hardware

Project Approach - Tank Cost Analysis
Cost Analysis Estimator Model

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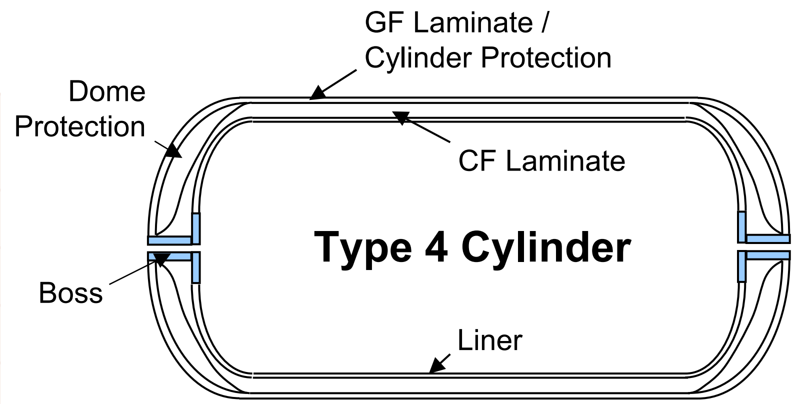
- Key cost estimating step was to establish the appropriate input assumptions
- Baseline material cost factors:

Description	Material	Volume	$/kg	Scrap	Cost + Scrap $/kg
Liner (Blow Mold)	HDPE	10k-100k	2.09	n/a	2.09
Carbon Fiber	T700-S	10k-30k	33.00	n/a	33.00
Carbon Fiber	T700-S	80k	30.80	n/a	30.80
Carbon Fiber	T700-S	100k	29.48	n/a	29.48
Carbon Fiber	T700-S	100k+	28.60	n/a	28.60
Resin	Epoxy	10k-100k	6.60	1.25	8.25
Aluminum (Boss)	Al 6061-T6	10k-100k	4.75	2.0	9.50



- Baseline performance factors:
  - Safety Factor: 2.25x NWP (70 MPa)
  - CF Tensile Strength: 4,900 MPa
  - Translational Efficiency: 83%
  - CF Variability Factor: 10%
  - CF Volume Fraction: 60%

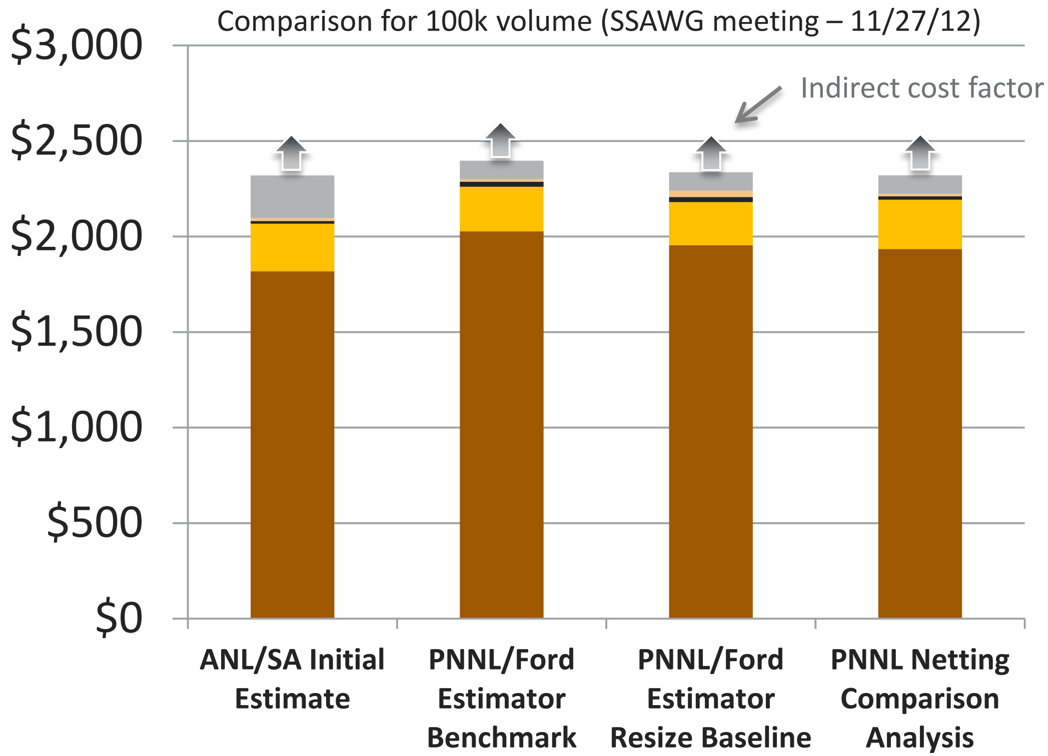
Note: baseline excluded optional dome and GF cylinder protection

Technical Accomplishment
Cost Analysis – Comparison

- Completed extensive cost estimating comparison with ANL and Strategic Analysis, resulting in consistent values
- Main differences are the translational efficiency and filament winding process assumptions

Baseline Tank
70 MPa H2 Type 4
5.6 kg H2 for 300 mile range

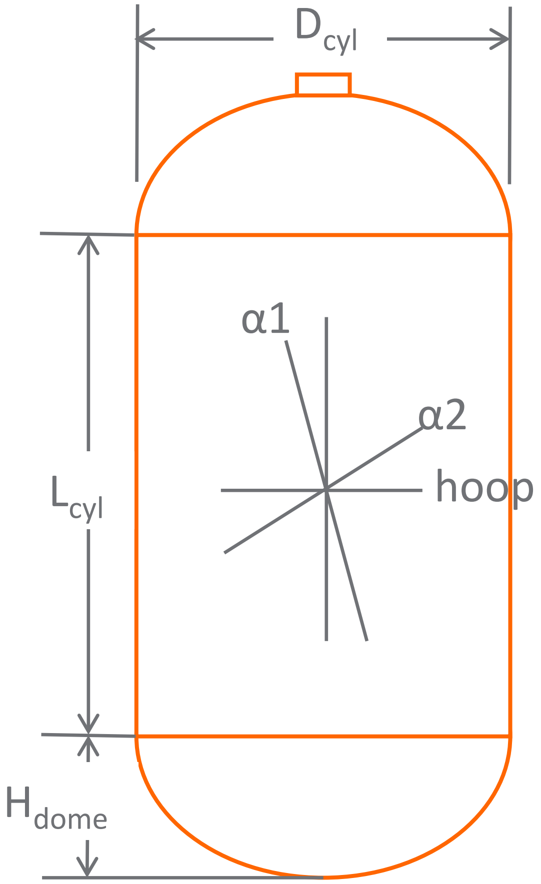
Optimal tank configuration based on single longitundinal tank package location
~Ø400 mm x 1900 mm



The PNNL/Ford cost estimator model has been successfully benchmarked (high volume comparison)

Technical Accomplishment - Cost Analysis Netting Analysis for Tank Mass Confirmation

- Netting analysis assumes:
  - Fibers are loaded in tension.
  - The matrix does not contribute to strength.
  - Shear stresses are small.
- Roylance* implementation for 2 helical and 1 hoop fiber direction.
  - α1 = low angle helical over polar bosses.
  - α2 = mid angle helical over tank shoulder.
  - Hoop fibers in the cylindrical section.
- PNNL refinements
  - Helical/Hoop stress = 0.6 to prevent end blow-out.
  - Thick-walled cylindrical and spherical stress concentrations
  - Through-thickness composite compression
- Tank Mass Comparison:
  - ANL finite element analysis 91.0 kg
  - Tank cost estimator tool 97.1 kg
  - PNNL netting analysis 99.0 kg



Good agreement between methods

* Roylance, D.K. 1976. Netting Analysis for Filament-Wound Pressure Vessels, AMMRC TN 76-3.

Technical Accomplishment - Cost Analysis Cost Reduction Opportunities Identified

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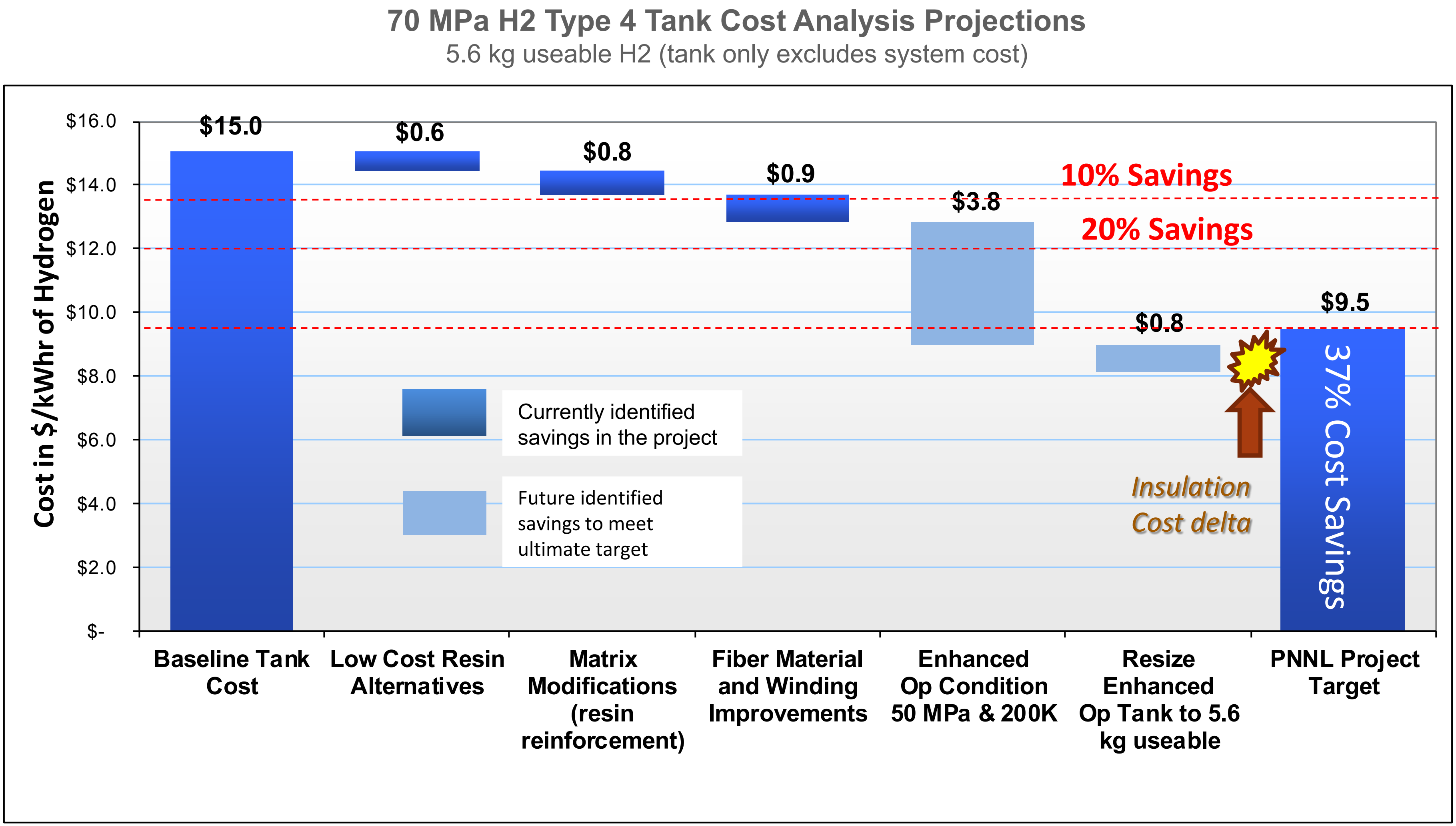
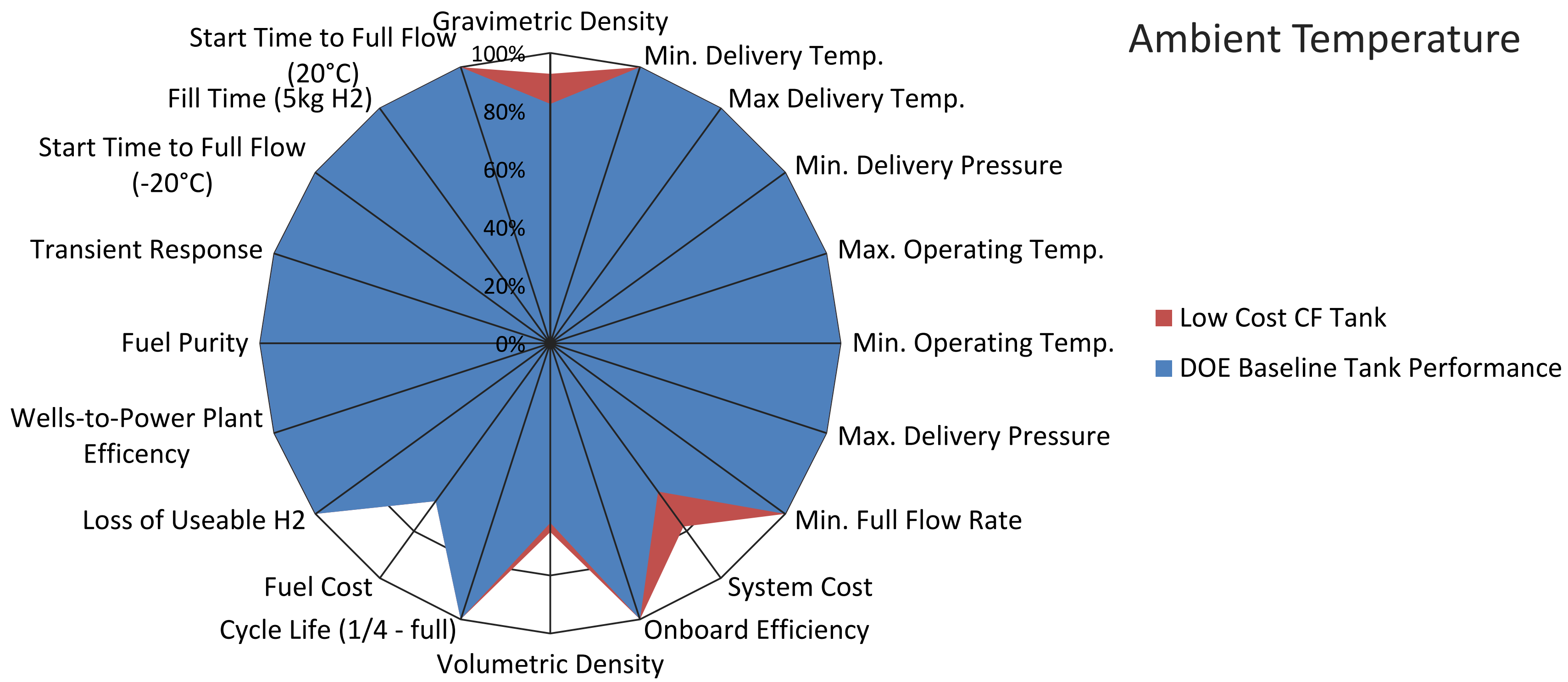


Currently identified reduction opportunities to achieve a 10% tank cost savings and projected path to target

Technical Accomplishment - Spider Chart

700 Bar Type IV Single Tank System Compared Against 2017 Targets



Technical Accomplishment – Low Cost Resin Alternative and Carbon Fiber Surface Modifications

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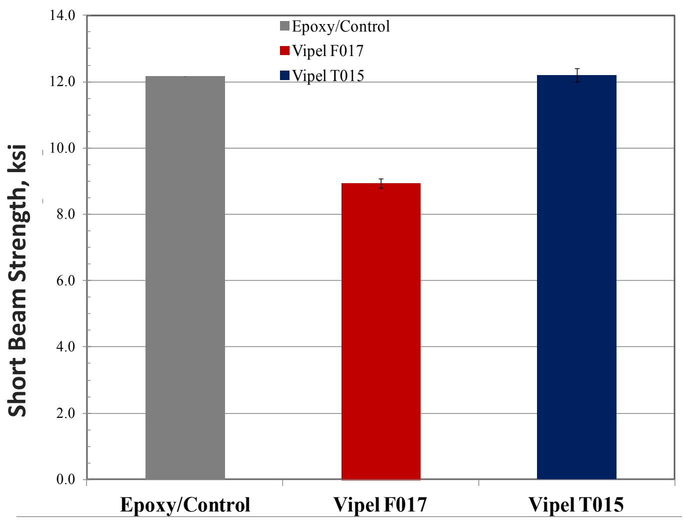
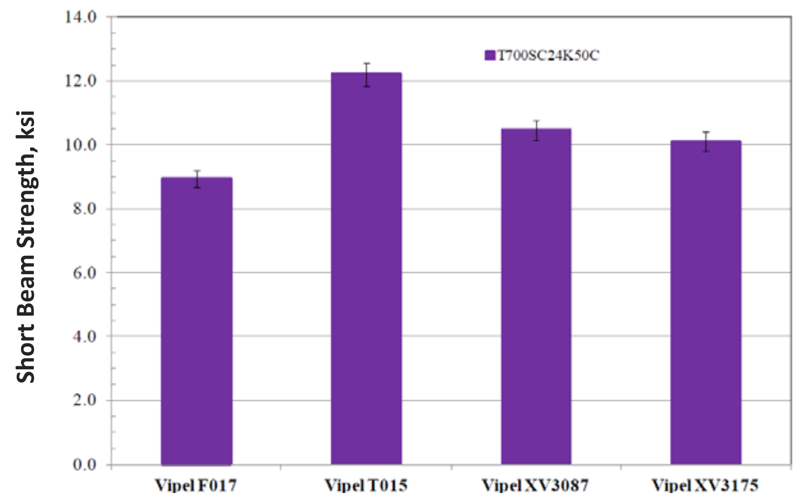
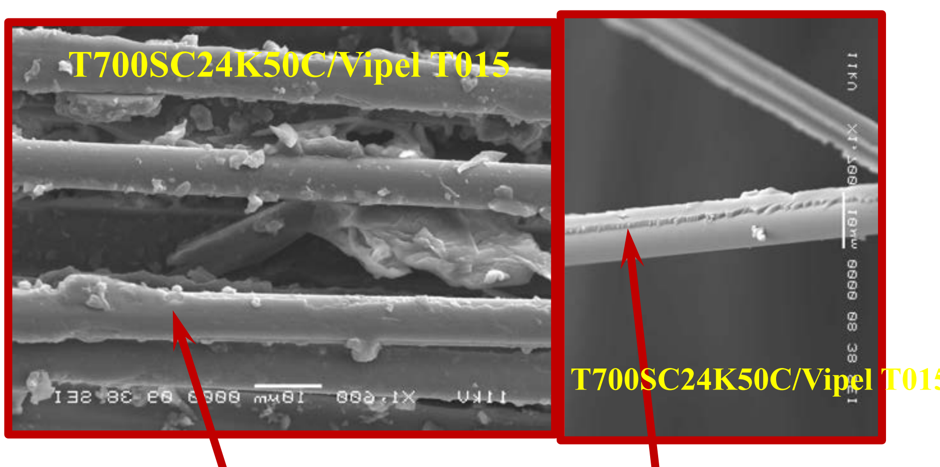


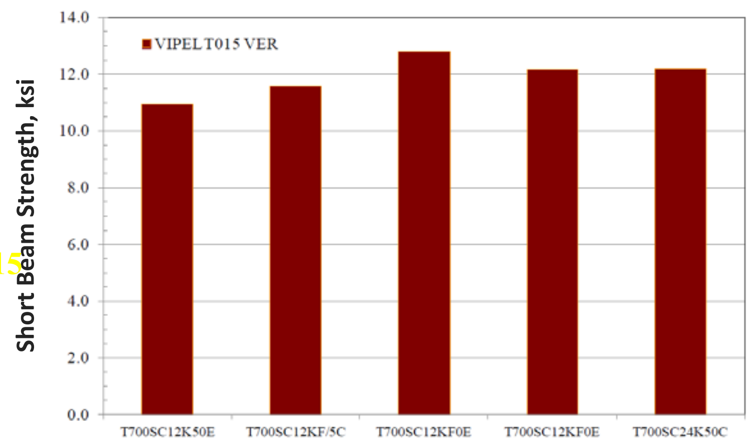
COMPARISON OF AOC VINYL ESTER RESIN SYSTEMS SHORT BEAM STRENGTH USING T700SC24K50C





Good Fiber-Matrix Adhesion

COMPARISON OF TORAYCA CARBON FIBERS SHORT BEAM STRENGTH USING VIPEL T015



Technical Accomplishment – Low Cost Resin Alternative and Carbon Fiber Surface Modifications

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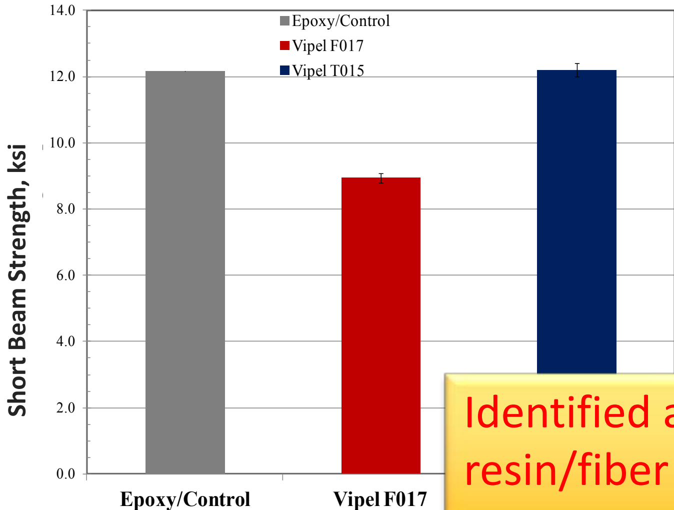

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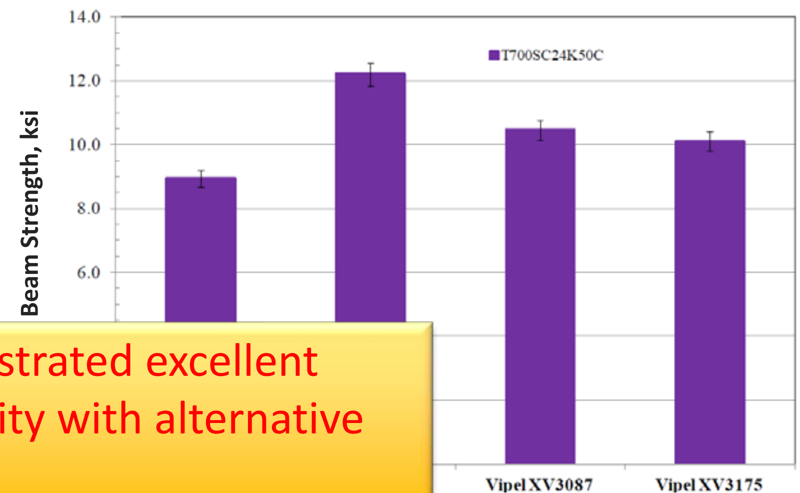
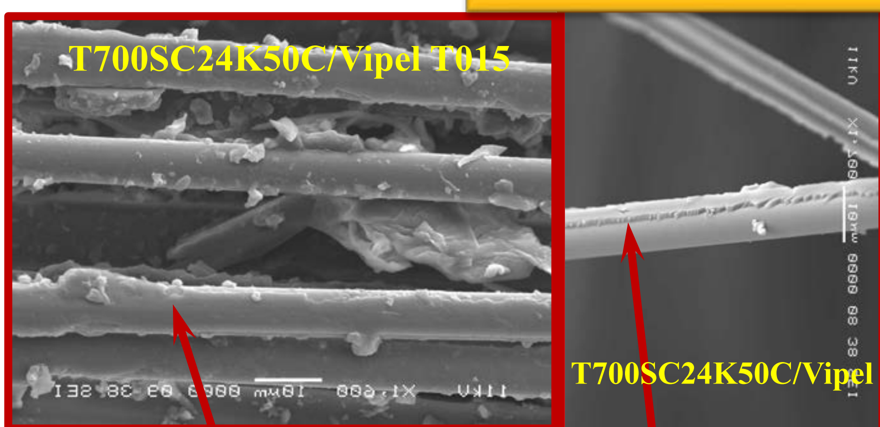
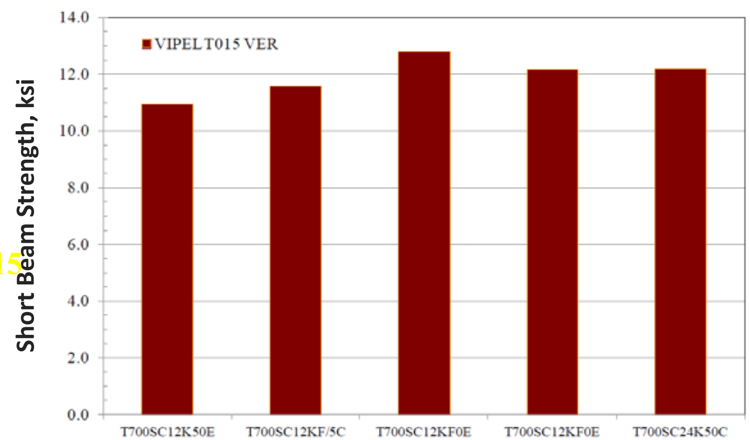


Identified and demonstrated excellent resin/fiber compatibility with alternative resin systems



COMPARISON OF TORAYCA CARBON FIBERS SHORT BEAM STRENGTH USING VIPEL T015



Good Fiber-Matrix Adhesion

Technical Accomplishments – Low Cost Resin Alternative: Resin Property Mechanical Testing

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- Low cost resin systems mechanical properties evaluated
- Sub ambient temperature testing of resins for future cold gas
- Resin systems tested are approximately 60-70% of the cost of epoxy systems
- Vinyl ester resins were similar to the epoxy system properties

				Vinyl ester resin systems						
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

AOC® World Leader in Resin Technology

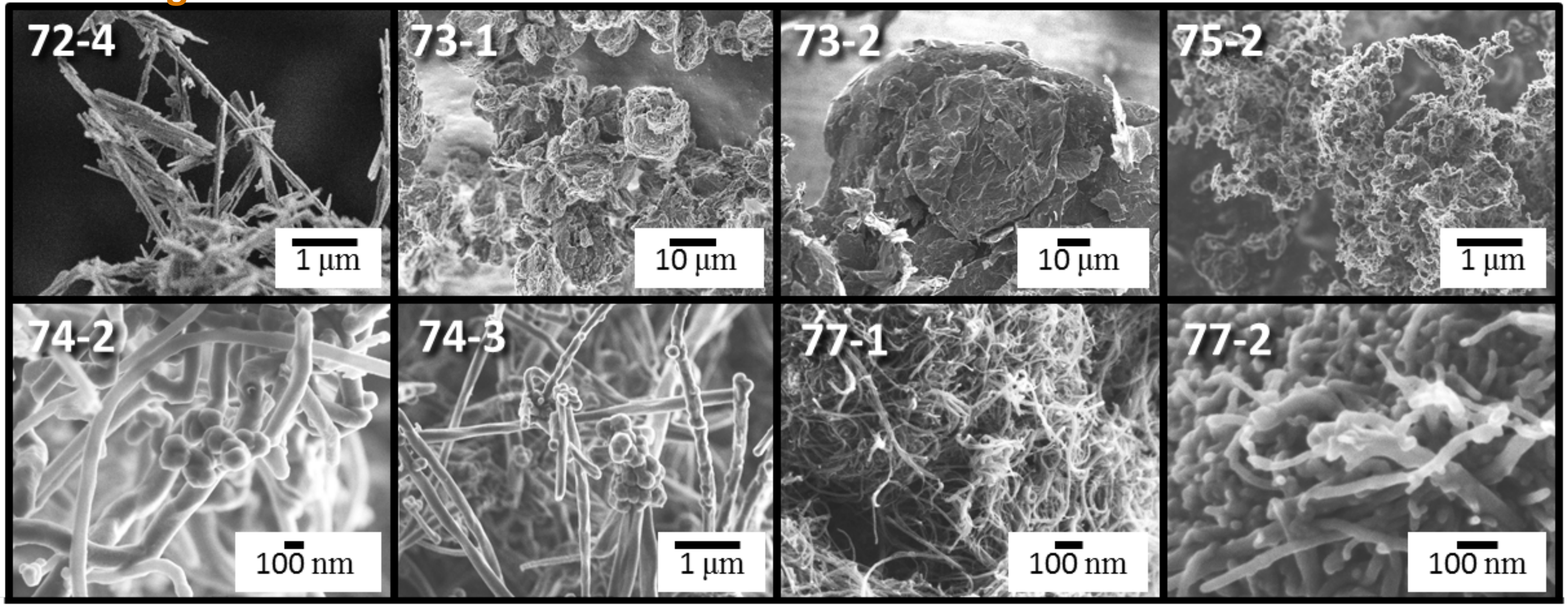
Identified and tested alternative resin systems similar to epoxy properties

Technical Accomplishment – Resin Modifications

Nanoscale additive	key
T015 neat resin	72-2
1wt% silica nano fibers	72-4
1wt% Cloisite 20A (nano clay)	73-1
1wt% xGnP-M-25 SN S070811 xGSciences (Graphene NanoPlatelets)	73-2
1wt% PR-24.XT-HHT-LD (Nano carbon fiber) carbon nanotubes	74-2
1wt% VGCF 06-06-108 (Vigin graphite carbon fiber) carbon nanotubes	74-3
1wt% Asbury online Nano307 (Nano graphite platelets)	75-2
1wt% multi wall carbon nanotubes	77-1
1wt% multi wall carbon nanotubes w/NH_2 functionalization	77-2

- Evaluated morphology effects on mechanical properties
- Clays, platelets, tubes, fibers
- Mixing with resins and performing tensile tests
- Down select based on price and material properties

SEM images of the nanoscale additives



Technical Accomplishment – Resin Modifications: testing of nanoscale additives in alternate resins

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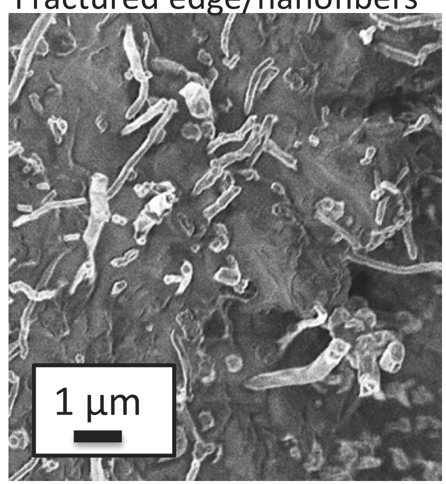
- Tensile samples fabricated from vinyl ester resins with nanoscale additives
- Testing shows significantly enhanced UTS and Elongation at break with nano-additives
- Additional testing with different cure recipes is needed and at cryogenic temperatures
- Based on cost and performance, nanoclays and nanoplatelets are top candidates at $3-10/lb

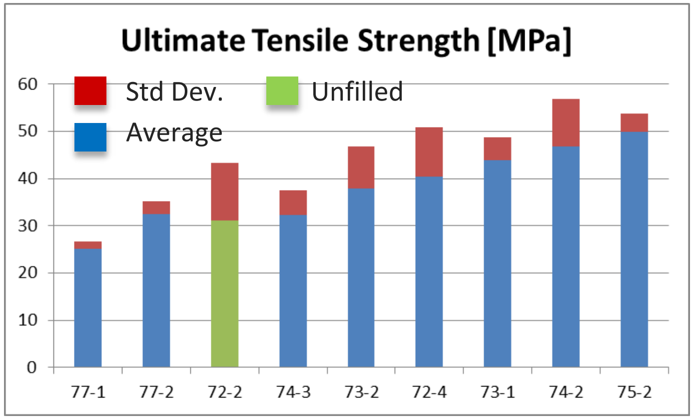
Tensile testing nano-filled resin

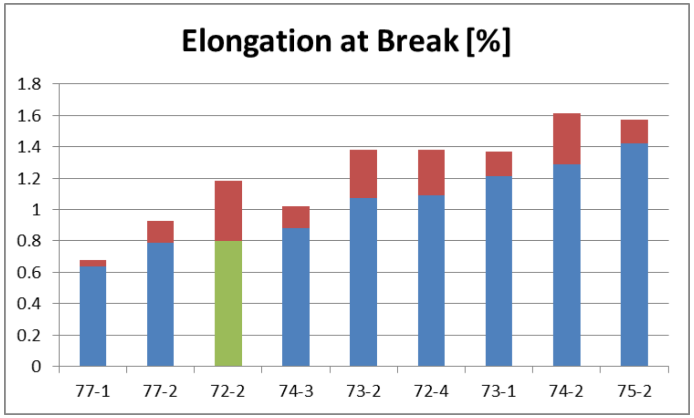
Fractured edge/nanofibers



neat resin

nano-filled resin





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- Additional testing with cure recipes is needed and at cryogenic temperatures
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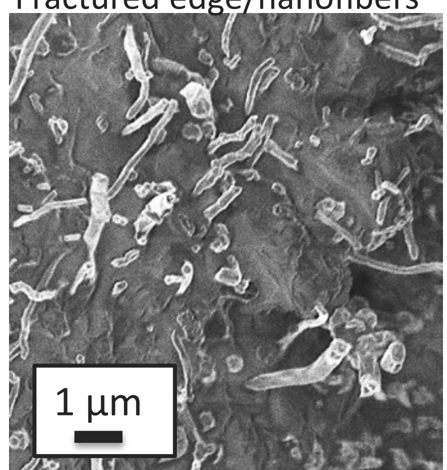
Filler morphology can significantly impact the resin properties

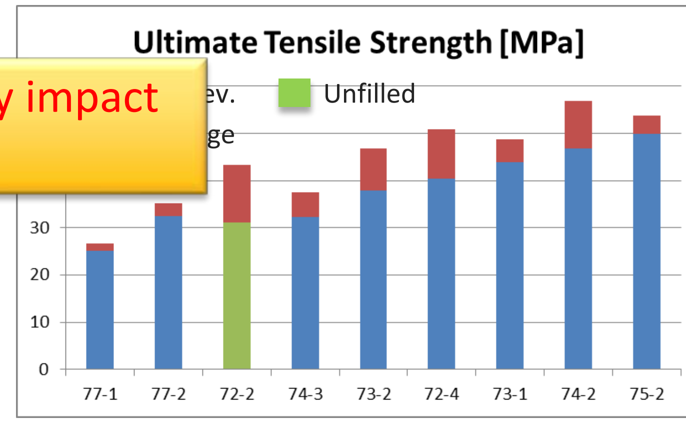
Tensile testing nano-filled resin

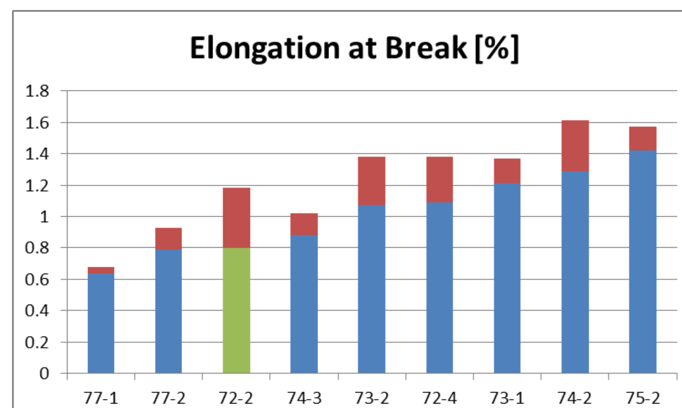
Fractured edge/nanofibers



neat resin

nano-filled resin





Technical Accomplishments – Resin Modifications: Predict Material Properties and Burst Pressures

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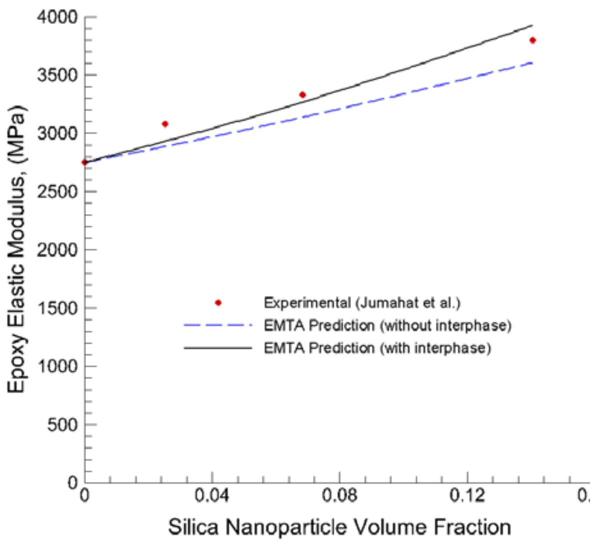
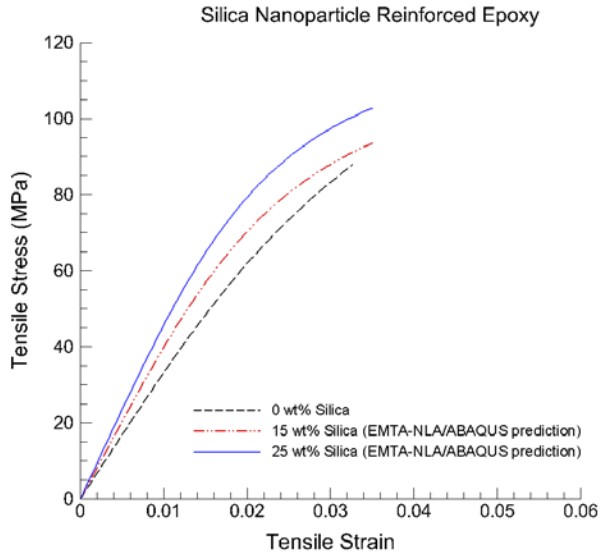
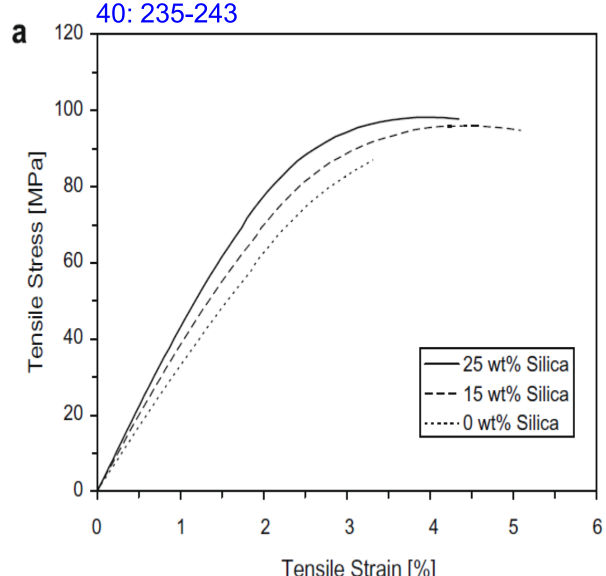


Resin property prediction validated with experimental data



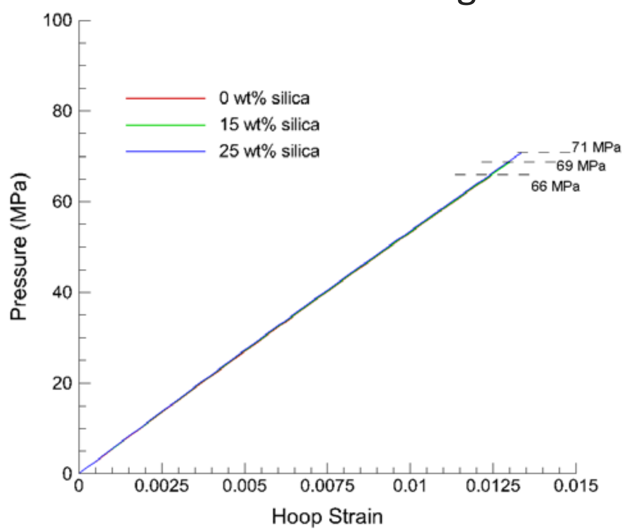
Resin property prediction at different filler loadings

Mahrholz et al. (2009), Composites: Part A 40: 235-243



Validated with experimental data comparison of predicted results

Finite element model with predicted material properties



Validated model for predicting burst pressures with experimental data

Technical Accomplishment - Alternate Fiber Placement and Multiple Fiber Types

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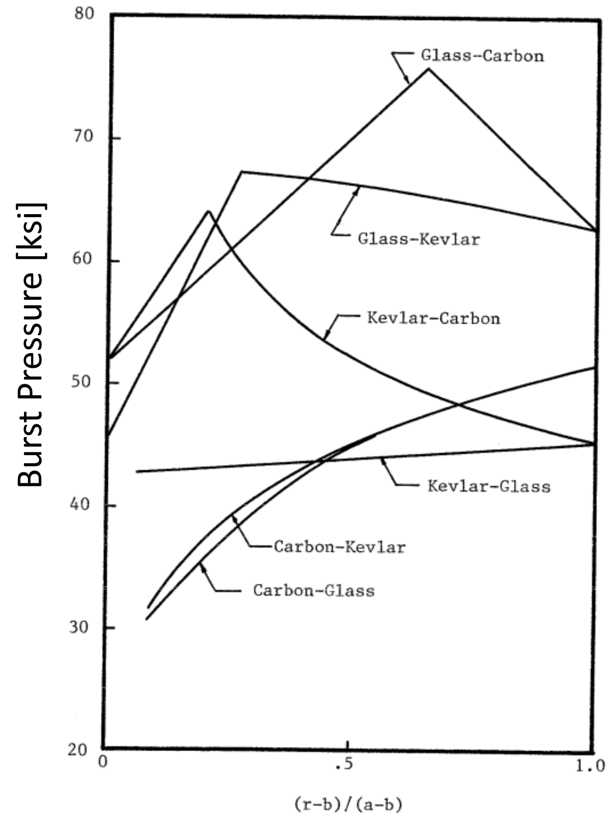

- Investigate alternate carbon fibers
  - Evaluate performance/price
  - Consider heavy tow fibers
- Investigate alternate low-cost fibers
  - Evaluate performance/price
  - Consider strength and other performance issues
  - Consider manufacturability
- Look at hybrid fiber reinforcement
  - Some materials 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

HEXAGON LINCOLN

Technical Accomplishment – Alternate Fiber Placement and Multiple Fiber Types

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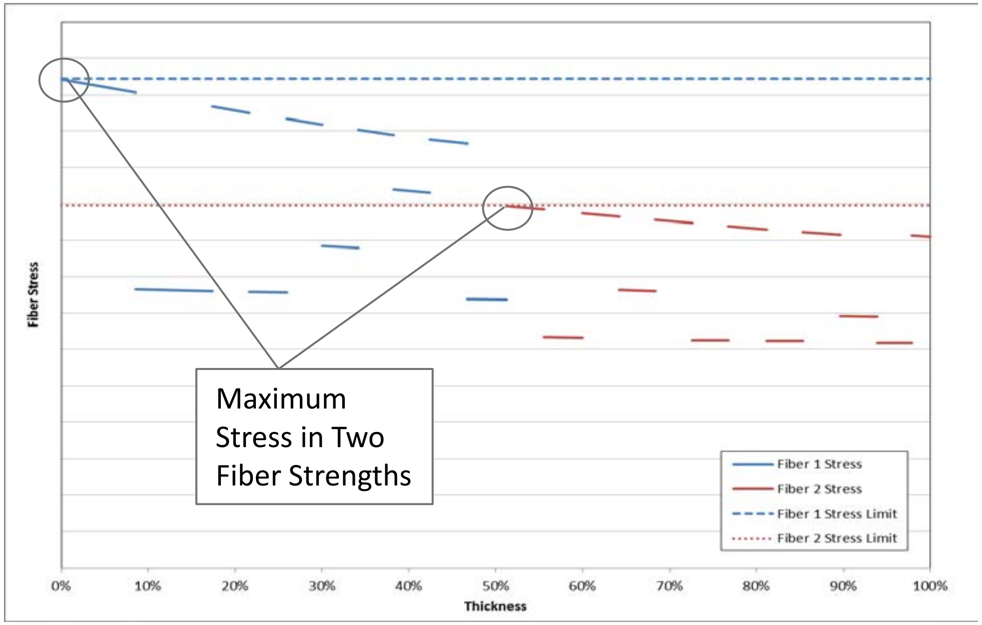


Single Fiber Designs

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%

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

Low and High Angled Helical 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%

HEXAGON LINCOLN

Gains in cost and mass savings up to 16% through controlled fiber placement

Collaborations

- Pacific Northwest National Laboratory: Kevin Simmons (PI), Ken Johnson, Kyle Alvine
  - 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

FY13

- Resin modifications with higher filler concentrations
- Tank dormancy for cold gas storage
- Tank modeling for resizing of cold gas storage
- Tooling for baseline tanks
- Fabricate baseline tanks: epoxy and vinyl ester
- Burst testing

FY14

- Fabricate tanks with baseline geometry with material property enhancements
- Fabricate tanks with baseline geometry with alternate fiber placement and multiple fiber types
- Material modifications with higher concentrations
- Mechanical testing of ASTM rings with resins and higher filler concentrations
- Burst testing

Project Summary

- Developed simplified estimator model for predicting tank parameters within +/- 5% of existing tank hardware
- Completed extensive cost estimating comparison with ANL and Strategic Analysis, resulting in consistent values
- The PNNL/Ford cost estimator model has been successfully benchmarked (high volume comparison)
- Identified reduction opportunities to achieve a 10% tank cost savings and projected path toward a 37% target
- Potential cost savings identified
  - Low cost resins 4%
  - resin modification improvements 5%
  - Alternative fiber placement and fiber types 6%
  - Total savings after cost model analysis is 15%

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: Developed a feasible pathway to achieve at least a 10% ($1.5/kWh) cost reduction, compared to a 2010 projected high-volume baseline cost of $15/kWh for 350 bar Type IV pressure vessels through detailed cost modeling and specific individual technical approaches

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

Proposed Future Research: Validate predictive models with experimental data

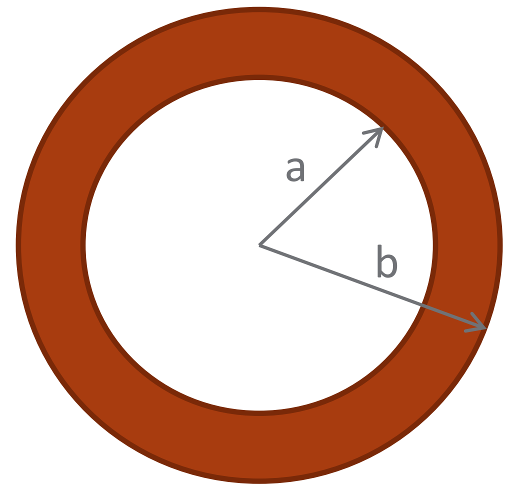
Back Up Slides

Netting Analysis Refinements

- Thick-walled stress concentrations:
  - Cylinder inner wall hoop
  - Dome inner wall axial

$$\frac{(b^2+a^2)}{(b^2-a^2)}\frac{(b-a)}{a}$$

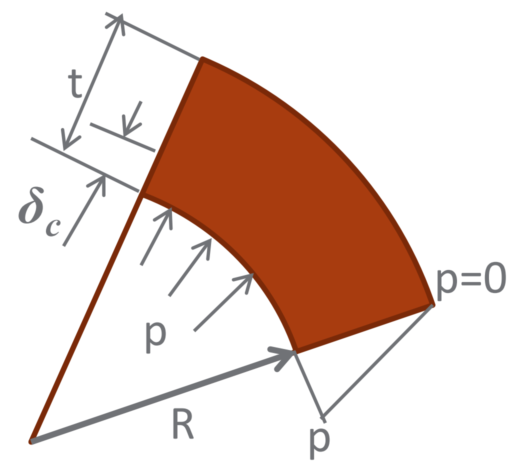
$$\frac{(2b^3+a^2)}{(b^3-a^3)}\frac{(b-a)}{a}$$



- Composite through-thickness modulus, E_2, causes additional hoop strain at inner wall due to composite compression
  - Composite compression
  - Additional hoop strain

$$\delta_c = \frac{Pt}{2E_2}$$

$$\varepsilon_h = \frac{\delta_c}{R}$$



- Tank Mass Comparison:
  - ANL finite element analysis 91.0 kg
  - Tank cost estimator tool 97.1 kg
  - PNNL netting analysis 99.0 kg

Netting Spreadsheet – Inputs in Blue

DOE Tank Mass Comparison Case, ID = 391mm, Cyl.Length = 1052mm, 70MPa, 147.3L													
Netting Analysis of Pressure Vessel Fiber Stresses, 3/14/2013													
Calculate lamina thickness and composite tank mass for a tank with 2 helical + hoop plys													
Based on:	Roylance, D.K. 1976. Netting Analysis for Filament-Wound Pressure Vessels, AMMRC TN 76-3.												
	Composites Division, Army Materials and Mechanics Research Center, Watertown, Mass.										**Outside Volume =**	**218.4**	**Liters**
Tank Inside Rad.		195.5	mm			**Densities**					**Outside Diameter =**	**469.6**	**mm**
Inside Dome Ht.		131	mm	Inside		Fiber =	1.8	g/cc			**Outside Length =**	**1366**	**mm**
Tank cylindrical length		1052	mm	L/D Ratio=	3.361	Matrix =	1.25	g/cc			**Outside L/D =**	**2.908**	
Liner thickness		5	mm			Composite =	1.58	g/cc	Rule of Mixtures				
CF-comp Inside Rad.		200.50	mm			HDPE Liner =	0.96	g/cc					
CF-comp Inside Dome Ht.		136.00	mm			**Matl Cost**			Material Costs from SA presentation, Nov. 28, 2012				
CF-comp Tank cyl. length		1052.00	mm			Carbon Fiber =	28.60	$/kg	$13/lb Toray T700S				
	Pressure	70.00	MPa			Matrix =	8.25	$/kg	$3.75/lb epoxy				
Fiber Strength =		4900	MPa			HDPE Liner =	2.09	$/kg	$0.95/lb				
E-Fiber-Axial =		225000	MPa				**Tank Internal Volume =**	**147.3**	**liters, Cyl.+Ellipt. Heads**				
E-Fib-Transv. =		13400	MPa				**Tank Composite Volume =**	**62.6**	**liters**	cyl=full thickness, ellipt heads=helical plys only			
E-matrix =		4000	MPa				**Tank Composite Mass =**	**99.0**	**kg**				
E-Lam-Transv.=		9640	MPa	Rule of Mixtures			**Carbon Fiber Mass =**	**67.6**	**kg**	**Carbon $**	**$1,935**		
	Vf =	0.6	Fiber Vol. Fraction				**Matrix Mass =**	**31.3**	**kg**	**Matrix $**	**$258**		
Lamina Strength =		**2425.5**	**MPa**				**Liner Mass =**	**8.6**	**kg**	**Liner $**	**$18**		
Safety Factor =		**2.25**					**Total Mass =**	**107.6**	**kg**	**Total $**	**$2,211**		
Coeff of Variation =		**0.1**	**fraction**										
Allow. Lamina Stress =		**970.20**	**MPa**										
Allow.Fiber Stress =		**1617.00**	**MPa**										
	Adjust layer												
	Thickness	Angle	Angle	FiberArea									
Layer	**mm**	deg.	rad.	per layer		k-Factors							
1	6.25	50	0.873	3.75	k1 =	1.019							
2	6.25	10	0.175	3.75	k2 =	4.167							
3-hoop	13.45	90	1.571	8.07	k3 =	9.365							
Stress Ratio =	0.60	Typical limit on Helical stress / Hoop stress to account for extra helicals needed in the dome region											
Total-Thick =	34.28	mm	1.350	inches	Thickness includes stress ratio applied to 2 helical layers								

Adjust layer thicknesses in blue until inner-layer stresses in orange are less than allowable fiber stress

Allow.Fiber Stress = 1617.00 MPa

Layer	**Adjust layer Thickness mm**	Angle deg.	Angle rad.	FiberArea per layer		k-Factors
1	6.25	50	0.873	3.75	k1 =	1.019
2	6.25	10	0.175	3.75	k2 =	4.167
3-hoop	13.45	90	1.571	8.07	k3 =	9.365
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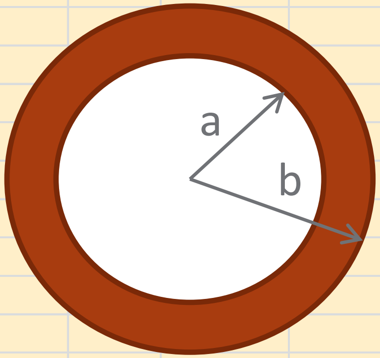


Thin Wall Strains		Thin Wall Stresses		
Hoop Strain, e1 =	6.006E-03	Stress in #1 Helicals, s1 =	1352.28	Mpa
Axial Strain, e2 =	6.015E-03	Stress in #2 Helicals, s2 =	1353.41	Mpa
		Stress in Hoop Fibers, s3 =	1351.44	Mpa

Thickwalled factor on hoop strain, sfac=(b**2+r**2)/(b**2-r**2)/(r/ttl) = Timoshenko thick cylinder (Art.28)

R,out = b = 234.78333 mm

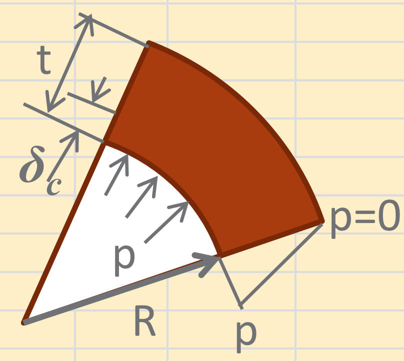
sfac = 1.092 Thickwall stress concentration at inside wall

Thickwalled factor on axial strain, sfac=(2*b**3+r**3)/(b**3-r**3)/(r/ttl) = Timoshenko thick sphere (Art.136)

Sfac(axial) = 1.189 Axial Thickwall stress concentration at inside wall

Transverse Mod. Effect = 6.208E-04 Additional Hoop strain due to lamina through thickness compression.

mod.fac = 1.103 Modulus ratio stress concentration at inside wall



Inner Surface Strains including Thickwall and Transverse Modulus effect

including Thickwall and Transverse Modulus effect		**Inner Surface Stresses**		
Inner Hoop Strain, e1 =	7.181E-03	**Stress in #1 Helicals, s1 =**	**1613.04**	**Mpa**
Inner Axial Strain, e2 =	7.152E-03	**Stress in #2 Helicals, s2 =**	**1609.36**	**Mpa**
		Stress in Hoop Fibers, s3 =	**1615.77**	**Mpa**

Composite Translation Efficiency = 0.825 Tested Lamina Strength / Theoretical Lamina Strength

Tank Structural Efficiency = 0.836 Thin Wall Hoop Stress / Thick Wall Hoop Stress

Combined Efficiency = 0.690