

Proudly Operated by Battelle Since 1965

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

#### P.I. KEVIN L. SIMMONS

Pacific Northwest National Laboratory May 15, 2013

### Project ID # ST101

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

# 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

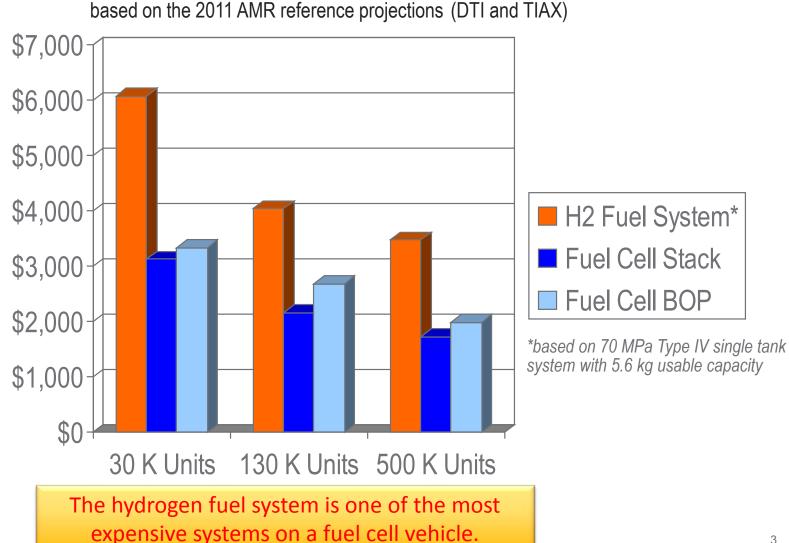
## Partners

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

### Relevance



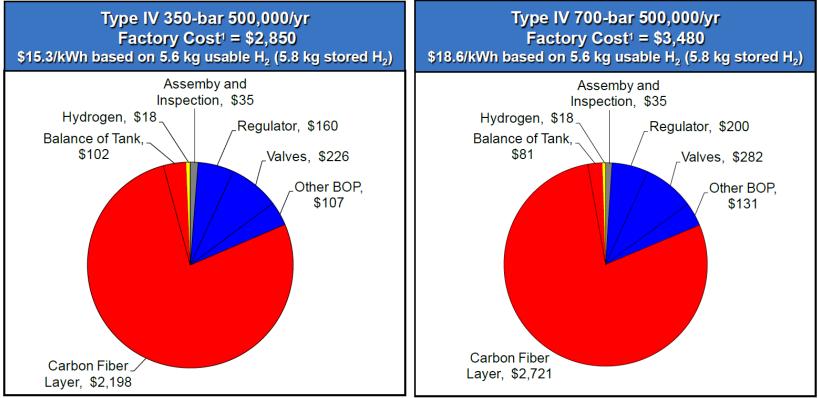
### Fuel Cell Vehicle Cost Analysis Study – Highest Cost Systems



### Relevance



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



<sup>1</sup> Cost estimate in 2005 USD. Includes processing costs.

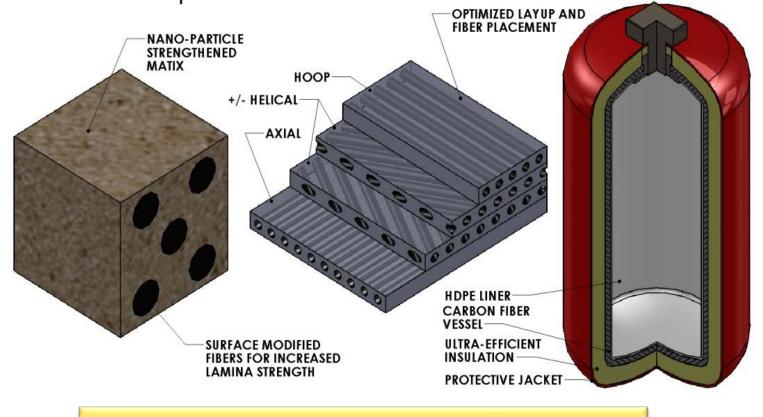
<sup>1</sup> Cost estimate in 2005 USD. Includes processing costs.

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**



Proudly Operated by Battelle Since 1965

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 <sub>2</sub> 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)

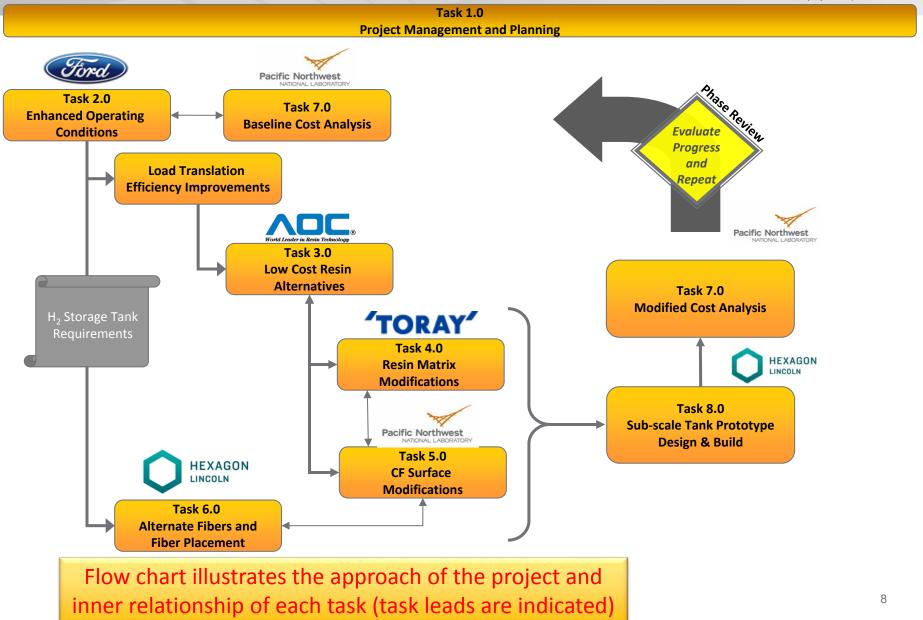
- Task 5.0 CF Surface modifications (Task Lead – Toray)
- Task 6.0 Alternative fibers & fiber placement (Task Lead – Lincoln)
- Task 7.0 Cost analysis (Task Lead – PNNL)
- Task 8.0 Sub-scale tank prototype (Task Lead – Lincoln)



### **Project Approach**



Proudly Operated by Battelle Since 1965



## **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.

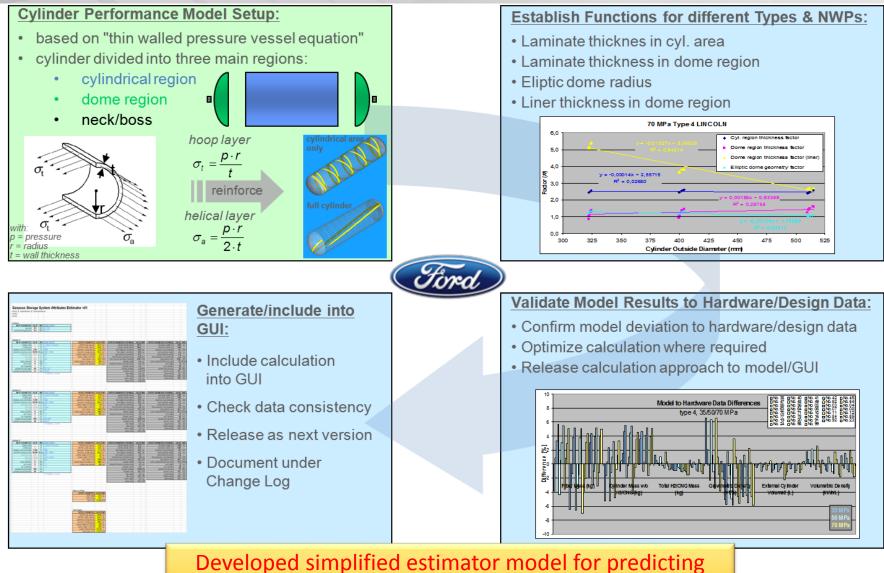
### Cost factors:

- 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



Proudly Operated by Battelle Since 1965



tank parameters within +/- 5% of existing tank hardware

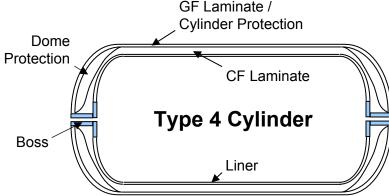
# Project Approach - Tank Cost Analysis Cost Analysis Estimator Model



Key cost estimating step was to establish the appropriate input assumptions

# Baseline material cost factors:

Description	Material	Volume	\$/kg	Scrap	Cost + Scrap \$/kg	Ρ
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	Ероху	10k-100k	6.60	1.25	8.25	
Aluminum (Boss)	Al 6061-T6	10k-100k	4.75	2.0	9.50	







## Baseline performance factors:

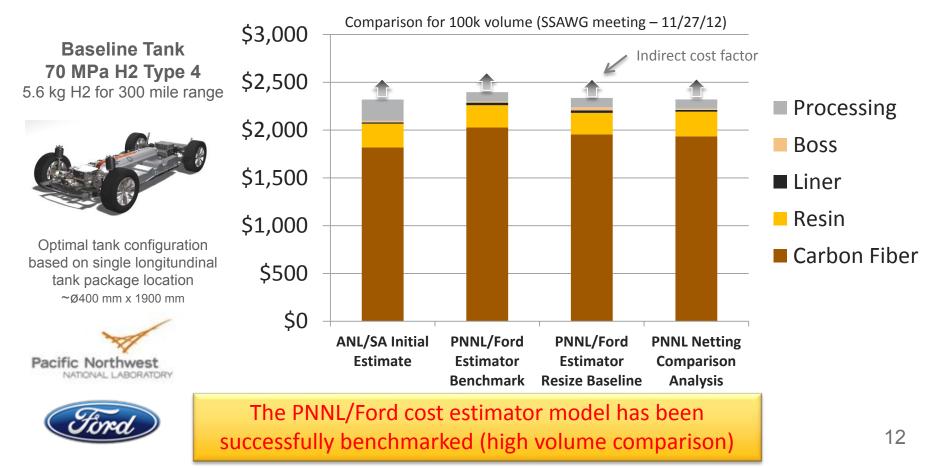
- Safety Factor: 2.25x NWP (70 MPa)
- CF Tensile Strength: 4,900 MPa
- Translational Efficiency: 83%
- CF Variability Factor: 10%
- CF Volume Fraction: 60%

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



### Technical Accomplishment - Cost Analysis Netting Analysis for Tank Mass Confirmation

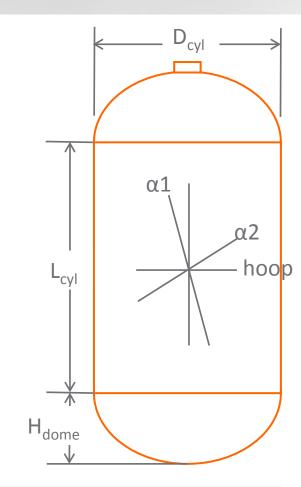
- Netting analysis assumes:
  - Fibers are loaded in tension.
  - The matrix does not contribute to strength.
  - Shear stresses are small.
- Roylance\* implementation for 2 helical and 1 hoop fiber direction.
  - $\alpha$ 1 = low angle helical over polar bosses.
  - $\alpha$ 2 = mid angle helical over 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

97.1 kg

99.0 kg

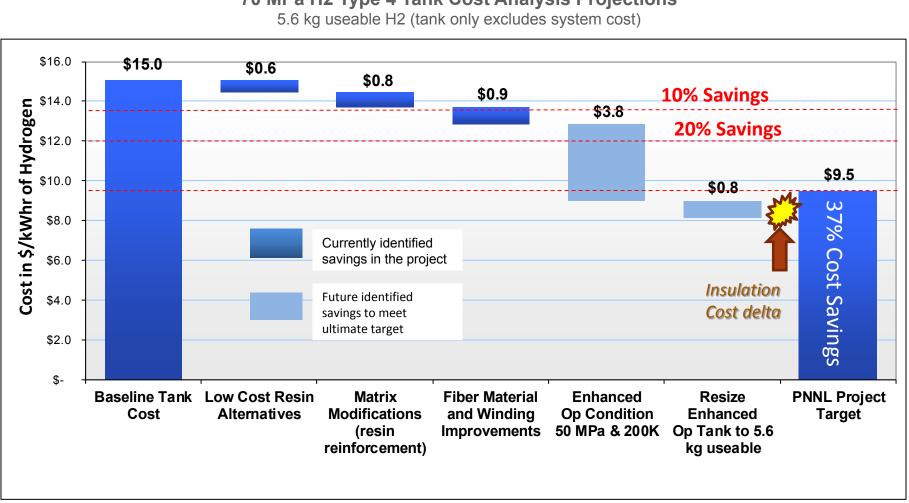
- Through-thickness composite compression
- Tank Mass Comparison:
  - ANL finite element analysis 91.0 kg
  - Tank cost estimator tool
  - PNNL netting analysis
  - \* Roylance, D.K. 1976. Netting Analysis for Filament-Wound Pressure Vessels, AMMRC TN 76-3.

Good agreement between methods





#### **Technical Accomplishment - Cost Analysis Cost** Pacific Northwest **Reduction Opportunities Identified** NATIONAL LABORATORY Proudly Operated by Battelle Since 1965



70 MPa H2 Type 4 Tank Cost Analysis Projections

Currently identified reduction opportunities to achieve

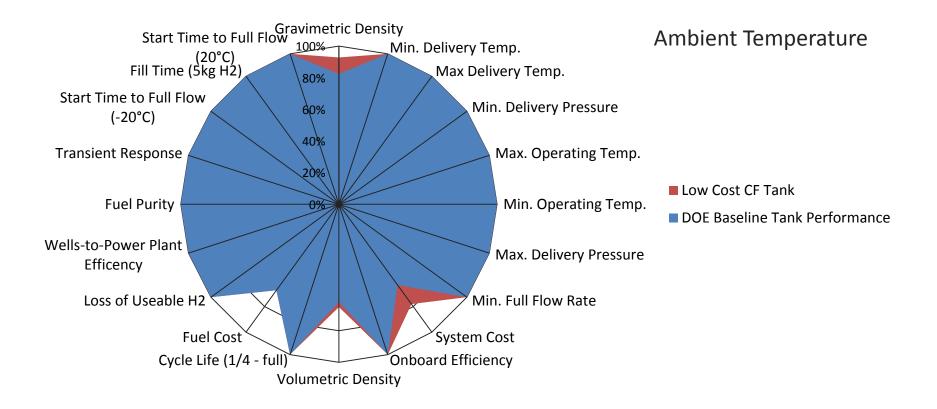
a 10% tank cost savings and projected path to target

April 17, 2013



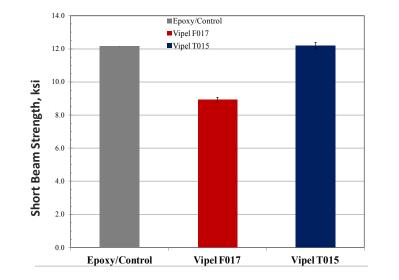


#### 700 Bar Type IV Single Tank System Compared Against 2017 Targets

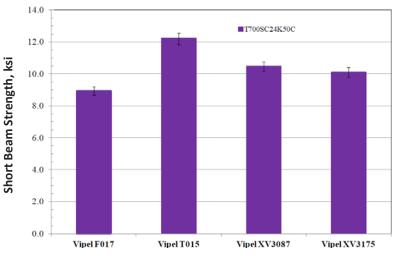


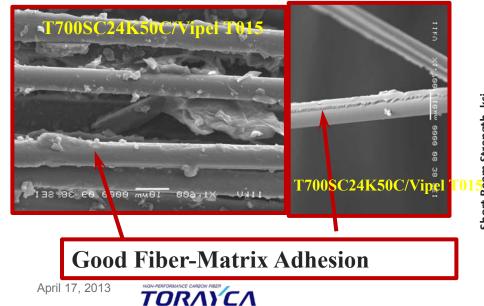
## **Technical Accomplishment** – Low Cost Resin Alternative and Carbon Fiber Surface Modifications



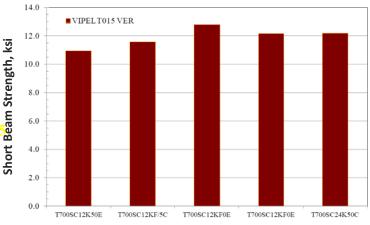






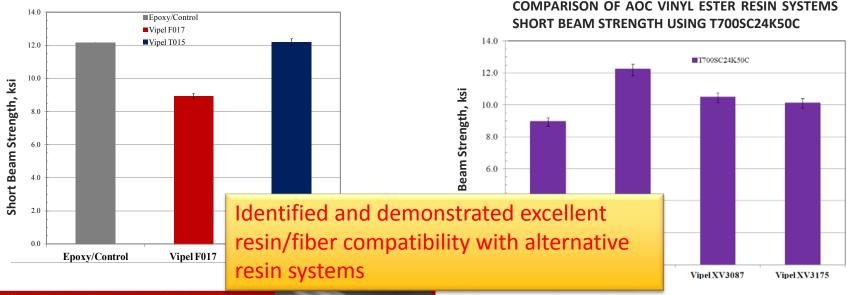


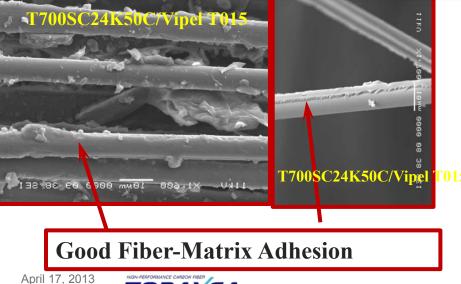
#### COMPARISON OF TORAYCA CARBON FIBERS SHORT BEAM STRENGTH USING VIPEL T015



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

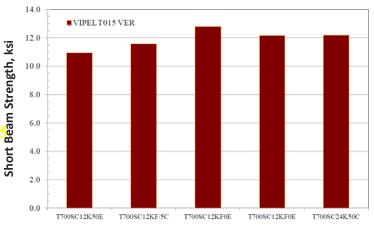






τοκλγζλ

#### COMPARISON OF TORAYCA CARBON FIBERS SHORT BEAM STRENGTH USING VIPEL T015



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



- 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

Test	Units	ASTM	015 RT	015 (-73C)	017 RT	017 (-73C)	XV-3175 RT	XV-3175 (-73C)	Epoxy RT	Ероху (-73С)
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



Identified and tested alternative resin systems similar to epoxy properties

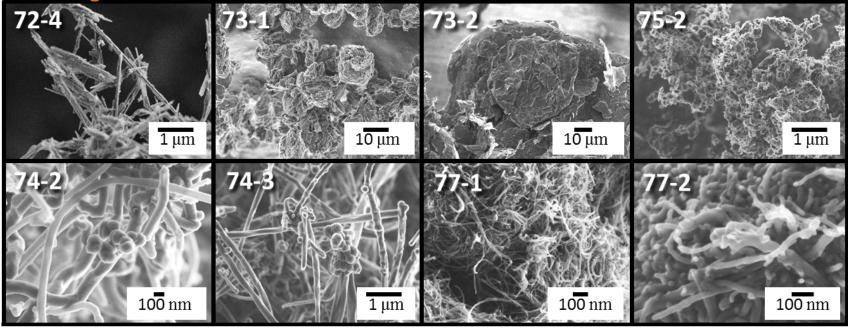
# Technical Accomplishment – Resin Modifications

NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

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 <sub>2</sub> functionalization	77-2

#### SEM images of the nanoscale additives

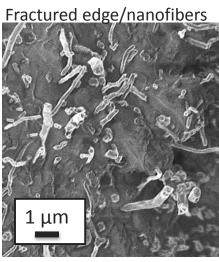
- Evaluated morphology effects on mechanical properties
- Clays, platelets, tubes, fibers
- Mixing with resins and performing tensile tests
- Down select based on price and material properties



#### Technical Accomplishment – Resin Modifications: testing of nanoscale additives in alternate resins Pacific Northwest National Laboratory Proudly Operated by Battelle Since 1965

- 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

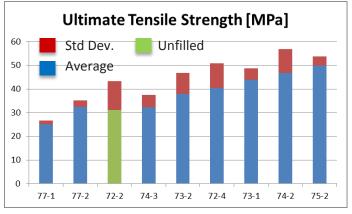


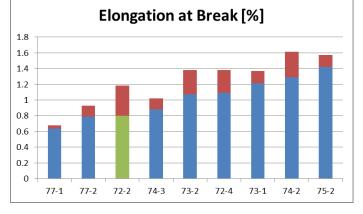


#### <u>neat resin</u>









#### Technical Accomplishment – Resin Modifications: testing of nanoscale additives in alternate resins Pacific Northwest National Laboratory Proudly Operated by Battelle Since 1965

- Tensile samples fabricated from vinyl ester resins with nanoscale additives
- Testing shows significantly enhanced UTS and Elongation at break with nano-activity Filler morphology can significantly impact

Tensile testing nano-filled resin

neat resin

30

20

10

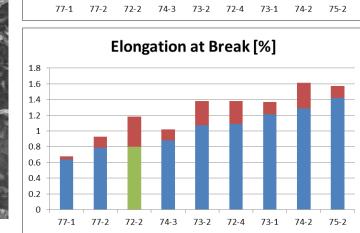
0



nano-filled resin

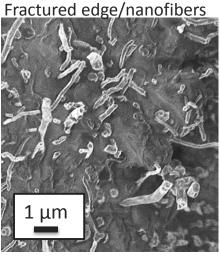


Ultimate Tensile Strength [MPa]



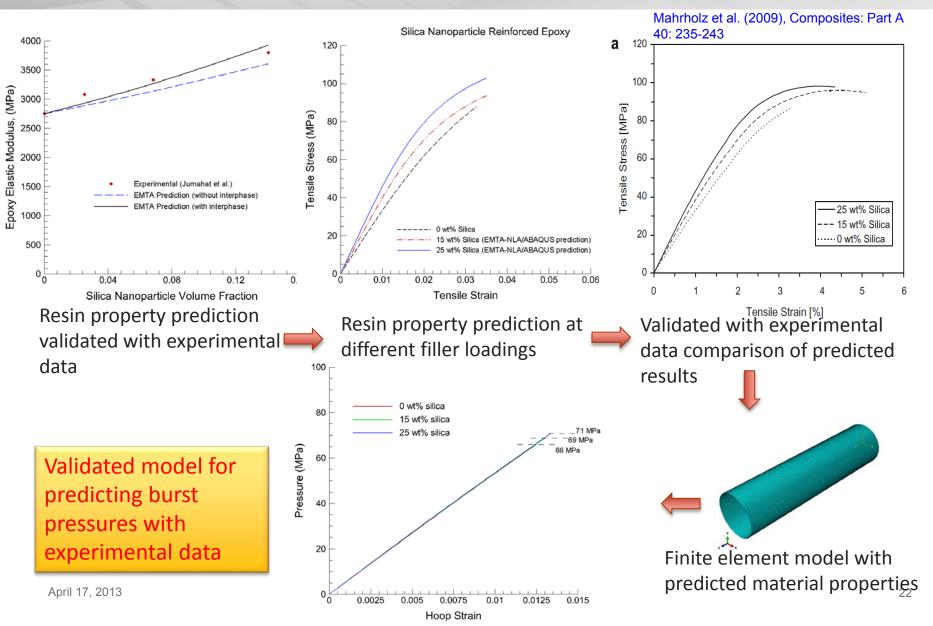
Additional testing with the resin properties cure recipes is needed and at cryogenic temperatures

 Based on cost and performance, nanoclays and nanoplatelets are top candidates at \$3-10/lb





### Technical Accomplishments – Resin Modifications: Predict Material Properties and Burst Pressures Provide Vision Pressures Provide Vision Pressures Provide Vision Pressures Provide Vision Pressure Visio

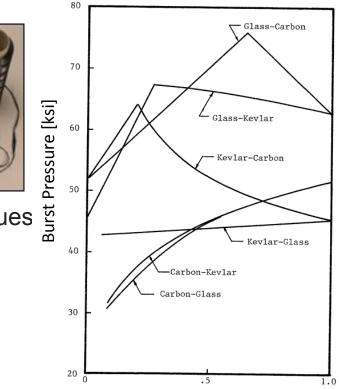


# **Technical Accomplishment - Alternate Fiber Placement and Multiple Fiber Types**



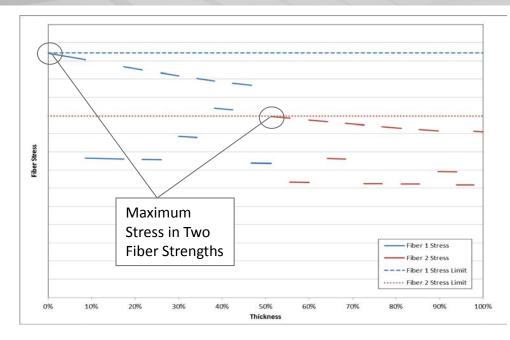
Investigate alternate carbon fibers

- 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



(r-b)/(a-b)

## Technical Accomplishment – Alternate Fiber Placement and Multiple Fiber Types



#### **Fiber Properties**

Material Property	E-Glass	Т300	T700	T720	Т800
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

#### Single Fiber Designs

<b>Evaluation Criteria</b>	Т300	T720	Т800
Percent Change in Cost	+19%	+9%	+63%
Percent Change in Mass	+59%	-30%	-30%

Pacific Northwest

NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

#### 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 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%



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%



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**



Proudly Operated by Battelle Since 1965

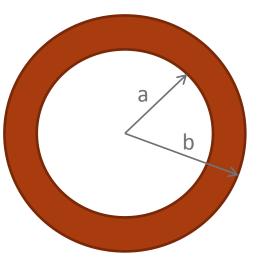
### **Netting Analysis Refinements**



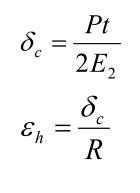
Proudly Operated by Battelle Since 1965

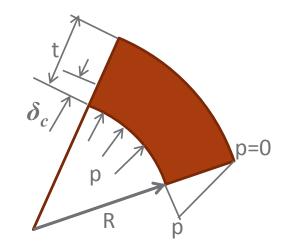
Thick-walled stress concentrations:
 Cylinder inner wall hoop
 Dome inner wall axial

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



- Composite through-thickness modulus, E<sub>2</sub>, causes additional hoop strain at inner wall due to composite compression
  - Composite compression
  - Additional hoop strain
- 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**



Proudly Operated by Battelle Since 1965

DOE Tank Mass	Comparison	Case, ID = 3	91mm, Cy	I.Length = 10	52mm,	70MPa, 147.3	L							
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														
	Composites Division, Army Materials and Mechanics Research Center, Watertown, Mass.											218.4	Liters	
Tanl	<mark>k Inside Rad.</mark>	195.5	mm			Densities				Outside Dia	ameter =	469.6	mm	
Insid	le Dome Ht.	131	mm	Inside		Fiber =	1.8	g/cc		Outside	Length =	1366	mm	
Tank cylin	drical length	1052	mm	L/D Ratio=	3.361	Matrix =	1.25	g/cc		Outsi	ide L/D =	2.908		
Lin	ner thickness	5	mm			Composite =	1.58	g/cc	Rule o	f Mixtures				
CF-comp	o Inside Rad.	200.50	mm			HDPE Liner =	0.96	g/cc						
CF-comp Insid	le Dome Ht.	136.00	mm			Matl Cost			Mater	ial Costs fro	m SA pres	esentation, Nov. 28, 2012		
CF-comp Tan	nk cyl. length	1052.00	mm		C	arbon Fiber =	28.60	\$/kg	\$13/lb	Toray T700	)S			
	Pressure	70.00	MPa			Matrix =	8.25	\$/kg	\$3.75/	lb epoxy/				
Fibe	r Strength =	4900	MPa			HDPE Liner =	2.09	\$/kg	\$0.95	/lb				
E-F	-iber-Axial =	225000	MPa			Tank Internal	Volume =	147.3	liters,	Cyl.+Ellipt.	Heads			
E-F	ib-Transv. =	13400	MPa		Tai	nk Composite	Volume =	62.6	liters	cyl=full thic	kness, ellip	ot heads	helical ply=	rs only
	E-matrix =	4000	MPa			Tank Compos	ite Mass =	99.0	kg					
E-La	m-Transv.=	9640	MPa	Rule of Mixt	ures	Carbon Fib	er Mass =	67.6	kg	Carbon \$	\$1,935			
	Vf =	0.6	Fiber Vol	. Fraction		Mat	rix Mass =	31.3	-	Matrix \$	\$258			
Lamina	Strength =	2425.5	MPa			Lin	er Mass =	8.6	kg	Liner \$	\$18			
	ety Factor =	2.25				То	tal Mass =	107.6	kg	Total \$	\$2,211			
	Variation =		fraction											
	ina Stress =	970.20												
	ber Stress =	1617.00	MPa											
	Adjust layer													
	Thickness	Angle	0	FiberArea										
Layer	mm	deg.	rad.	per layer		k-Factors								
1	6.25	50			k1 =	1.019								
2	6.25	10			k2 =	4.167								
3-hoop	13.45	90				9.365								
Stress Ratio =				Helical stress / Hoop stress to account for extra helicals needed in t							gion			
Total-Thick =	34.28	mm	1.350	inches	Thickne	ess includes sti	ress ratio a	pplied to 2	2 helica	al layers				

# Adjust layer thicknesses in blue until inner-layer stresses in orange are less than allowable fiber stresses ince 1965

	iber 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 Helica	al stress / Hoo	op stre	ss to account fo	or extra hel	licals nee	ded in	the dome	region			
Total-Thick =	34.28	mm	1.350	inches	Thickn	ess includes str	ess ratio a	oplied to	2 helic	al layers				
Thin Wall Strain	<u>s</u>		Thin Wal	l Stresses										
Ноор	Strain, e1 =	6.006E-03	Stress	s in #1 Helical	ls, s1 =	1352.28	Мра						27	
Axia	l Strain, e2 =	6.015E-03	Stress	s in #2 Helical	ls, s2 =	1353.41	Мра						d	
			Stress	in Hoop Fiber	rs, s3 =	1351.44	Мра						$\leq$	b
Thickwalled fact	tor on hoop s	train, sfac=(l	o**2+r**	2)/(b**2-r**2	2)/(r/ttl	) = Timoshenko	thick cylin	der (Art.2	28)					17
	R,out = b =	234.78333	mm											
	sfac =	1.092	Thickwa	all stress cond	centrat	ion at inside wa	all							
Thickwalled fact	tor on axial st	rain, sfac=(2	*b**3+r*	**3)/(b**3-r*	*3)/(r/	ttl) = Timoshen	ko thick spl	here (Art.	136)					
	Sfac(axial) =	1.189	Axial Thi	ckwall stress	concer	tration at insid	e wall					X		
		6.208E-04	Additio	nal Hoop stra	in due	to lamina throu	ugh thickne	ss compr	ession			t / 🔰		
	mod.fac =	1.103	Modulu	s ratio stress	concei	ntration at insid	le wall					1K		
Inner Surface St	rains includin	g Thickwall a	nd Transv	verse Modulu	is effec	t								
including Thic		-				Surface Stresse	<u>es</u>				6	6/1-		
Inner Hoop	Strain, e1 =	7.181E-03		Stre	ss in #1	Helicals, s1 =	1613.04	Мра				7 ' /	1	0=q
	l Strain, e2 =					Helicals, s2 =		•				/ σ΄		
				Stress	in Hoo	p Fibers, s3 =	1615.77	Мра						
											1	R	р	
Composite	Translation I	Efficiency =	0.825	Tested Lam	nina Str	ength / Theore	tical Lamin	a Strengt	h				1-	
Tan	k Structural I	Efficiency =	0.836	Thin Wall H	loop St	ress / Thick Wa	ll Hoop St	ress						
32	Combined I	Efficiency =	0.690											