COMPOSITE TECHNOLOGY DEVELOPMENT, INC.

ENGINEERED MATERIAL SOLUTIONS

Optimizing the Cost and Performance of Composite Cylinders for H_2 Storage using a Graded Construction

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June 18, 2014

Project ID # ST110

Overview

Timeline

- Project Start Date:
  - Phase I: Feb 2013
  - Phase II: May 15, 2014
- Project End Date: May 2016
- Percent Complete: 30% (Phase I)

Barriers

- Type IV Pressure Vessel Cost
- Price and availability of low cost carbon fiber
- Composite properties of lower cost carbon fibers

Budget

- FY13 DOE Funding: $155K
- Planned FY14 DOE Funding: $208K
- Total Project Value: $ 1.15M

Partners

- Oak Ridge National Laboratory
  - Low cost carbon fiber
- Adherent Technologies, Inc.
  - Specialty sizing
- Heyliger Consulting
  - Model optimization
- Luxfer Gas Cylinders
  - Cost analysis
  - High rate manufacturing

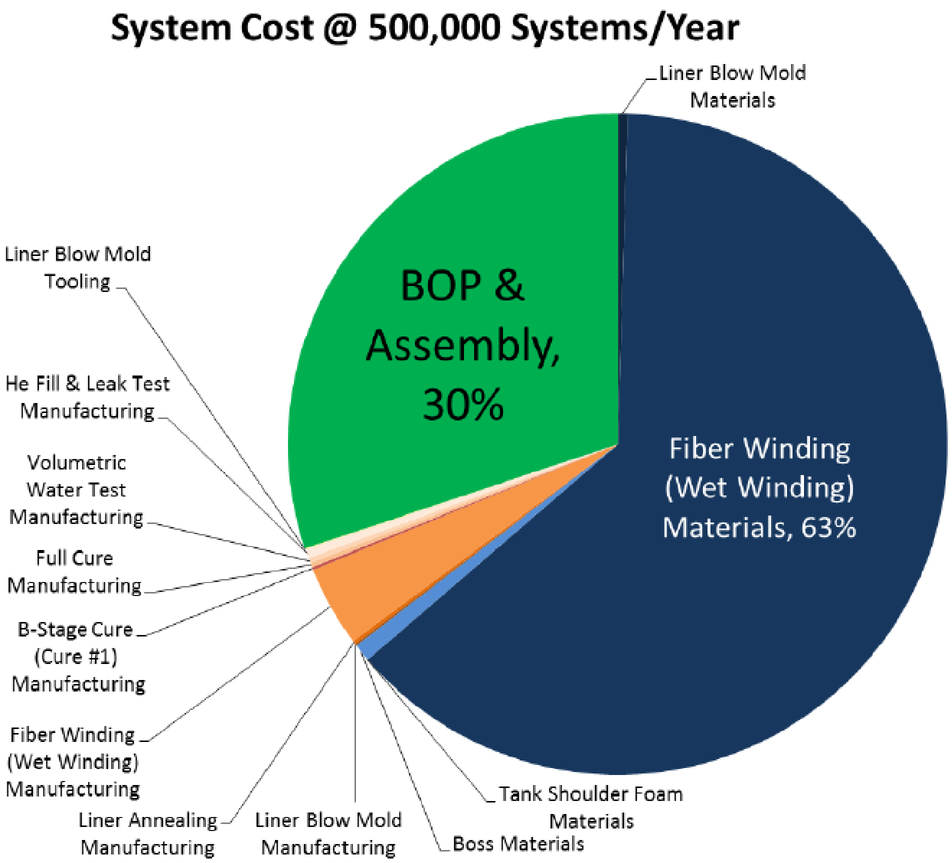
Relevance

- Hydrogen fuel cell vehicles require on-board H_2 storage systems to support driving distance of >300 miles
  - 5 kg H_2 storage required
  - Requires 700 bar (10,000 psi) storage capability
  - Current Type III and Type IV COPV will not meet long term cost/performance targets*
    - Storage system cost significantly higher than 2017 targets
  - Carbon fiber identified as primary driver of storage system cost

Phase II Goal: Demonstrate technology to reduce cost of Type IV H2 Storage vessel by 10 – 25 %

* "Technical Assessment of Compressed Hydrogen Storage Tank Systems for Automotive Applications", September 2010, published on the DOE/FCT website: http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/compressedtank_storage.pdf

Relevance – Cost Breakout for Type IV H_2 Storage Systems

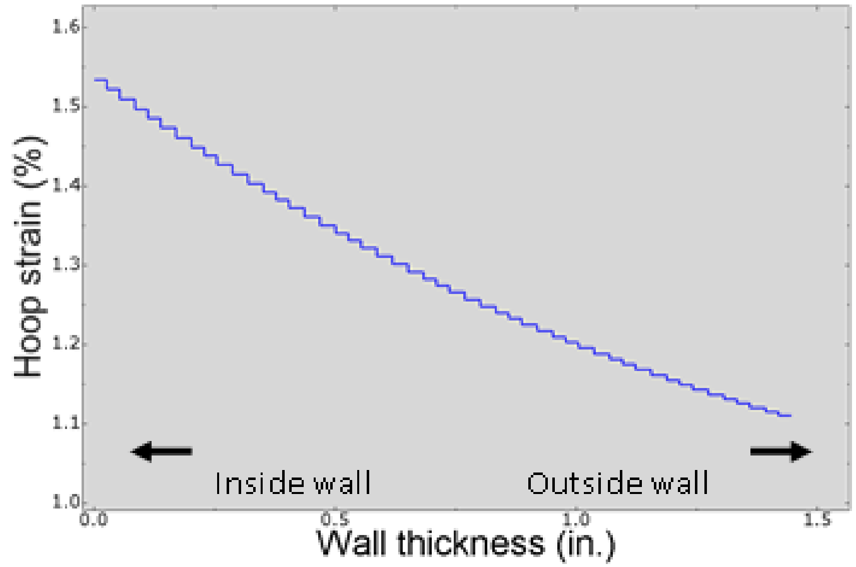


Reducing quantity and cost of carbon fiber represents an excellent opportunity to reduce Type IV tank cost while maintaining performance properties

Graphic from "Hydrogen Storage Cost Analysis", U.S. Department of Energy's (DOE's) 2013 Annual Merit Review and Peer Evaluation Meeting (AMR) for the Hydrogen and Fuel Cell Technologies (FCT) Program, http://www.hydrogen.energy.gov/pdfs/review13/st100_james_2013_o.pdf

Approach – Pressure Vessel Mechanics

- **Efficient composite maximizes fiber strain**
- **700 Bar tank analyzed as thick walled shell**
  - **Thickness/radius > 0.1 invalidates uniform hoop stress distribution through wall**
  - **In thick shell there is a gradation of strain from inner to outer wall**
  - **The outer fibers are strained 20-30% less than the inner fibers at incipient burst failure**

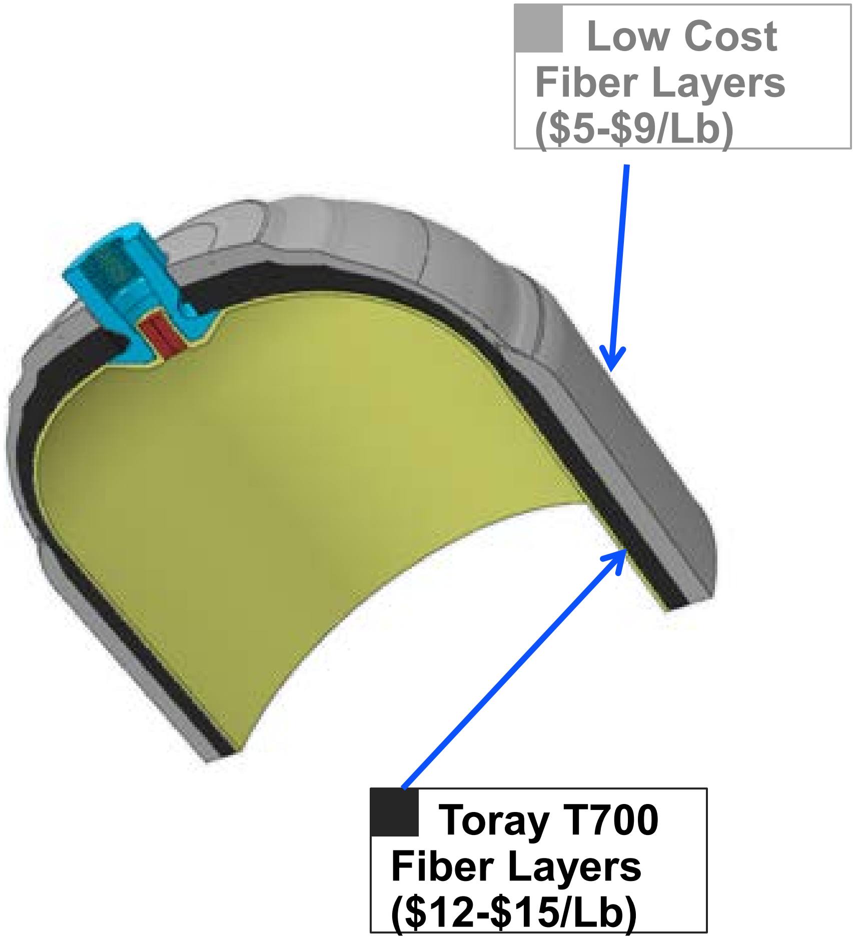


- **Thick composite performance also depends on**
  - **Damage due to microcracking and delamination during hydrostatic pressurization as well as fatigue cycling**
  - **Understanding and incorporation of progressive failure mechanisms is essential to optimize design**

CTD Approach – Graded Composite

- **Carbon fiber is the highest cost component in 700 Bar composite tanks**
  - **Reducing the cost or quantity of carbon fiber in a tank can yield the biggest savings**
- **Lower cost carbon fibers tend to have lower strain capabilities than high priced fibers**
  - **In thick walled shell – outer most fibers are stained to lower levels**
  - **By using a graded composite where high strain fibers are used in the inner portion and lower strain fibers on the outside can reduce tank cost**

Graded Composite Structure



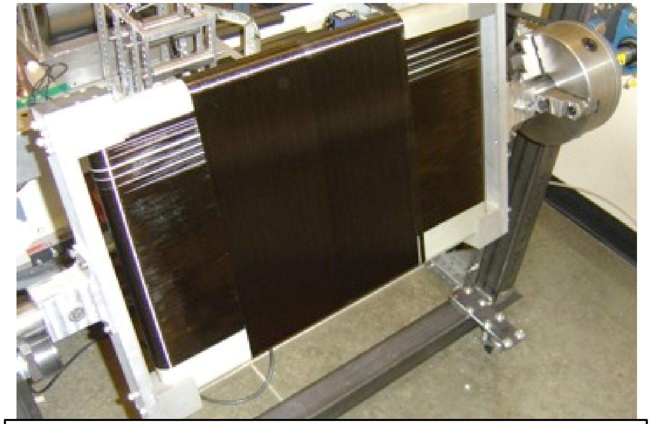
Approach – Project Goals

- **ORNL's textile-PAN based fibers are making significant progress in strength and modulus**
  - **Material properties have only been explored at the fiber level**
- **Composite properties under investigation in this program**
  - **Fiber translation in epoxy matrix composites**
  - **Compatibility with the filament winding process**
  - **How composite design rules apply**
- **Optimize fiber sizing and epoxy matrices to → maximum properties of these carbon fibers**
  - **Prevent fiber damage during handling and filament winding**
  - **Damage can reduce burst, fatigue, and stress rupture performance**
  - **Promotes chemical compatibility and adhesion between the fiber and matrix**

Provide highly efficient composite with excellent fiber translation at a minimal cost due to grading with low cost fibers through tank thickness

Approach – Composite Manufacturing and Test Coupons

- **Evaluate performance of T700 and low cost carbon fiber options**
- **Processing of materials for program**
  - **Unidirectional panels for coupon testing**
  - **Wet winding**
- **Coupon Testing**
  - **Tensile (ASTM D3039)**
    - **Data for design model**
  - **Short Beam Shear (ASTM D2344)**
    - **Some information regarding sizing effects**
  - **Data to verify/refine design models**

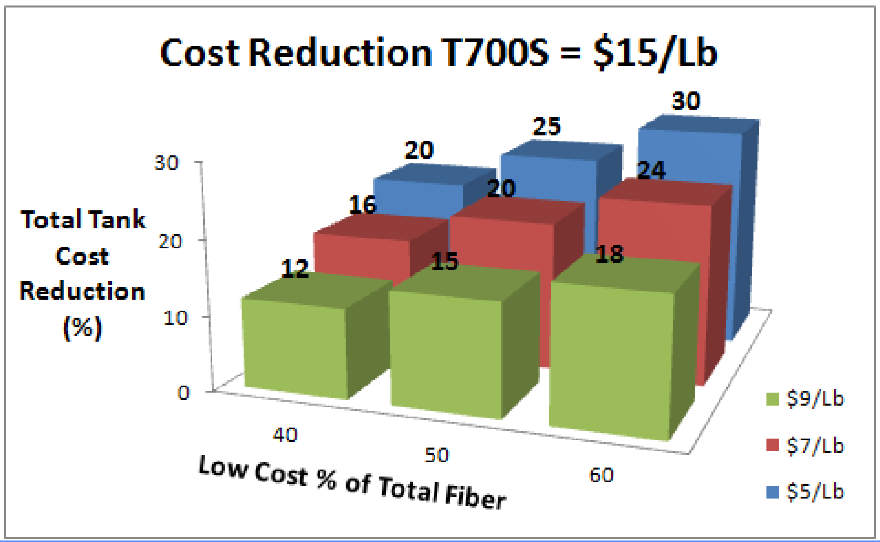


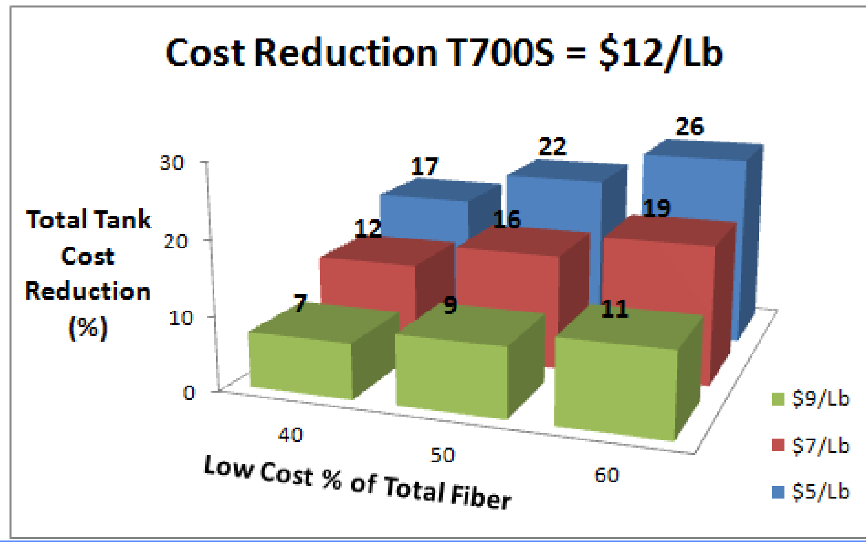
Uni and Cross Ply Panel Winding

Short Beam Shear Test

Accomplishments & Progress – Phase I Cost Analysis

- **Cost reduction potential based on**
  - T700S over cost range of $12-15/Lb
  - ORNL low cost carbon fiber range of $5-9/Lb
  - Percentage of low cost fibers used in tank wall between 40%-60%
  - Assumed zero mass change relative to current design





Lower Cost Fibers and Graded Composite Can Enable 25% Cost Reduction

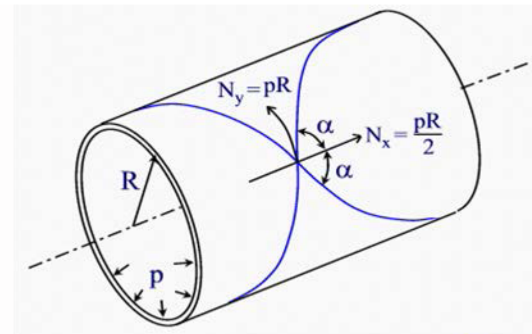
Values Calculated using cost breakout from "Technical Assessment of Compressed Hydrogen Storage Tank Systems for Automotive Applications", September 2010, published on the DOE/FCT website: http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/compressedtank_storage.pdf

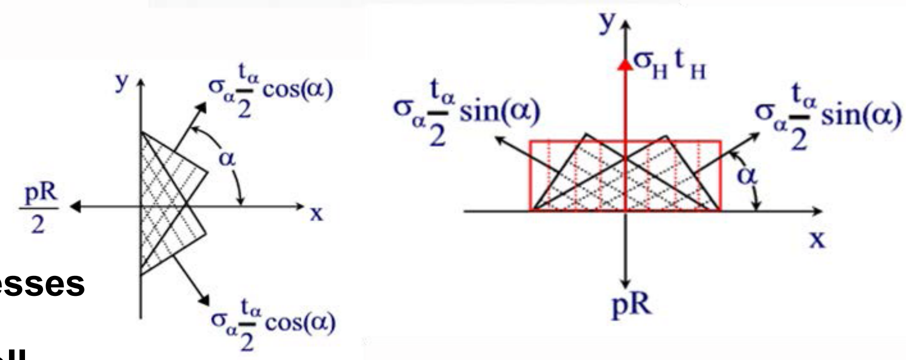
Accomplishments & Progress – Phase I Analytical Model

- **Basic shell design determined using netting analysis**

$$\sigma_\alpha = \frac{pR}{2\left(\cos^2\alpha\right)t_\alpha}$$

$$\sigma_H = \frac{pR}{t_H}\left(1 - \frac{\tan^2\alpha}{2}\right)$$





- **α is the helical wind angle**
- **σ_a and σ_H are the stresses in the helical and hoop plies**
- **t_a and t_H are the helical and hoop ply thicknesses**
- **p is the internal pressure**
- **R is the average radius of the cylindrical shell**

- **The equations are solved for t_a and t_H by assuming that the cylinder bursts when the stresses reach the ultimate fiber failure stress.**

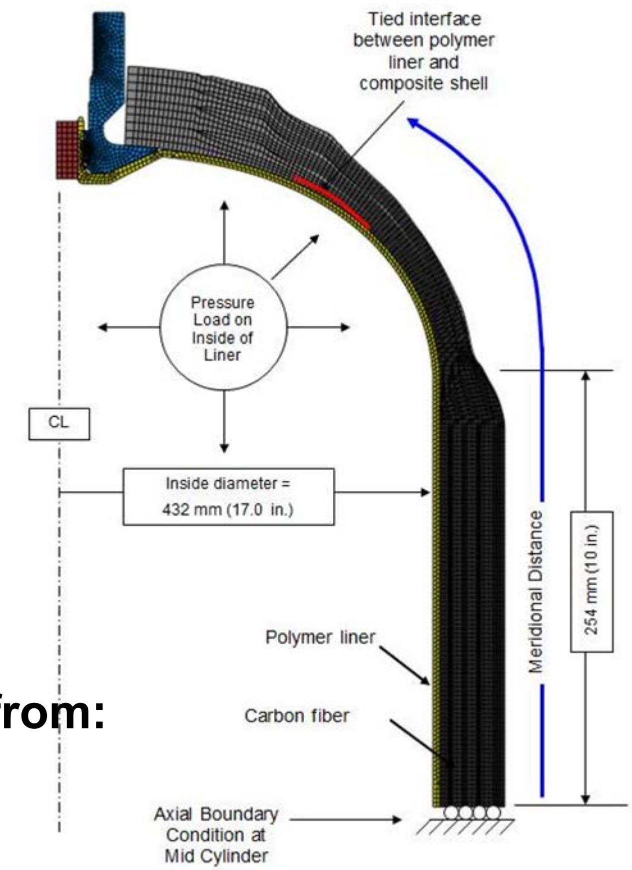
Accomplishments & Progress – Solution for Toray T700 Case

- **Assumptions**
  - Liner ID = 437 mm (17.2 in.)
  - Cylindrical length = 698.5 mm (27.5 in.)
  - Total length of tank = 1041.2 mm (41 in.)
  - Water volume of unpressurized tank = 127.75 Liters
  - Volume of pressurized tank = 131 Liters
- **p = 164.5 MPa → thickness of the composite shell**

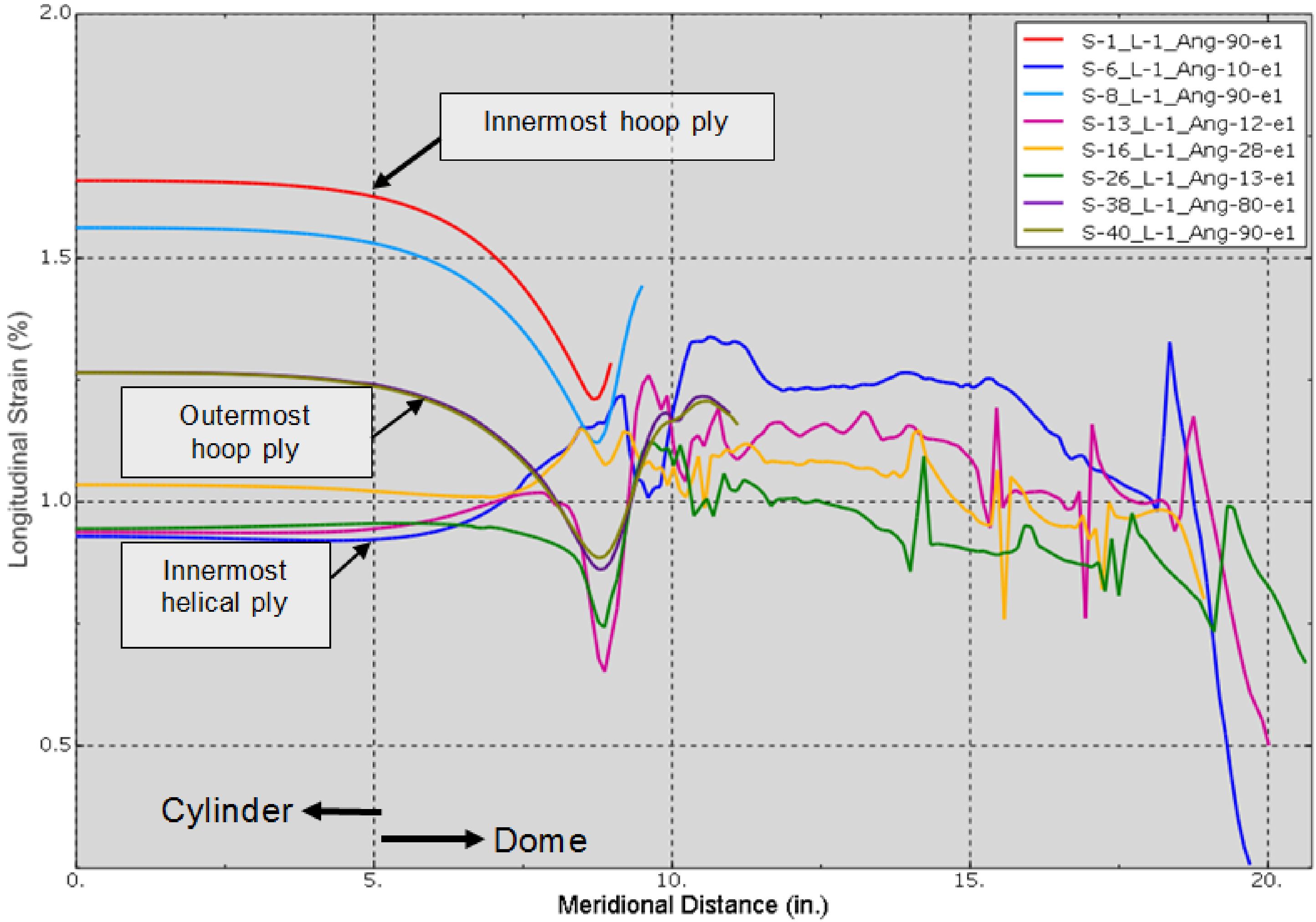
Design Input		
Burst Pressure	bar (psi)	1645 (23,852)
Ultimate Fiber Stress	GPa (ksi)	4.9 (711)
Average Helical Angle		10°
Helical : Hoop Stress Ratio		0.6
Computed Parameters		
Number of Hoop Layers		59
Number of Helical Layers		27
Total Hoop Thickness	mm (in.)	19.0 (0.75)
Total Helical Thickness	mm (in.)	16.5 (0.65)
Total Thickness of Composite Shell	mm (in.)	35.6 (1.4)

Accomplishments & Progress – Finite Element Analysis

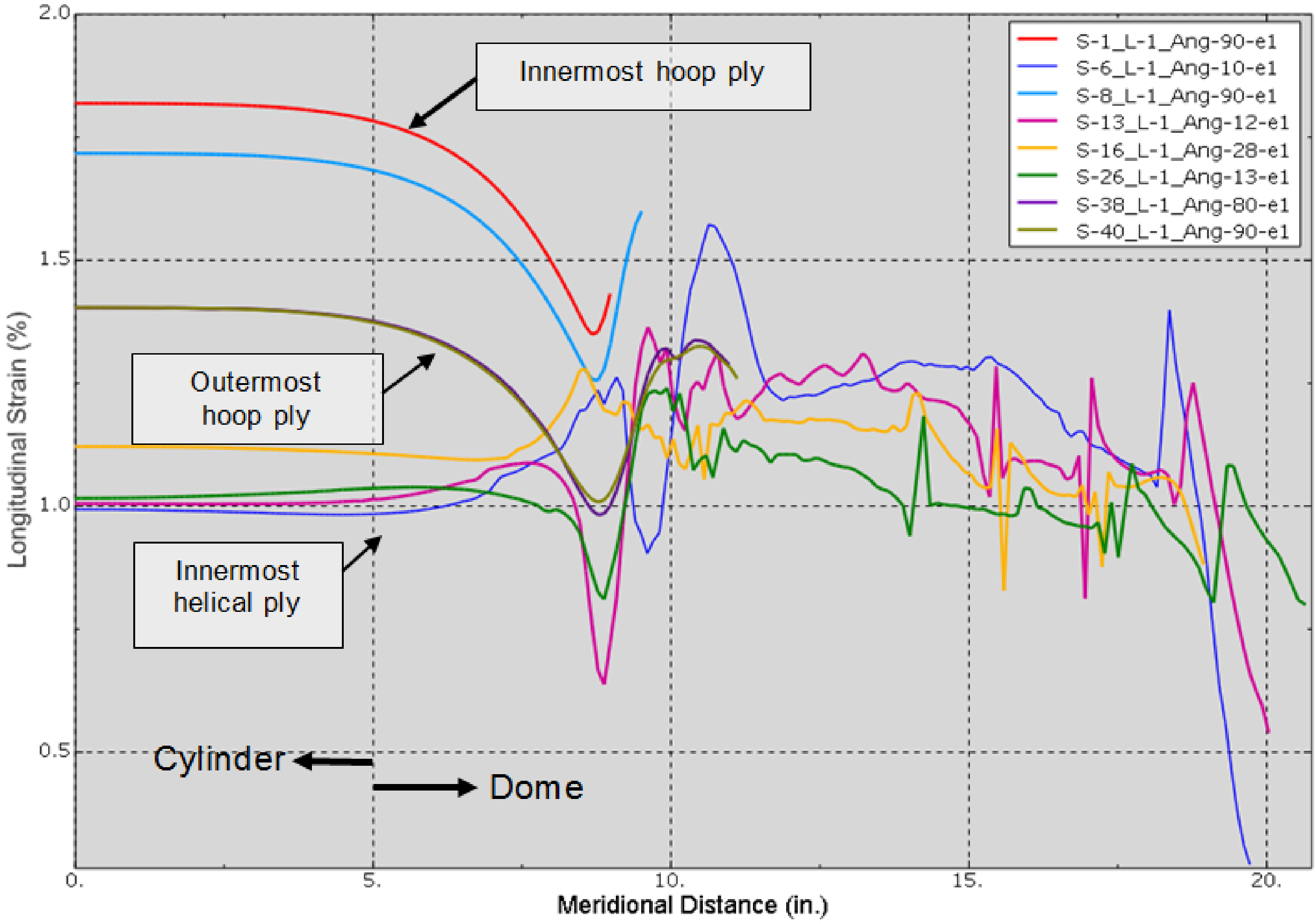
- **FEA accounts for:**
  - Orthotropic properties of the composite layers, properties and thickness of each element
  - Polar buildups during filament winding
  - Hoop stagger at the cylinder-to-dome transition region
- **Geodesic isotensoid dome**
  - Uniform tension in helical plies
  - Minimizes slippage of fibers during helical winding
- **Frictional interface**
- **Material properties for each element generated from:**
  - Unidirectional composite properties
  - COPV geometry
  - Initial wind angle



Accomplishments & Progress – FEA Results – T700 Case



Accomplishments & Progress – FEA Results – Graded Case

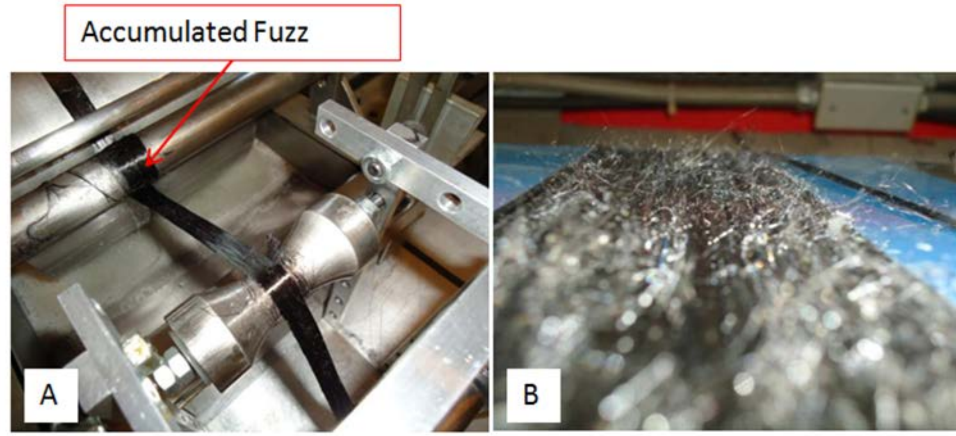


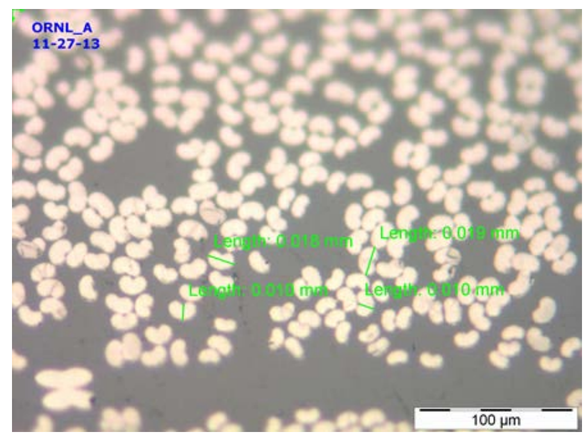
Approach – Phase I Baseline Materials

Material	Description	Comments
Toray T700	Commercial carbon fiber	• Currently used in Type IV tank construction • $12-15/lb
ORNL Low Cost Carbon Fiber	Non-commercial carbon fiber	• Textile PAN feedstocks • Target price point $5-$9/lb • ORNL-A: specialty sizing applied by Adherent Technologies • ORNL-B: conventional sizing applied at ORNL • ORNL-C: conventionally sized, different variant
Zoltek Panex 35	Commercial low cost carbon fiber	• Targeted for automotive applications • $10/lb
Standard Epoxy Sizing	Commercially available, applied during manufacture	• Primarily handling function • Some improvement in wetting/adhesion
Adherent Technologies AT-9307E finish	Reactive finish	• Dramatic improvements in composite strength and environmental durability
CTD-7.1	Toughened epoxy	• Wet winding • Used in KIBOKO® linerless composite tanks

Accomplishments & Progress – Phase I Test Coupons

- **Target 60% fiber volume fraction**
- **Limited quantities of ORNL fiber available**
- **Significant fuzzing noted for ORNL-A and ORNL-B variant fibers**
  - **Kidney-shaped cross-section → fiber breakage**
- **ORNL-C fiber showed significantly less fuzzing**
  - **Round cross-section**





Accomplishments & Progress – Unidirectional Laminate Data

	Experimental - Normalized to 60% VF			Expected @ 60% VF			
	Strength (ksi)	**Modulus (Msi)**	**Ult Strain (%)**	**Strength (ksi)**	**Modulus (Msi)**	**Ult Strain (%)**	**Strength Translation (%)**
Toray T700	343.2	18.4	1.86	425	20	1.7	81
Zoltek Panex	232.8	19.1	1.18	355	20	1.2	66
ORNL A	179.3	17.6	0.97	315	20	1	57
ORNL B	165.3	16.5	0.96	315	20	1	52
ORNL C	190	16.8	1.1		17.4		

ORNL A = PAN-VA with custom sizing applied by Adherent Technologies (Albuquerque, NM)
ORNL B = PAN-VA with 0.5% sizing applied by ORNL
ORNL C = PAN-VA with 2% sizing applied by ORNL – NOTE: different precursor than ORNL A or B

Accomplishments & Progress – Phase I Summary & Keys to Success

- **Finite element models generated required failure strains for T700 segments and low cost composite segments**
  - **1.8% strain requirement for T700 close to being met in Phase I**
    - **80% translation vs 85% translation**
  - **1.5% strain requirement for low cost variants not close**
    - **Options under consideration for Phase II are closer to this target**
- **High translation of fiber properties ($\geq$ 85%) required**
  - **Challenging for large tows (~50K) characteristic of low cost carbon fibers**

Approach – Phase II Goals

- Identify best low cost carbon fiber candidates
  - Combination of strength, modulus and strain to failure
  - Strength and modulus on target for current variants, strain to failure remains an issue
- Maximize fiber property translation
  - Large tow handling
  - Sizing/matrix interactions
    - specialty sizing has been shown to improve fiber property translation
    - Comparison with commercially applied sizing
- Generate experimental data to validate graded structure models

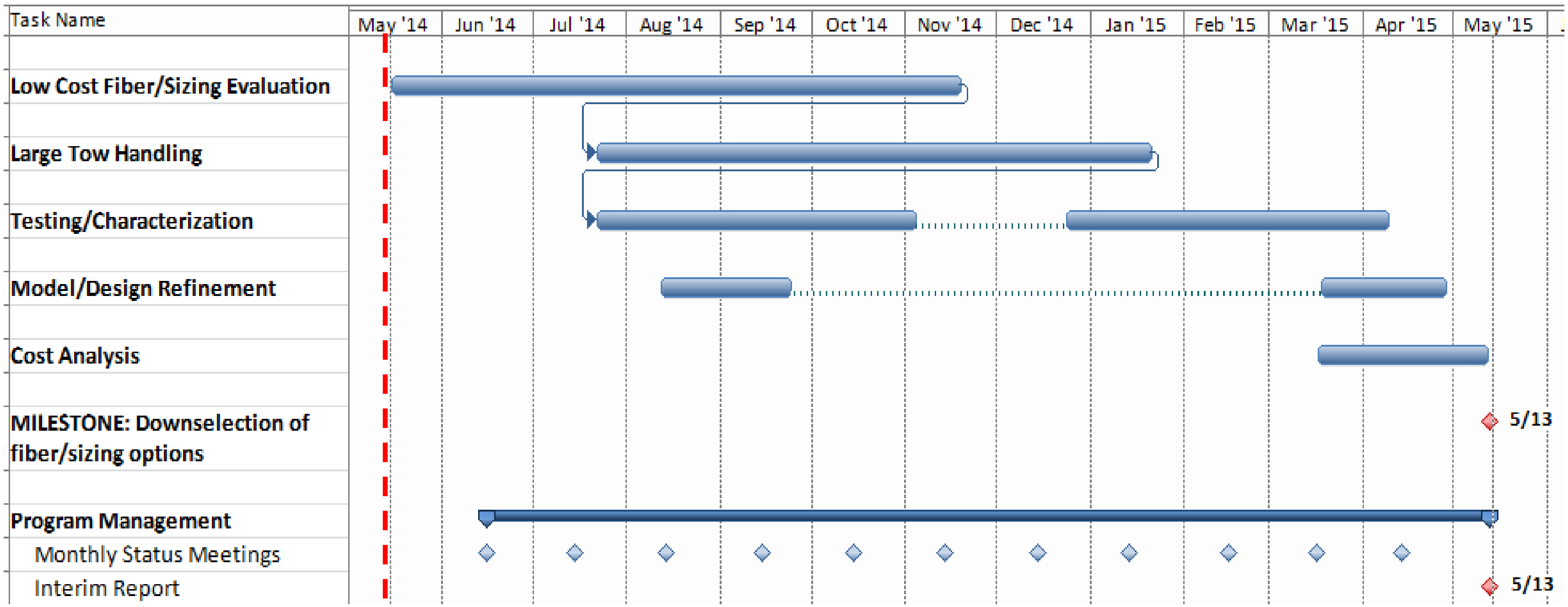
Approach – Phase II Goals (cont'd)

- **Optimize structure for highest content of low cost fiber**
  - **Based on experimental data obtained from unidirectional composites**
- **Comprehensive cost analysis**
  - **Material components**
    - **Primarily carbon fiber cost**
    - **Wet winding will be standard**
    - **Towpreg might still be considered as an option in cost analysis**
  - **Process-related costs**
    - **Use of multiple fibers in tank winding**
      - **Multiple winding stations**
      - **robotic tow handling**

Approach – Phase II Baseline Materials

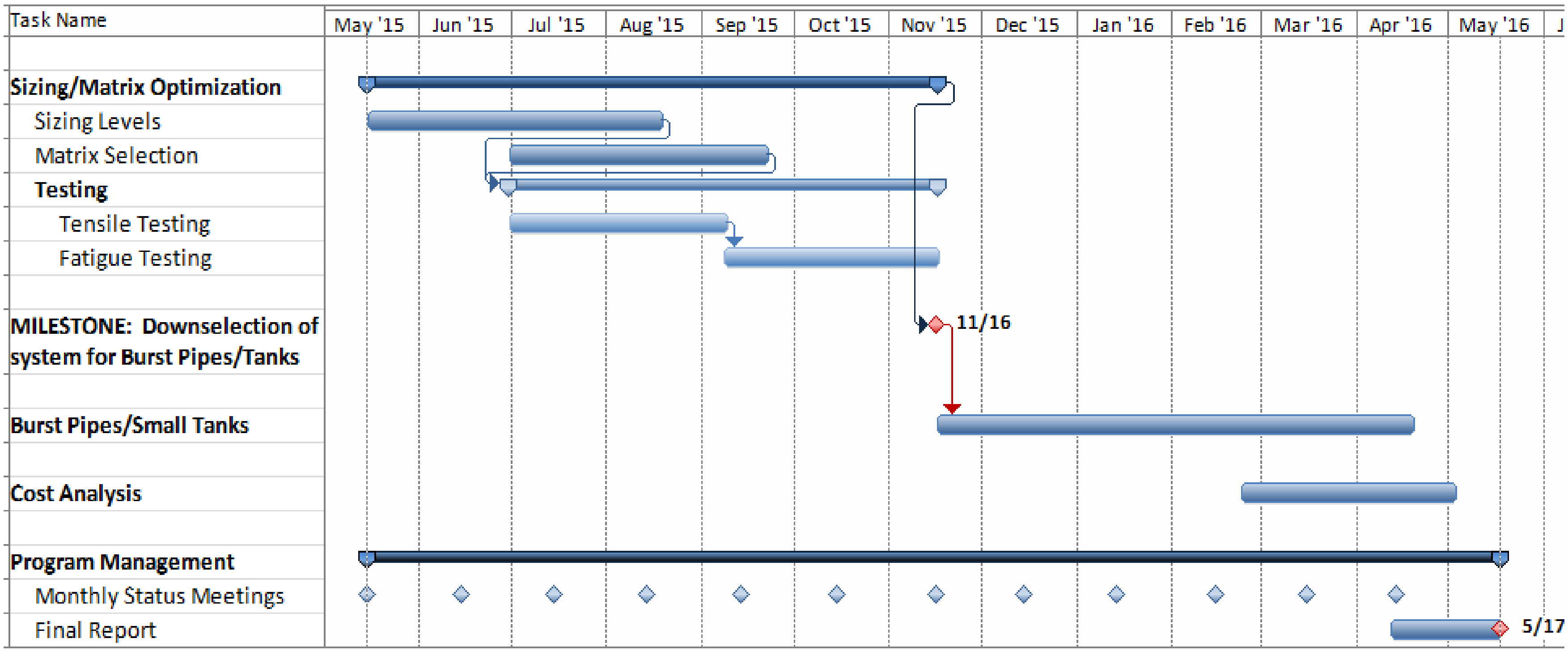
Material	Description	Comments
Toray T700	Commercial carbon fiber	• Currently used in Type IV tank construction • $12-15/lb
ORNL Low Cost Carbon Fiber	Non-commercial carbon fiber	• Alternate feedstocks for low cost carbon fiber production • Target price point $5-$9/lb
SGL Sigrafil® C30	Commercial lower cost carbon fiber	• $11/lb
Standard Epoxy Sizing	Commercially available, applied during manufacture	• Primarily handling function • Some improvement in wetting/adhesion
CTD Sizing	Reactive sizing	• Improved interlaminar shear properties
Adherent Technologies AT-9307E finish	Reactive finish	• Dramatic improvements in composite strength and environmental durability
CTD-9.1PX	Toughened epoxy	• Prepreg resins • Will be modified for wet winding

Approach – Phase II Schedule, Year 1



- **Downselection criteria**
  - Improved handling – i.e., reduced fuzzing of low cost fiber options
  - Improvement of fiber translation for large tows from 55% to at least 70%
  - Composite strain to failure approaching 1.5%

Approach – Phase II Schedule, Year 2



Collaborations

- **CTD**
  - **Material trials – includes sizing, tow handling, etc.**
  - **Product design**
  - **Commercialization**
- **Oak Ridge National Laboratory (ORNL)**
  - **Provide non-commercial low-cost carbon fiber for evaluation**
- **Adherent Technologies, Inc.**
  - **Specialty fiber sizing**
- **Heyliger Consulting**
  - **Analytical model optimization**
  - **Laminate optimization**
- **Luxfer Gas Cylinders**
  - **Aid with cost analysis – primarily process-related components**
  - **Test cylinder fabrication**

Project Summary

Relevance	Decrease overall cost of on-board hydrogen storage for fuel cell powered vehicles
Approach	Type IV hydrogen storage tank based on graded composite structure incorporating low cost carbon fibers
Technical Accomplishments & Progress	Preliminary parametric cost analysis performed; preliminary design trade studies completed; coupon testing has identified target areas for improvement (composite strain to failure, fiber property translation, handling of large fiber tows)
Technology Transfer/ Collaborations	Active collaborations with ORNL (low cost carbon fiber), Adherent Technologies (specialty sizing), and Luxfer Gas Cylinders (cost analysis, high rate manufacturing)
Proposed Future Research	Optimization of graded composite tank construction; demonstrate a lower cost Type IV pressure vessel using graded composite construction; work with Luxfer to build and test Type IV tanks