2010 DOE Hydrogen Program

Development of Advanced Manufacturing Technologies for Low Cost Hydrogen Storage Vessels

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QUANTUM TECHNOLOGIES BOEING Pacific Northwest NATIONAL LABORATORY Lawrence Livermore National Laboratory

Overview

Timeline

- Project start date 09/2008
- Project end date: 03/2012
- Percent complete: 33%

Budget

- **Total Budget: $5,486,848**
- DOE Share: $2,566,451
- QT/Boeing Share: $1,920,397
- FFRDC Share: $1,000,000
- FY08 Funding: $475,845
- Funding for FY09: $350,000
- Funding for FY10: $800,000

Barriers

- Material system costs
- Manufacturing processes

Partners

- Quantum Technologies, Inc.
- The Boeing Company (Boeing)
- Pacific Northwest National Laboratory (PNNL)
- Lawrence Livermore National Laboratory (LLNL)

Project Objectives- Relevance

To manufacture Type IV H_2 storage pressure vessels, utilizing a new hybrid process with the following features:

- Optimal elements of advanced fiber placement (AFP) & commercial filament winding (FW).
- Reduced production cycle times by adaptations of high-speed "dry winding" methodology.
- Improve understanding of polymer liner H_2 degradation.

With the aim of achieving:

A manufacturing process with lower composite material usage, lower cost, and higher efficiency.

Milestones

Time	Milestone
09/08-04/09	Program Kick-off Material development investigation; 100% complete Composite design literature review & optimum liner dome profile; 100% complete Fiber placement delivery head modification; 100% complete Initial cost model; input/output & approach; 100% complete
05/09	Merit Review
05/09-12/09	Manufacture & test best effort tank using hybrid process: build & test two tanks Baseline cost model complete Go/NoGo decision→ data shows AFP & FW processes can manufacture a tank → GO Decision
11/09-04/10	Dry tape technology evaluation
06/10	Merit Review
03/10-01/11	Manufacturing process development; manufacture & test best effort tank Revised cost model Go/NoGo decision→ demonstrate process can reduce material usage and cost
03/11-06/11	Hybrid manufacturing technology refinement
05/11	Merit Review
06/11-01/12	Produce hybrid manufacturing technology tanks; test per EIHP Final cost model

Approaches

- Material study to address material compatibility, cure profile, AFP process requirements.

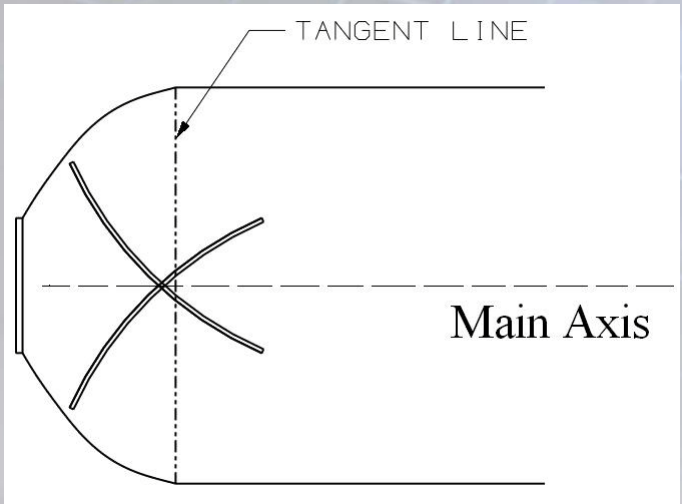
- Composite design & stress analysis

Governing Equilibrium Equation

$$\frac{N_\alpha}{R_m} + \frac{N_\beta}{R_P} = p$$

Assumed dome profile in parametric form

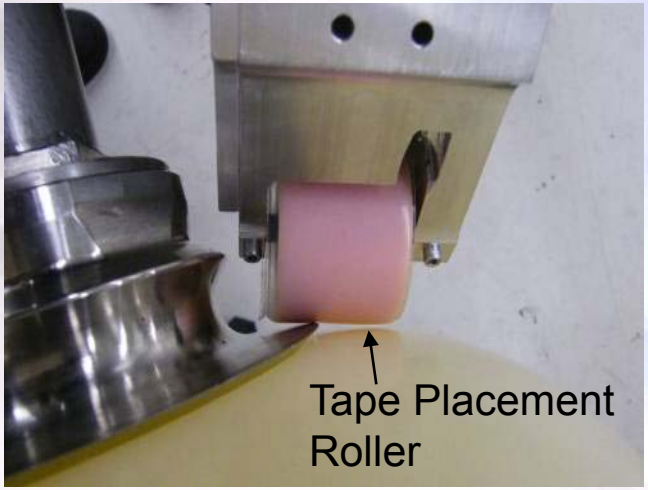
$$S(r,\beta) = \{r\cos\beta, r\sin\beta, z(r)\}$$

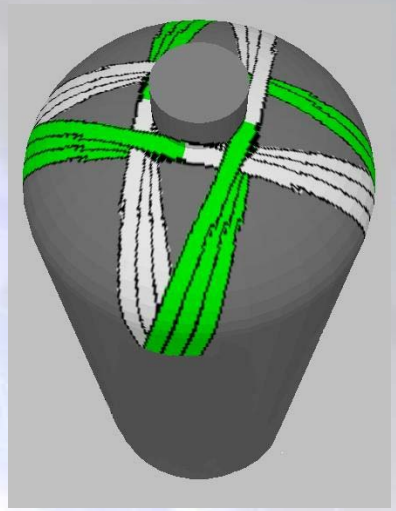


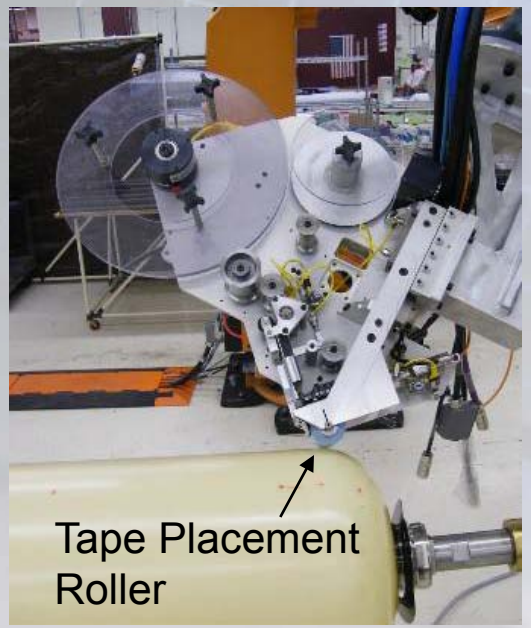
➡ **Optimum liner dome profile, composite lay-up**

Approach: Advanced Fiber Placement- Boeing

- **Advanced Fiber Placement:** A CNC process that adds multiple strips of composite material on demand.
  - Maximum weight efficiency - places material where needed
  - Fiber steering allows greater design flexibility
  - Process is scalable to hydrogen storage tanks
  - Optimize plies on the dome sections with minimal limitation on fiber angle
  - Reinforce dome without adding weight to cylinder







Approach: Advanced Fiber Placement- Boeing

- Integration of Filament Winding and Advanced Fiber Placement
  - In the same cell
  - In parallel cells
  - Off line fiber placement of reinforcement details

Technical Progress: Advanced Fiber Placement - Boeing

- Boeing Advanced Fiber Placement (AFP) Process

  Boeing has successively modified their AFP head

  - Smaller polar openings, more optimal structural design
    - 2.5-inch aft dome, and a 3.7-inch forward dome
  - Local heating and cooling of the towpreg.
    - Control of “tackiness” and “boardiness”
    - Enhances feeding and lay-down, reduces wrinkling

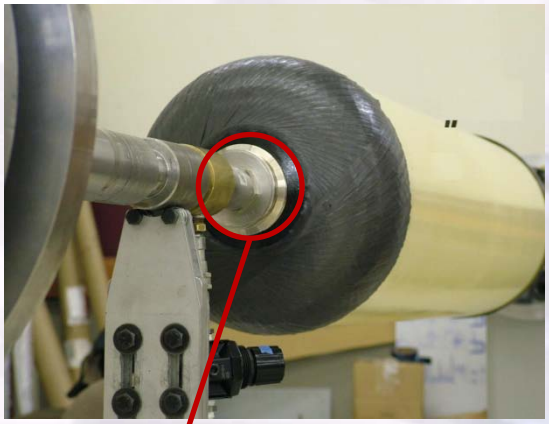
Technical Progress: Advanced Fiber Placement - Boeing

Developed an alternative build approach (Off-line AFP process)

- Stand-alone mandrel for the AFP operations
  - Sub-laminate is released and then re-mounted onto the liner
  - Same shape and dimensions as the liner
  - Cantilevered full head access to the end regions
  - Eliminates head interference problems
  - No polar-opening issues
  - Versatile build options

Approaches

- Tank preparation and validation test



Representative smallest polar opening that the AFP process can currently make

The localized reinforcement protected the dome regions very well

- Static Burst Result: 23420 PSI > 22804 PSI, EN standard (New European Standard superseding EIHP)
- 64.9 kg composite usage in the 1st hybrid vessel vs. 76 kg in the baseline tank (FW alone)

11.1 kg (14.6%) Savings!

Approach: Tank Cost Analysis

- Quantum and Boeing's manufacturing experience was used to estimate the $/kg of Filament Wound (FW) and Advanced Fiber Placed (AFP) Composites.
- Hybrid composite design provided the mass of Filament Wound and Advanced Fiber Placed Composites.
- Cost model included materials, labor, overhead, balance of system, manufacturing equipment and factory space costs.

Approach: Tank Cost Analysis

Baseline and two bounding manufacturing scenarios were investigated:

1. Baseline = Quantum Filament Wound 129 Liter, Type IV Tank.
2. Fully Integrated FW and AFP – Composite layup optimized for high strength, but inefficient machine usage.
3. Fully Separate FW and AFP - 100% machine usage, but composite strength may be slightly reduce.

Technical Progress: Tank Cost Analysis

500,000/yr, $11/lb Carbon Fiber

		Type IV Tank	Hybrid FW + AFP Reinforced	
Summary Table		Baseline 129L	Fully Integrated	Separate
		Filament Wound	FW and AFP	FW and AFP
Composite Mass, kg	FW	76	63.4	63.4
	AFP		1.5	1.5
Total Composite Mass, kg		76	64.9	64.9
Comp. Placement Speed, kg/hr	FW	13.2	13.2	13.2
	AFP		0.9	0.9
Comp. Placement Time, hr/tank	FW	5.75	4.80	4.80
	AFP		2.48	1.65
Total Comp. Place Time, hr/tank		5.75	7.27	4.80
# Manuf. Cells for 500K/yr	FW	191	242	159
	AFP		484	165
Tank Costs				
FW Composite		$2,290	$1,910	$1,910
AFP Composite			$90	$90
End Boss		$250	$250	$250
Manufacturing Equipment		$36	$66	$41
Factory Space		$7	$10	$7
Total Tank Cost		$2,583	$2,326	$2,299
% Tank Cost Savings		0%	10%	11%
DOE Measures				
Specific Energy, kWh/kg [1]		1.50	1.67	1.67
Cost Efficiency, $/kWh [2]		$23.45	$21.91	$21.75

[1] 5 kg H2 * 33.31 kWh/kgH2 / (Tank+OtherComponents+H2 mass, kg) OtherCompMass=30kg

[2] (Tank+OtherComponents $$) / (5 kg H2 * 33.31 kWh/kgH2)

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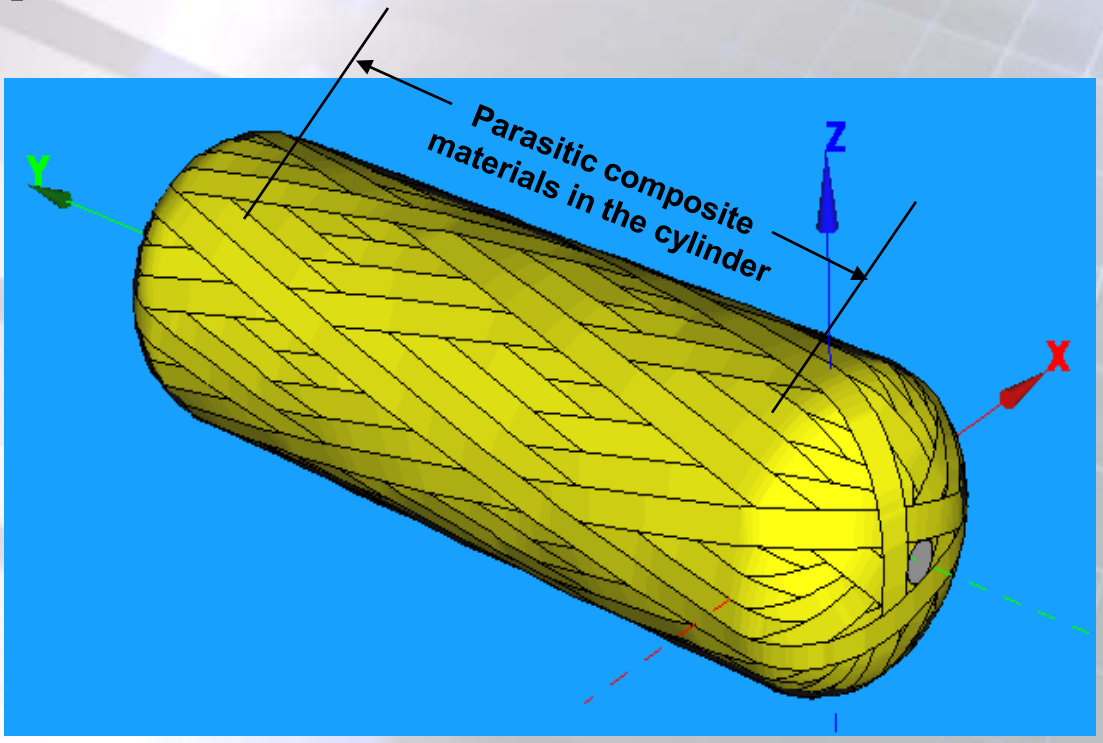
Accomplishment: Material & Cost Saving



64.9 kg composite usage in the 1st hybrid vessel vs. 76.0 kg in the baseline tank (FW alone)

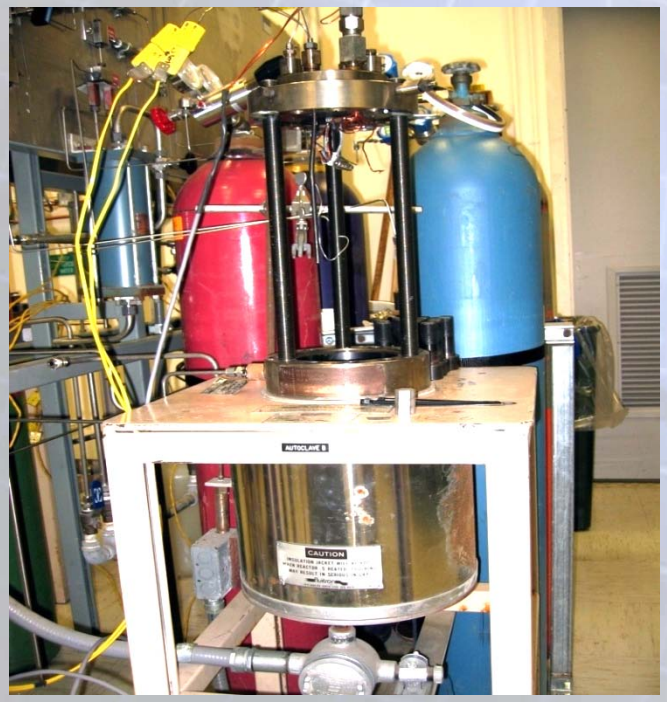
- The end-user H_2 storage system weight efficiency = 1.67 kWh/kg vs. 1.50 kWh/kg in the system with the baseline tank
- The end-user H_2 storage system cost efficiency:

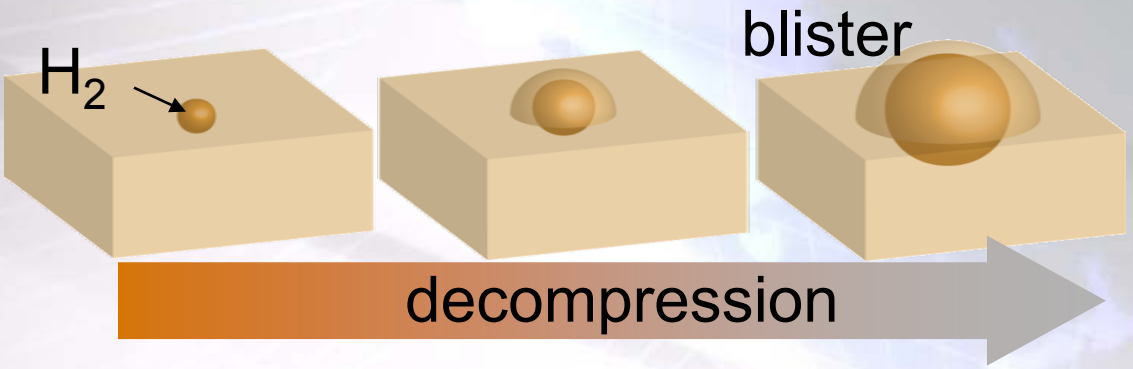
•<u>$11/lb CF</u>	Baseline	$23.45	Fully Integrated	$21.91	Fully Separate	$21.75
• <u>$6/lb CF</u>	Baseline	$18.74	Fully Integrated	$17.79	Fully Separate	$17.63

Approach: Hydrogen Liner Compatibility

Relevance:
- Polymer liner prevents H_2 diffusion
- Exposed to high pressure H_2, decompression
- H_2 embrittles, blisters metals, ceramics
- Little is known about H_2 effect on Polymers

Approach:
- Charge Polymers in high pressure H2
- Investigate degradation: blistering
  - Function of temperature, decompression
  - Function of crystallinity
- Bulk Modulus tests planned to look for changes

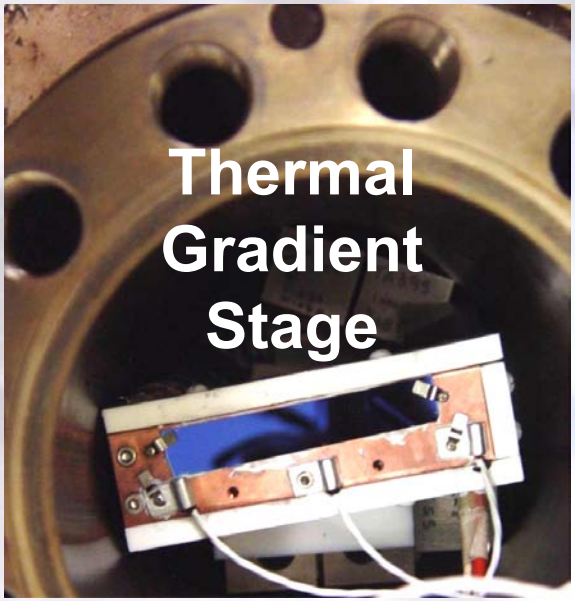


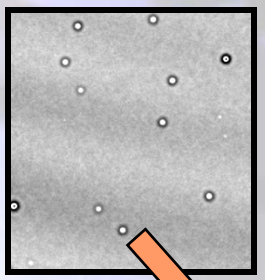


PNNL High Pressure H_2 Setup
- 100% H_2 or D_2 atmosphere
- up to 5,000 psi
- RT to 200C temperature
- large samples possible

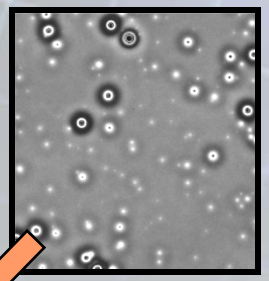
Technical Progress: Hydrogen Liner Compatibility

- Developed Thermal Gradient Stage for ***in-situ*** Combinatorial testing
- Preliminary testing of amorphous polymers with temperature
- Preliminary testing of 100% crystalline polymers with temperature
- Observed blistering dependent of temperature, crystallinity





- Blister size/density increase with Temp.
- 100% crystalline polymer do not appear to blister

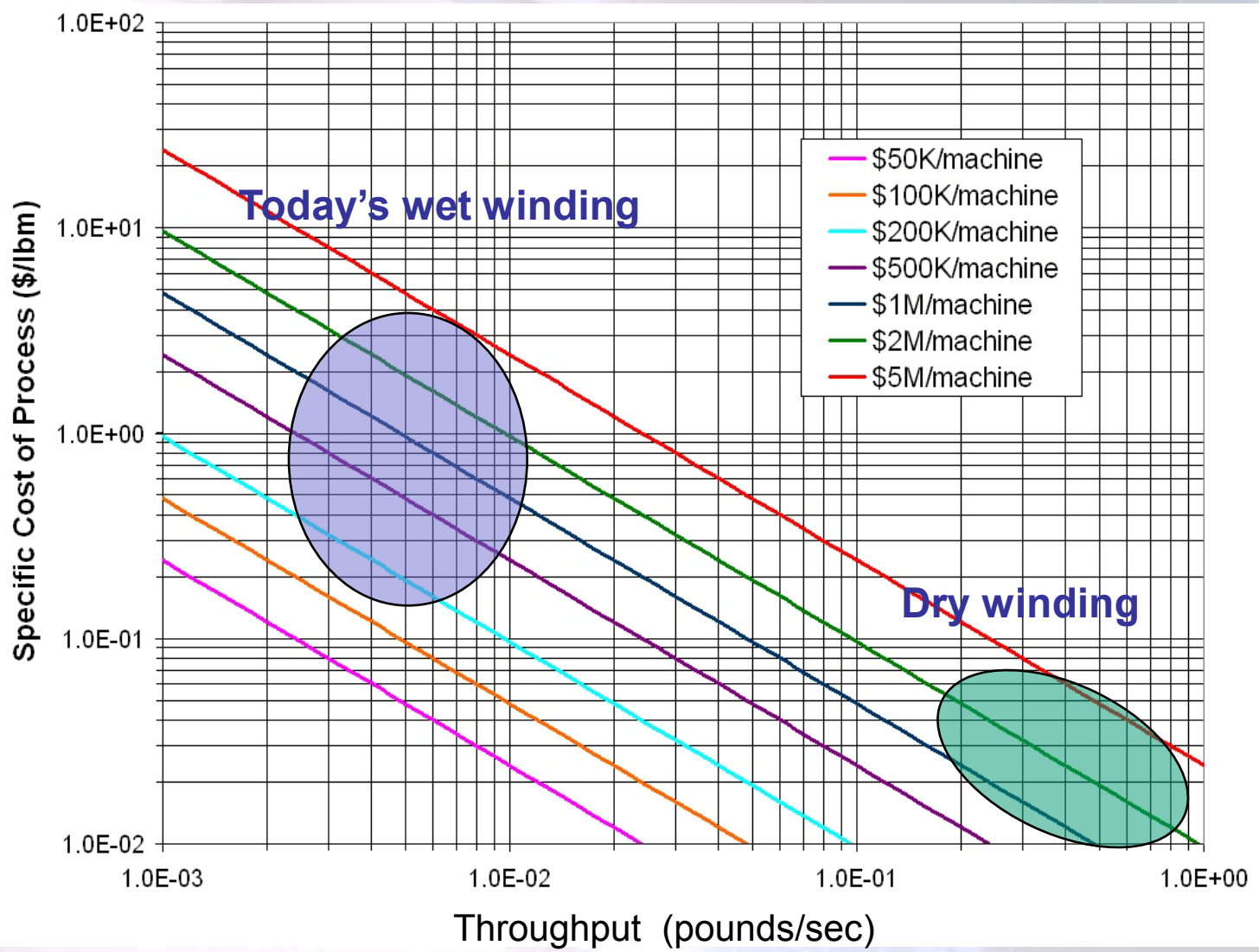


Hydrogen Liner Compatibility: Future Work

- Further H_2 blistering studies semi-crystalline Polymers
  - HDPE, PVDF, other standard materials
  - Function of crystallinity (LDPE, HDPE, UHMWPE)
  - XRD measurements to confirm crystallinity
  - Function of temperature (aging)
- Tests on Quantum Polymers
- Bulk Modulus testing (bulk rods)
  - HDPE, other materials
  - Function of H2 exposure
  - Recovery time

PNNL mechanical testing lab

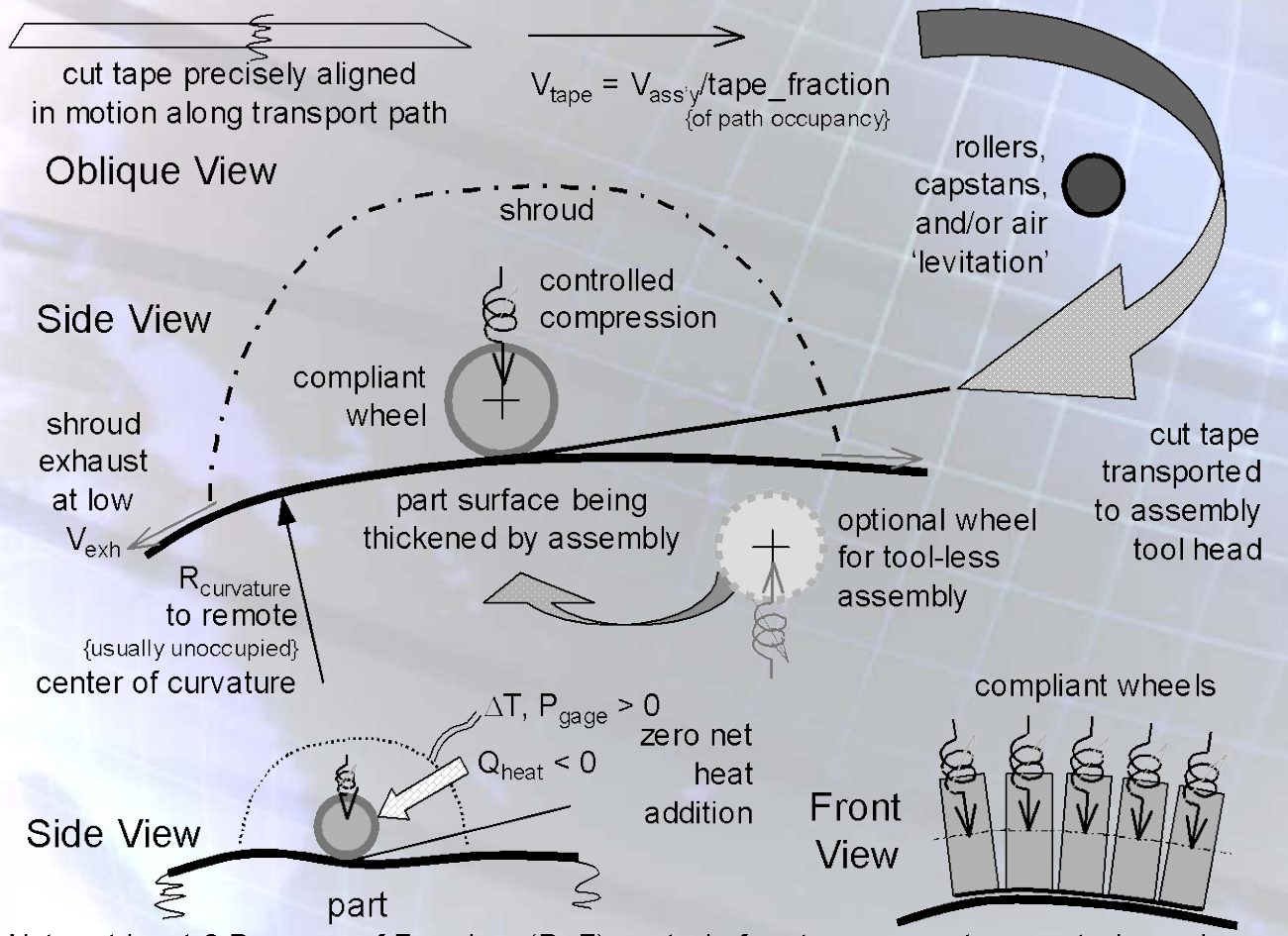
Approach: Dry Tape Winding



Manufacturing cost is inversely proportional to Throughput → *Significant* cost reductions require *fast* winding

Approach: Dry Tape Winding

How to implement ultra fast bonding? Our approach retains full fiber strength, improves tensile strength, and produces precise parts (like tires, instead of like baskets)

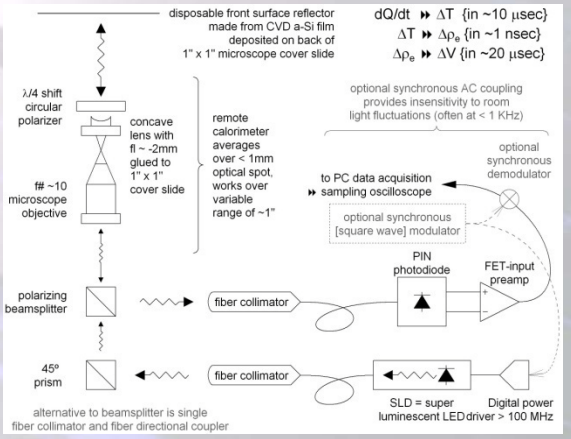


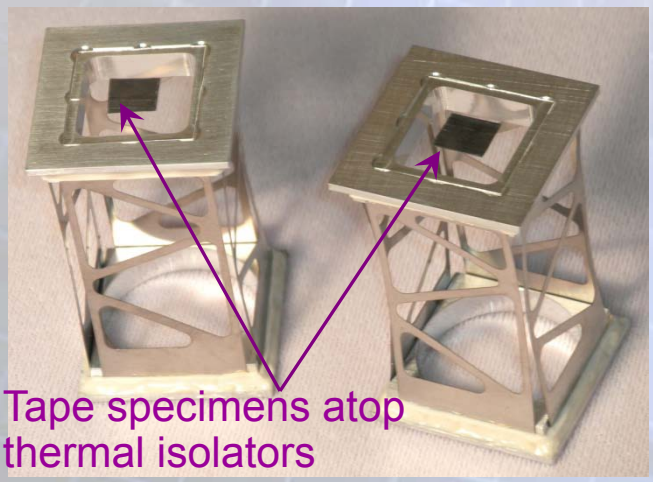
Note: at least 6 Degrees of Freedom (DoF) control of part location+orientation plus 2 DoF tool head vs. 2 plus 2 for pressure vessel vs. 2 plus 1 for tubing

curvature control may be required to assist compliance in providing uniform compression

Approach: Dry Tape Winding

We are measuring tape-to-tape bonding process speed with calorimeters (exothermic plastic + endothermic solder bonds)

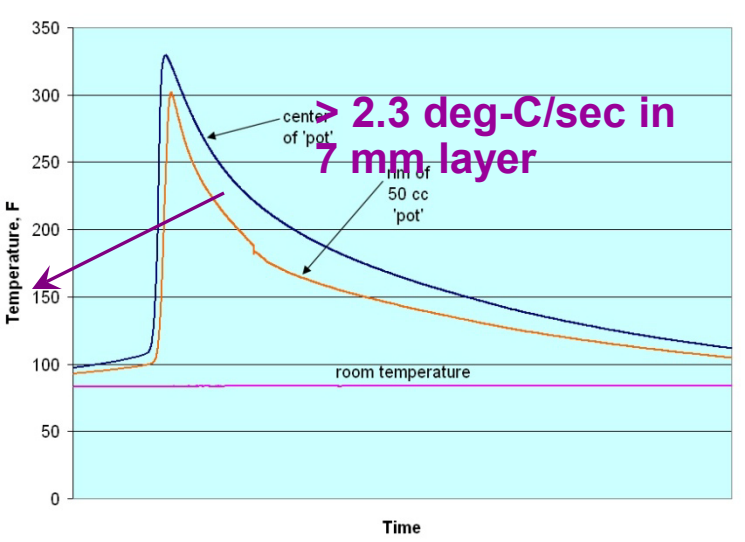




Design for 1st generation RTD remote infrared calorimeter measures heat emissions from >> T's (found in Go-No-Go trial)

Scaled by heat diffusion (from 280 to 1 mil thick bond layers) gains 10 x viscosity in ~0.14 msec

Thermocouple-instrumented hot pot experiment Achieved Go-No-Go Milestone in August 2009



Future Work: Strategies for Program Goals

- Continued improvement on advanced fiber placement (AFP) processes and structural design
  - Flexibility in AFP to cover more regions
  - Off-line AFP process for automation platforms
- More testing to validate the AFP/FW hybrid process
  - Ambient temperature cycle fatigue
  - Extreme temperature cycle fatigue
  - Accelerated stress rupture
- Cost model update including consideration of textile performing approaches as compared to our hybrid AFP/FW process.
- Continuous evaluation of polymer liner candidate material resistance to H_2 environment
- Improve tape processes speed and test performance
  - Measure strength: bond shear stress and strain, tensile stress
- Evaluation of alternative materials: S-Glass, Basalt fibers

Project Summary

- A Boeing/Quantum Composite Tank Has Been Produced Using a Hybrid AFP/FW Process:
  - Significant step towards DOE's efficiency goals
  - The first hybrid tank exceeded the required burst pressure and saved 11.1kg of the 76 kg baseline (14.6% !!)
  - Composite cost is high compared to factory equipment and space costs. The composite layup can be optimized without significant cost from machine inefficiencies.
  - Reduced tank mass improves:
    - Specific energy increased from 1.5 to 1.67 kWh/kg.
    - Cost efficiency reduced from $23.45 to $21.75/kWh (7.2% reduction) for $11/lb carbon fiber.

Project Summary (Con't)

- PNNL Hybrid Process Cost Model Development and Polymer Liner Hydrogen Compatibility:
  - Initial cost model shows additional costs of equipment required for hybrid process is insignificant compared to cost saving achieved from fiber usage reduction.
  - Polymer liner compatibility testing in hydrogen indicates crystalline density and temperatures have direct effect on formation of blisters in liner material.

- LLNL Dry Tape Winding Development:
  - Dry tape initial feasibility showed positive results. Development of process still in early stages.