System Level Analysis of Hydrogen Storage Options

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2013 DOE Hydrogen and Fuel Cells Program Review

Arlington, VA

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Project ID: ST001

Overview

Timeline

- Project start date: Oct 2009
- Project end date: Sep 2016
- Percent complete: 50%

Barriers

- H_2 Storage Barriers Addressed:
  - A: System Weight and Volume
  - B: System Cost
  - C: Efficiency
  - E: Charging/Discharging Rates
  - J: Thermal Management
  - K: Life-Cycle Assessments

Budget

- FY12: $700 K
- FY13: $480 K

Partners/Interactions

- Storage Systems Analysis Working Group (SSAWG)
- Hydrogen Storage Engineering Center of Excellence (HSECoE): SRNL, UTRC
- Ford, PNNL, Tank OEMs
- University of Oregon
- SA

Objectives and Relevance

- Conduct independent systems analysis for DOE to gauge the performance of H_2 storage systems
- Provide results to material developers for assessment against performance targets and goals and help them focus on areas requiring improvements
- Provide inputs for independent analysis of costs of on-board systems.
- Identify interface issues and opportunities, and data needs for technology development
- Perform reverse engineering to define material properties needed to meet the system level targets

Approach

- Develop thermodynamic and kinetic models of processes in physical, complex metal hydride, sorbent, and chemical H_2 storage systems
  - Address all aspects of on-board and off-board storage targets, including capacity, charge/discharge rates, emissions, and efficiencies
  - Perform finite-element analysis of compressed hydrogen storage tanks
  - Assess improvements needed in materials properties and system configurations to achieve storage targets
- Select model fidelity to resolve system-level issues
  - On-board system, off-board spent fuel regeneration, reverse engineering
  - Conduct trade-off analyses, and provide fundamental understanding of system/material behavior
  - Calibrate, validate, and evaluate models
- Work closely with DOE technology developers, HSECoE and others in obtaining data, and provide feedback
- Participate in SSAWG meetings and communicate approach and results to foster consistency among DOE-sponsored analysis activities

Summary: FY2013 Technical Accomplishments

1. Physical storage
    - Carbon fiber (CF) composite requirements: Calibration and validation of ABAQUS model for 700-bar Type-4 tanks
    - CF composite use reduction: Advanced winding and fabrication
    - Updated SA cost analysis: CF requirements and component data for single and multi tank 700 and 350-bar storage systems
2. H_2 storage in metal hydrides
    - Reverse engineering to determine material properties needed to meet system targets
    - Comparison of initial results and methodology with SRNL and UTRC of HSECoE
3. H_2 storage in sorbents
    - Reverse engineering to determine material properties needed to meet system targets, comparison with HSECoE pending*
4. Off-board regeneration
    - Alane regeneration by organo-metallic route and AB regeneration using benzophenone for hydrazine production (SA support)*
    - CBN regeneration by formic acid and MeOH/$NaAlH_4$ routes*

*Not covered in this presentation

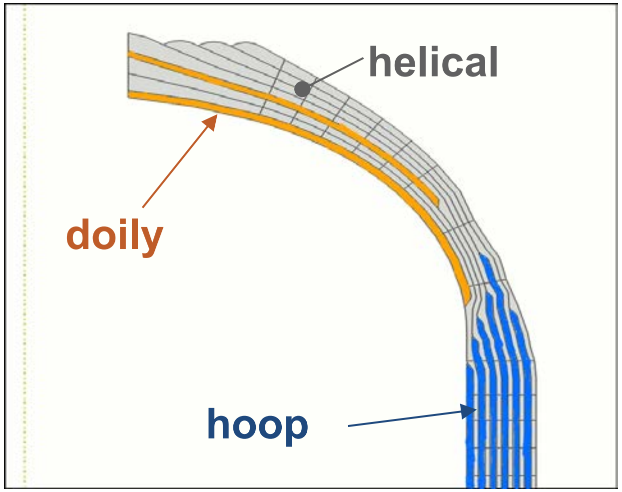
Compressed H_2 Storage

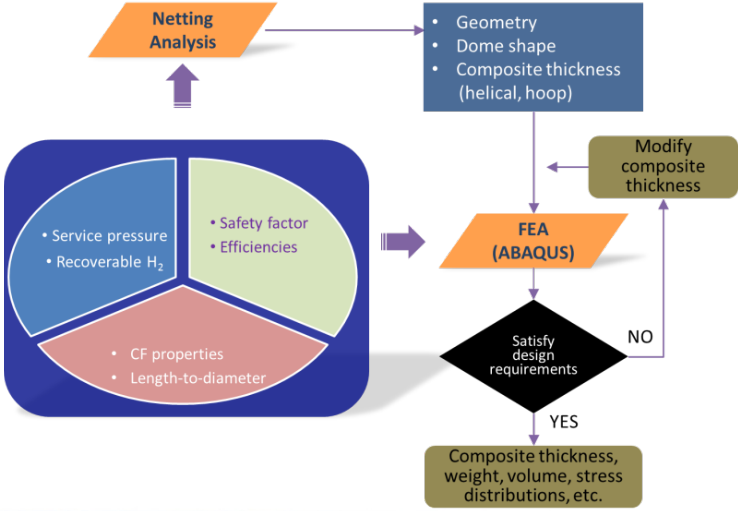
3-D finite element analysis using ABAQUS and Wound Composite Modeler

- Iterative method combining netting and finite-element analyses
- Held meetings with Ford, Lincoln Composites, PNNL, and SA to arrive at common definitions and assumptions for T700 CF composites
- Validated/calibrated model with OEM data and other models

Proposed and evaluated methods to reduce carbon fiber composite usage

- Winding doilies over dome to reduce stresses in shoulder and boss areas
- Varying hoop winding angles for more uniform sharing of loads
- Integrated end cap concept to reduce helical windings
- Increasing stress ratio to reduce helical windings




Netting Analysis

- Geometry
- Dome shape
- Composite thickness (helical, hoop)

- Service pressure
- Recoverable H_2

- Safety factor
- Efficiencies

- CF properties
- Length-to-diameter

FEA (ABAQUS)

Modify composite thickness

Satisfy design requirements

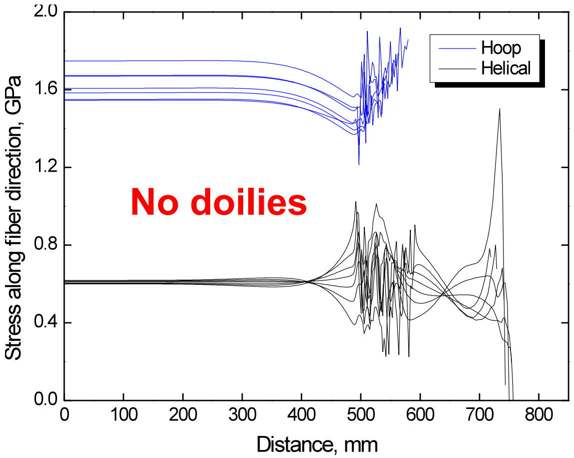
NO

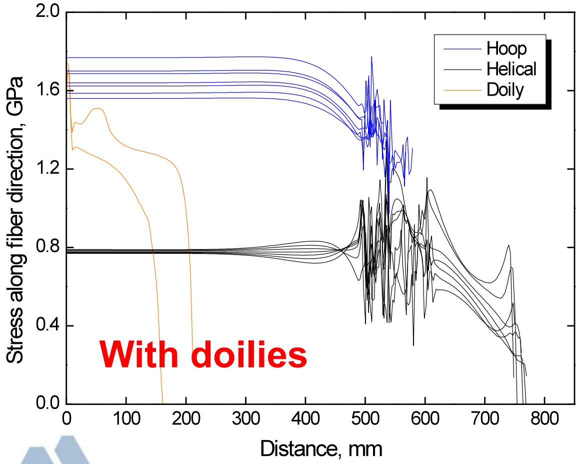
YES

Composite thickness, weight, volume, stress distributions, etc.

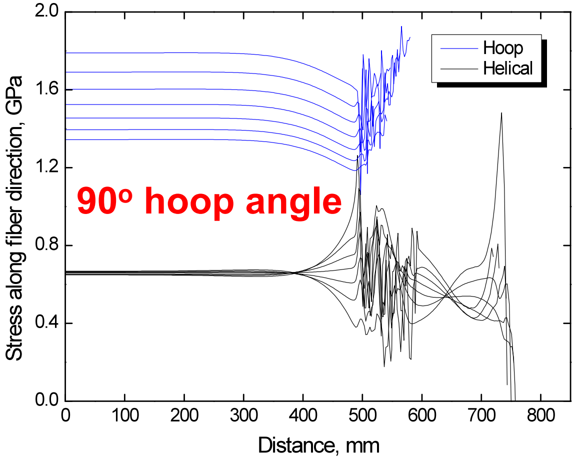
Stress Profiles in Carbon Fiber

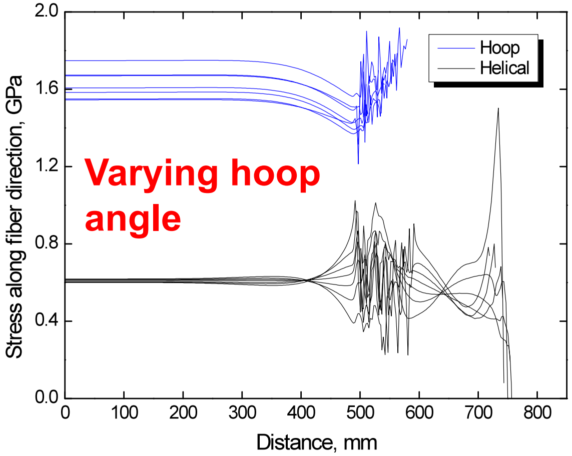
Stress in shoulder and boss areas reduced with doilies: tank more likely to fail in cylinder section



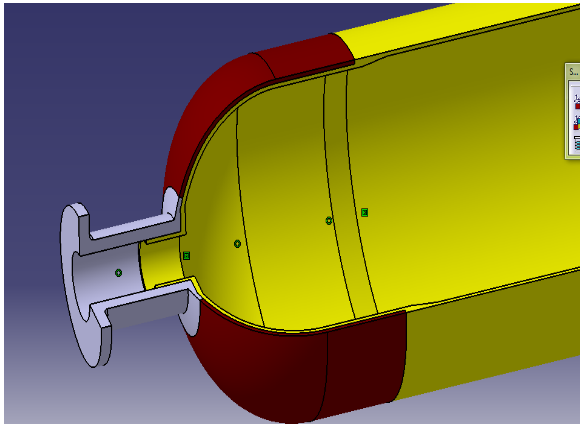


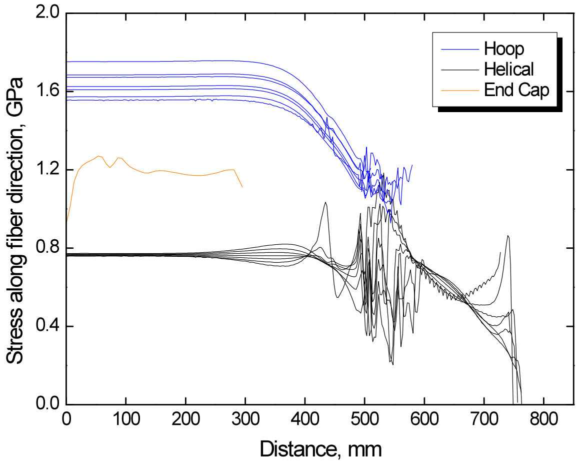
Stress distribution more uniform across the layers if hoop winding angle is varied





Domes reinforced with end caps made by resin transfer molding: end caps blow-molded with boss and liner*





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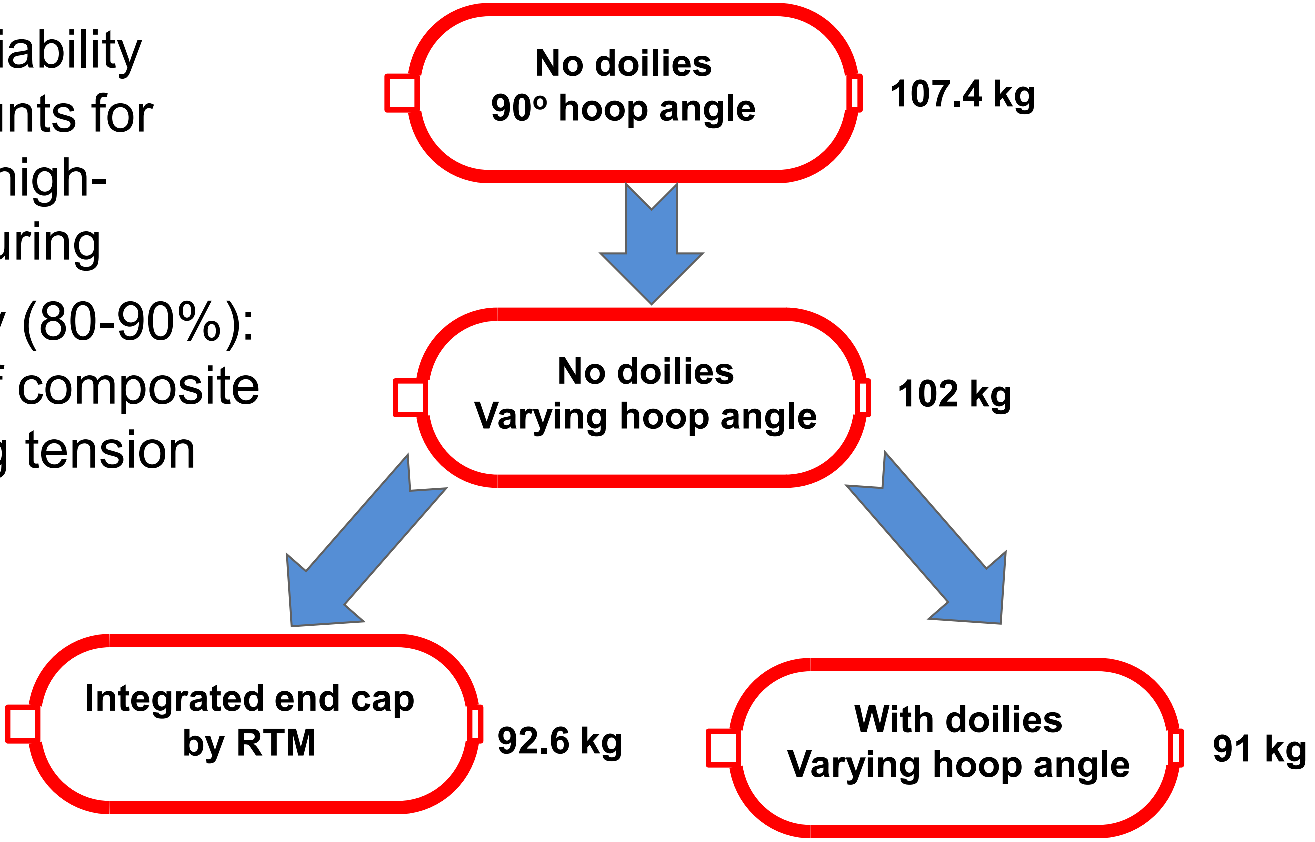
*Tensile strength of end cap assumed to be 75% of the composite used in filament winding

Carbon Fiber Requirement for 700-bar Type-4 Tank

Established consensus baseline for 700-bar Type-4 tank, 5.6 kg usable H_2, outside L/D = 3, P = 700 bar

Harmonized assumptions and definitions with PNNL led tank project

- Composite efficiency (87%): ratio of composite strength normalized to fiber volume (60% nominal)
- Fiber strength variability factor (0.9): accounts for fiber variability in high-volume manufacturing
- Winding efficiency (80-90%): includes effects of composite thickness, winding tension



No doilies
90° hoop angle
107.4 kg

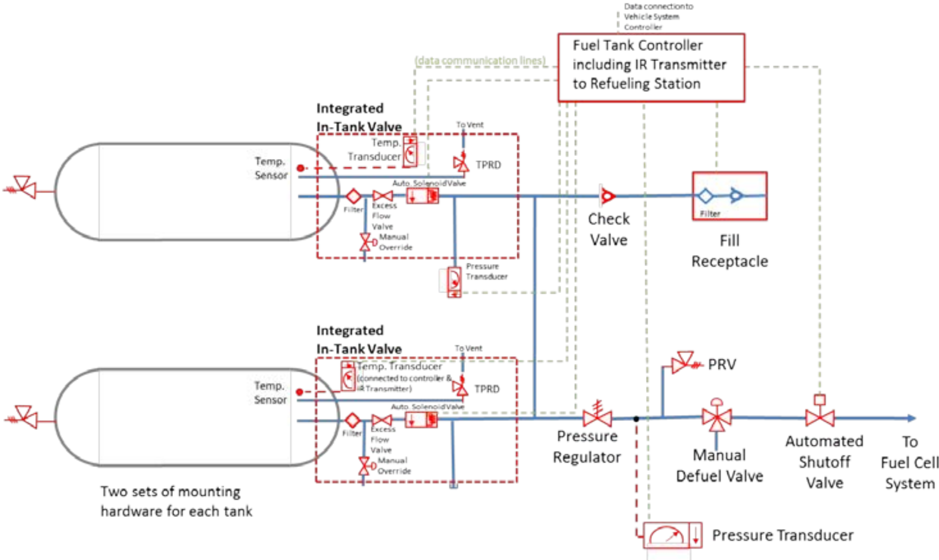
No doilies
Varying hoop angle
102 kg

Integrated end cap by RTM
92.6 kg

With doilies
Varying hoop angle
91 kg

Baseline Gravimetric and Volumetric Capacities

- Revised BOP components layout for 1-tank and 2-tank systems (ANL+SA and OEMs)
- Gravimetric capacities: 4.7-5.4 wt% for 350-bar and 4.1-4.4 for 700-bar systems
- Volumetric capacities: 17.1-17.7 g/L for 350-bar and 24.2-25 g/L for 700-bar systems
- CF accounts for 67-71% by weight and 25-26% by volume of the 700-bar system; 55-59% by weight and 12.5% by volume of the 350-bar system



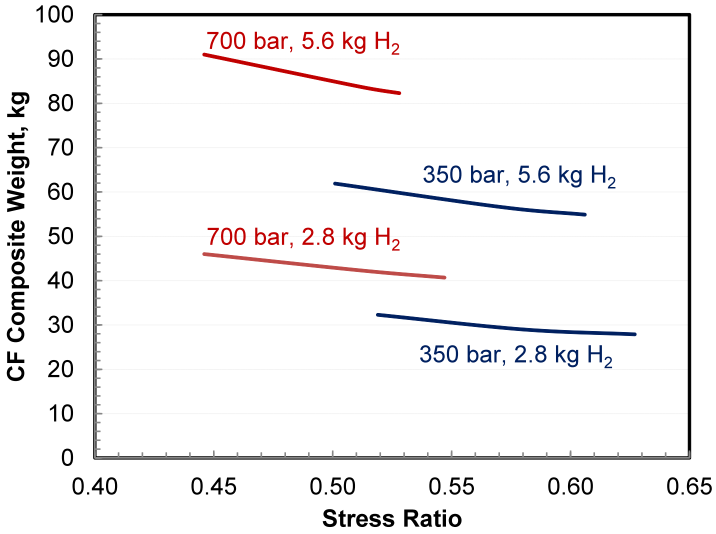
Type 4 Tank	350 bar One-Tank		350 bar Two-Tank		700 bar One-Tank		700 bar Two-Tank	
	W (kg)	V (L)	W (kg)	V (L)	W (kg)	V (L)	W (kg)	V (L)
Stored Hydrogen	6.0	250.4	6.0	250.4	5.8	145.2	5.8	145.2
HDPE Liner	11.4	12.0	14.4	15.2	8.0	8.4	10.1	10.6
Carbon Fiber Composite	61.9	39.2	64.6	40.9	91.0	57.6	92.0	58.2
Dome Protection	5.2	7.7	7.1	10.4	4.0	5.9	5.5	8.1
BOP	19.9	7.1	26.1	9.9	18.7	6.9	24.7	9.7
System Total	**104.5**	**316.4**	**118.2**	**326.8**	**127.6**	**224.0**	**138.2**	**231.8**
Gravimetric Capacity, wt%	**5.4**		**4.7**		**4.4**		**4.1**	
Volumetric Capacity, g H_2/L		**17.7**		**17.1**		**25.0**		**24.2**

*

Increasing Stress Ratio to Reduce CF Composite Usage

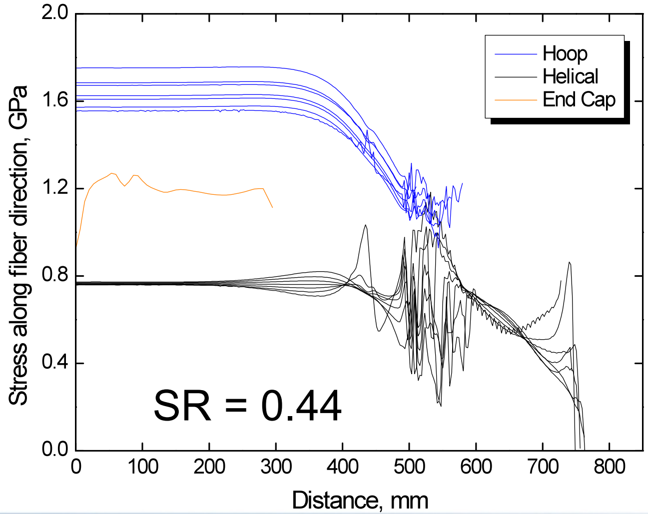
>10% reduction in CF composite possible in filament-wound only tank

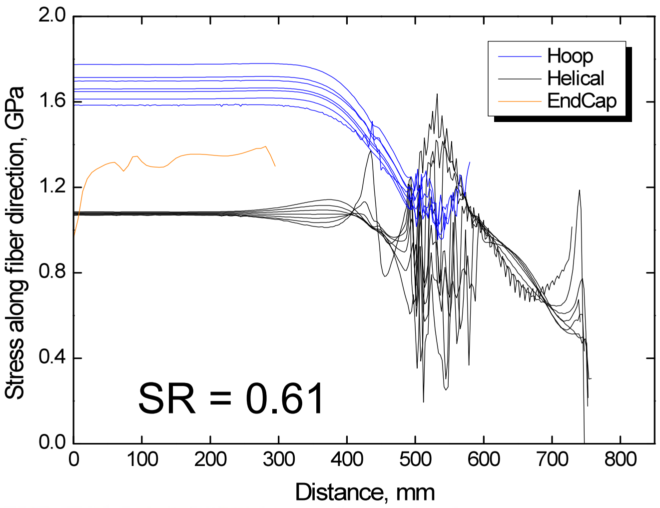
- SR* is generally limited to prevent end dome rupture. Lower SR helps pass 45° drop test and provides extra dome reinforcement and prevents dome failure or boss blowout.
- With doilies, stress concentration in shoulder limits SR to 0.53-055 in 700-bar tank.



~17% reduction in CF composite possible with integrated end caps

- Higher SR possible with end caps than doilies because of reduced stress concentration in shoulder and boss areas (improved stiffness continuity)



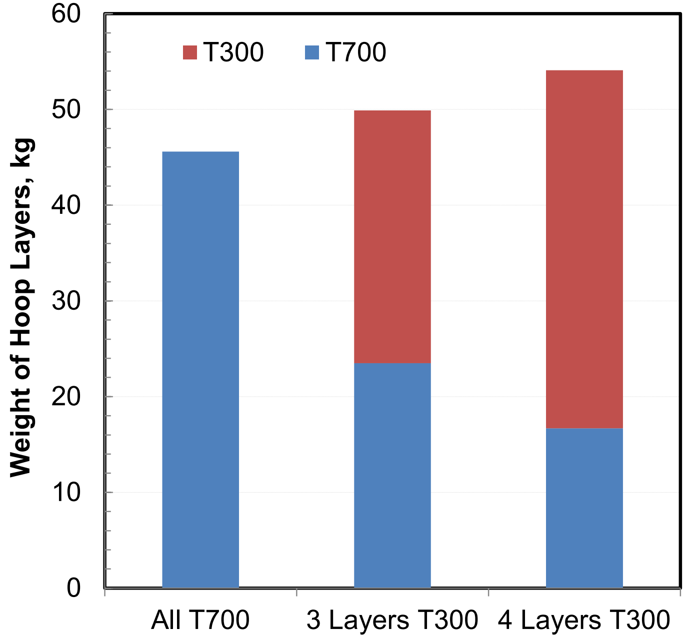


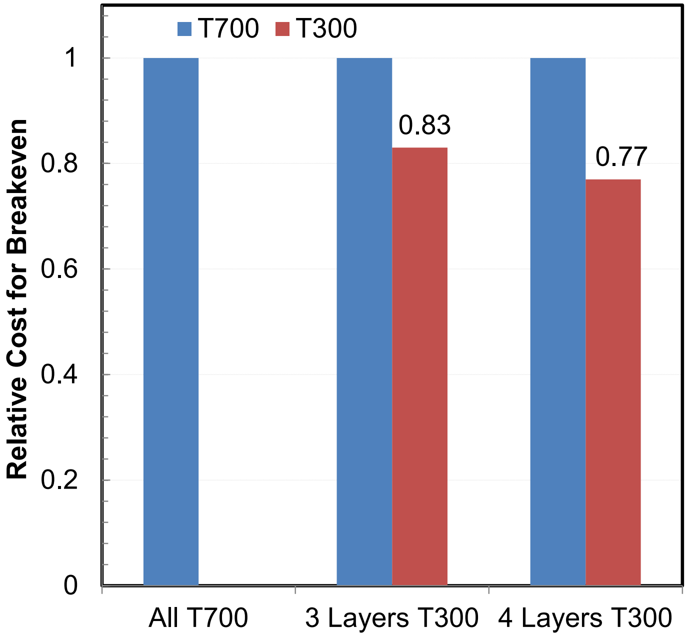
*SR: Ratio of helical to hoop stress in the cylinder section

Combined High and Low Grade Carbon Fiber

Replace outer 3 or 4 hoop layers of T700 CF with lower grade T300

- Total of 7 hoop layers varying in thickness from 2.4 to 4 mm. Hoop stresses in the outer 4 layers are 15-25% lower than in the innermost layer.
- T300 has 28% lower tensile strength, larger amount of CF is needed for the same pressure loading and fiber volume fraction. Weight of hoop layers increased by 9.4-18.6%
- Breakeven in composite material cost if T300 costs 17-23% less than T700

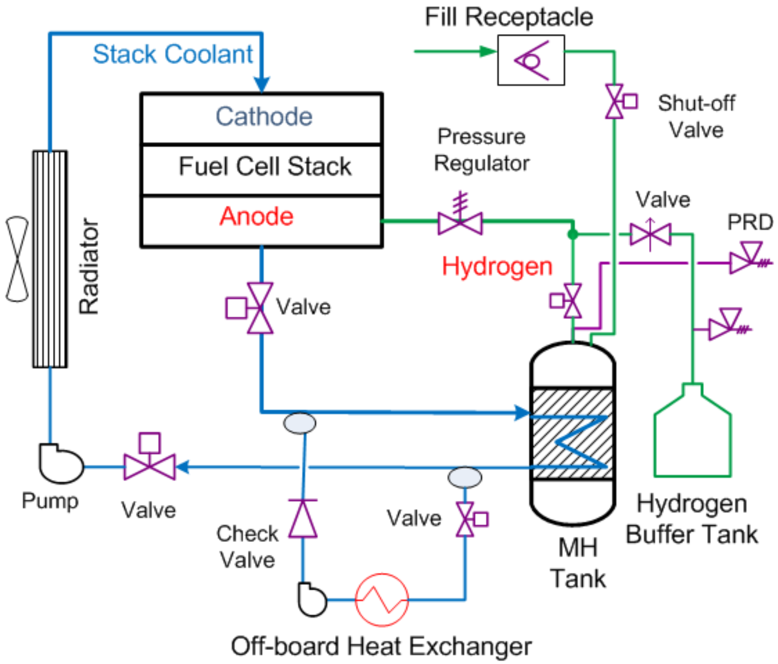




Reverse Engineering to Determine Target MH Properties

Low-temperature MH H_2 storage system

- Thermally integrated with FCS
- No H_2 burner - 100% on-board storage system efficiency
- Expanded natural graphite for conductivity enhancement
- Buffer tank for start-up from -40°C
- Type 3 containment tank

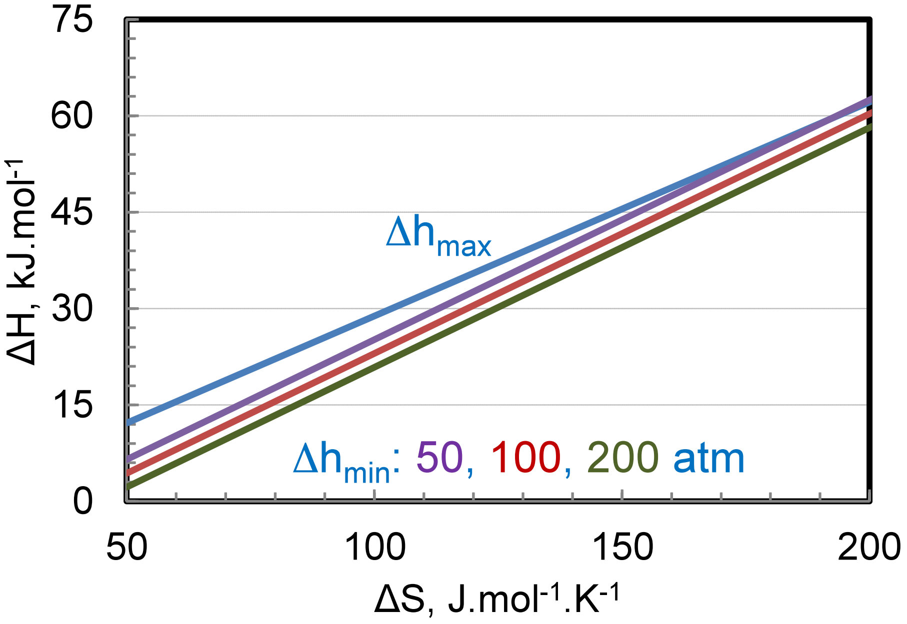


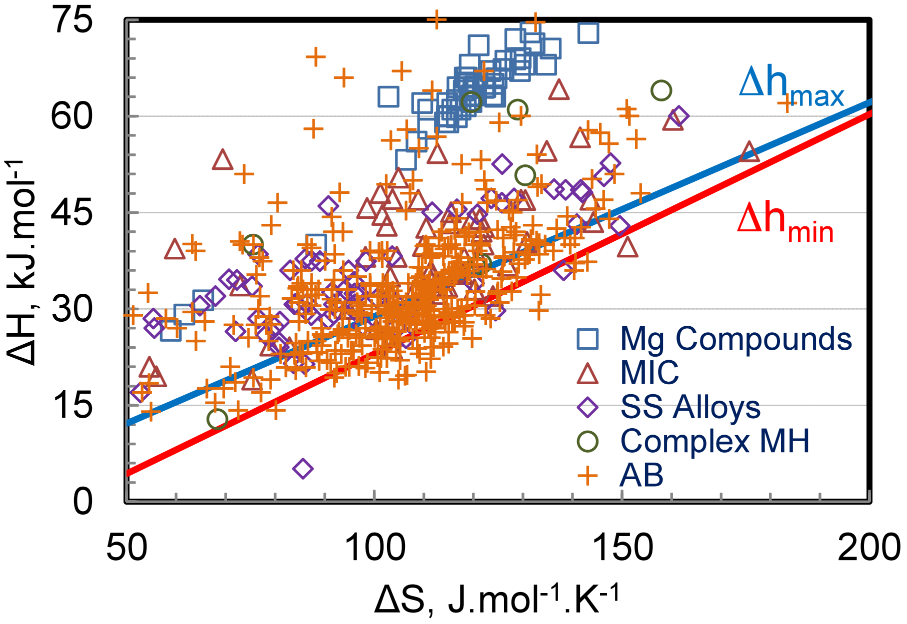
	Units	Reference Values	Range of Values	Comments
FCS Coolant Temperature	°C	62 - 85		ANL 2012 Reference FCS
Off-Board Coolant Temperature	°C	80	60 - 100	
MH Thermodynamics	ΔS, J/mol.K	110	TBD	Δh_{min} = 26.8 kJ/mol
	Dh, kJ/mol	28	TBD	Δh_{max} = 32.2 kJ/mol
Activation Energy for Discharge	E_c, kJ/mol	45	TBD	$NaAlH_4$ data
Minimum Delivery Pressure	atm	5		DOE target
Minimum Full Flow Rate of H_2	g/s	1.6		DOE target
Refueling Pressure	atm	100	50 - 200	
Expanded Graphite/MH Mass		0.1	0.05 - 0.25	IJHE 28 (2003) 515-527
System Gravimetric Capacity	%wt.	5.5		DOE target
System Volumetric Capacity	g/L	40		DOE target

Metal Hydrides: Thermodynamic Requirements

van't Hoff equation for equilibrium (plateau) pressure

- Δh_{max}: Equilibrium pressure of the MH at the minimum FC stack coolant temperature (60°C) should be higher than the minimum delivery pressure (5 atm)
- Δh_{min}: Equilibrium pressure at the maximum allowable bed temperature (100-150^{o}C) should be lower than the H_2 supply pressure (50-200 atm)





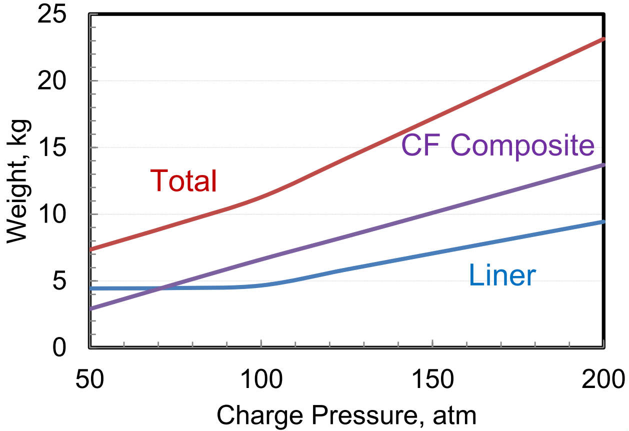
Containment and Buffer H_2 Tanks

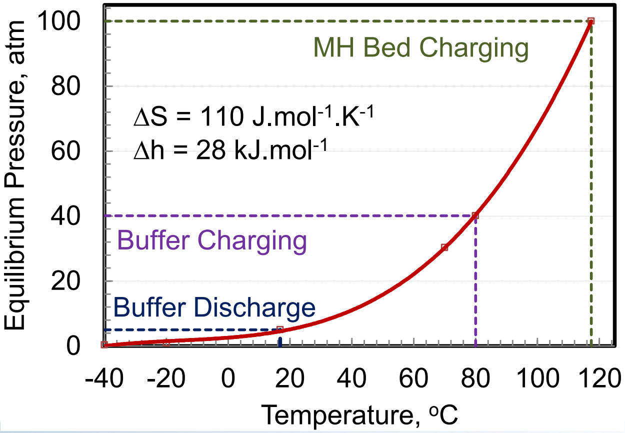
Type-3 carbon fiber (CF) wound storage tank with Al 6061-T6 alloy liner and Toray T700S CF, 60% fiber volume in composite

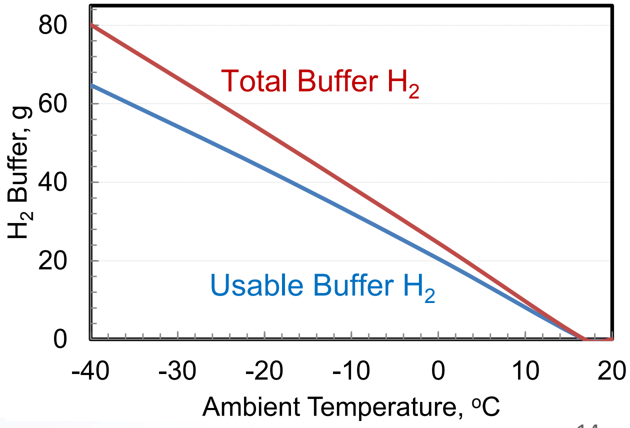
- Netting analysis to determine tank geometry, dome shape, helical and hoop thicknesses, 2.25 safety factor
- Fatigue analysis of auto-frettaged liner, 5500 pressure cycles at 1.25 NWP (SAE J2579)

H_2 buffer capacity for FCS startup from -40ÁC

- Buffer to supply H_2 until the MH bed reaches temperature at which it can release H_2 at a fraction (25% nominal) of the minimum full flow rate, 5-atm back pressure
- Buffer replenished with H_2 released from MH bed during normal operation when the stack coolant is at peak temperature



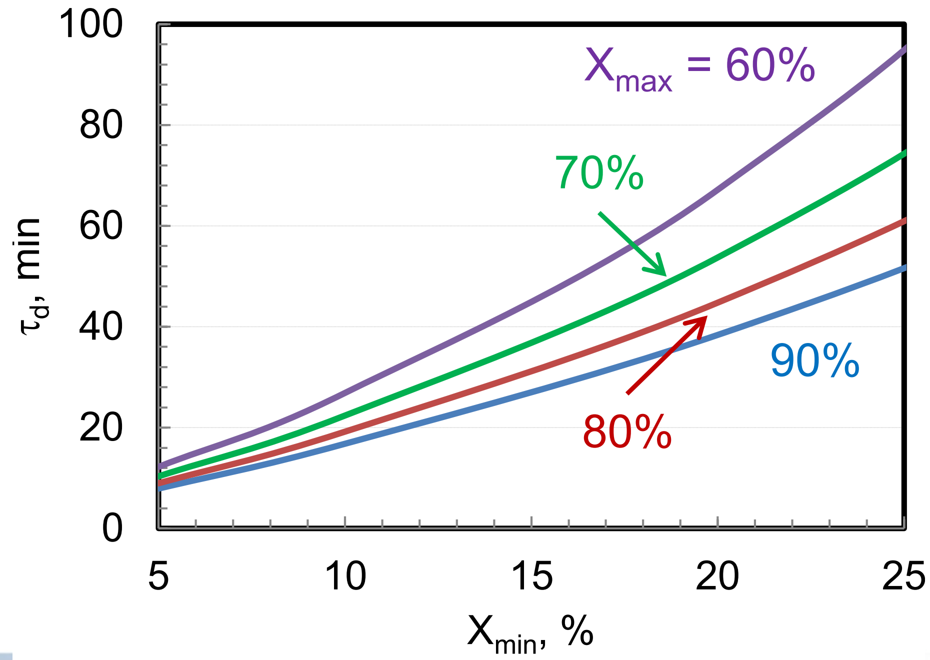




Discharge Kinetics Requirement

Usable storage capacity is related to 1) β: the intrinsic material capacity, 2) X_{min}: the minimum state-of-charge (SOC, 10% nominal), and 3) X_{max}: the maximum SOC (90% nominal)

- Minimum SOC (or maximum SOD) determined by the kinetic requirement that the bed should be able to supply the minimum full flow of H_2 (1.6 g/s)
- τ_d: Kinetic time for isothermal dehydriding from 100% SOC to X_{min} at the minimum FC stack coolant temperature (60°C), 5-atm back pressure

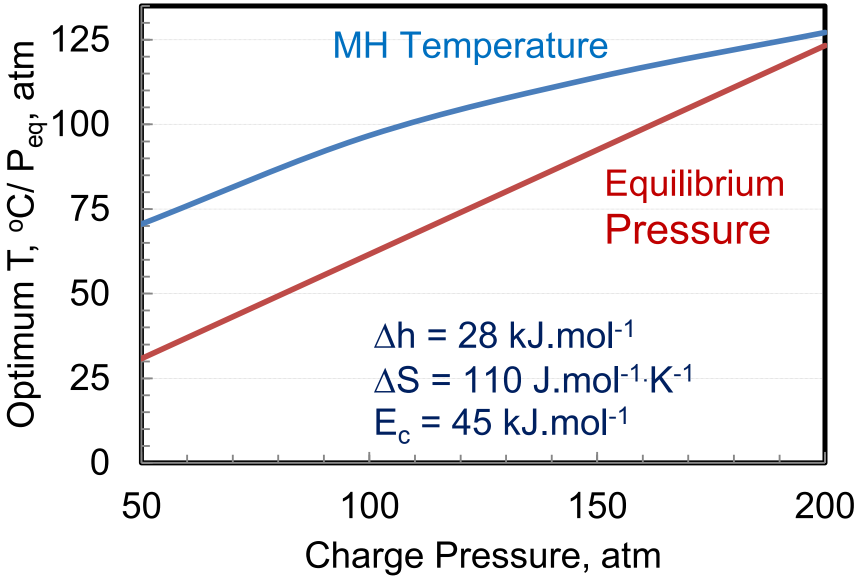


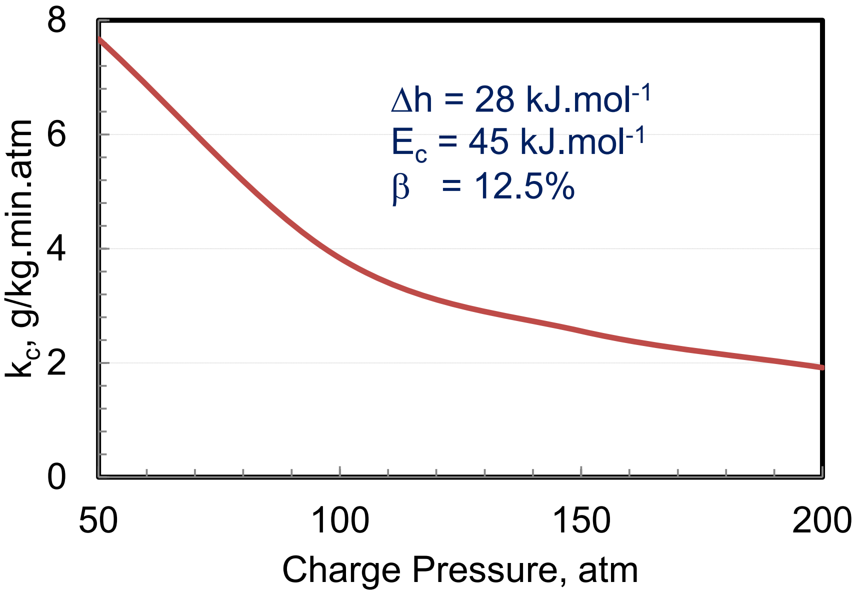
SOD: State of discharge; SOC: State of charge;

Charge Kinetics Requirement

The candidate MH must have sufficiently fast kinetics (and thermal conductivity) to permit complete refueling in 3.7 mins (τ_r).

- For given thermodynamics (Δh), activation energy (E_c) for charge kinetics, and charge pressure, there is an optimum temperature (T_{opt}) at which the charge rate is the fastest. The off-board coolant temperature should always be below T_{opt}.
- τ_c: Kinetic time for isothermal hydriding from X_{min} to X_{max} at T_{opt} and specified charge pressure, set to 50% of τ_r.

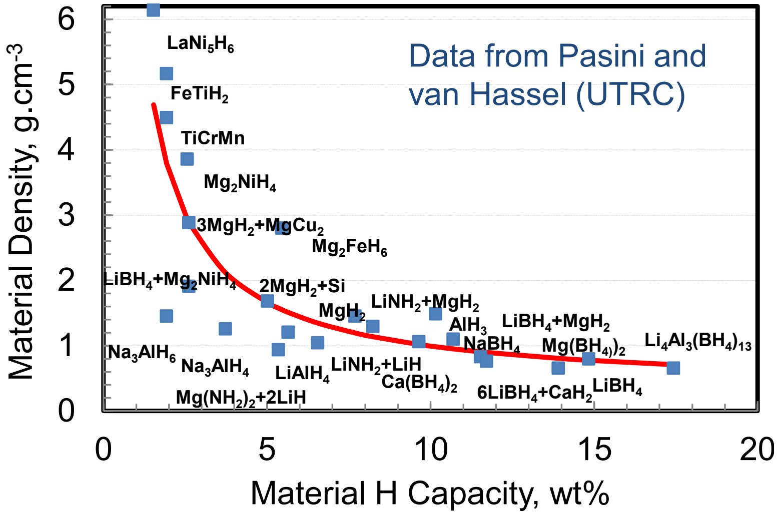


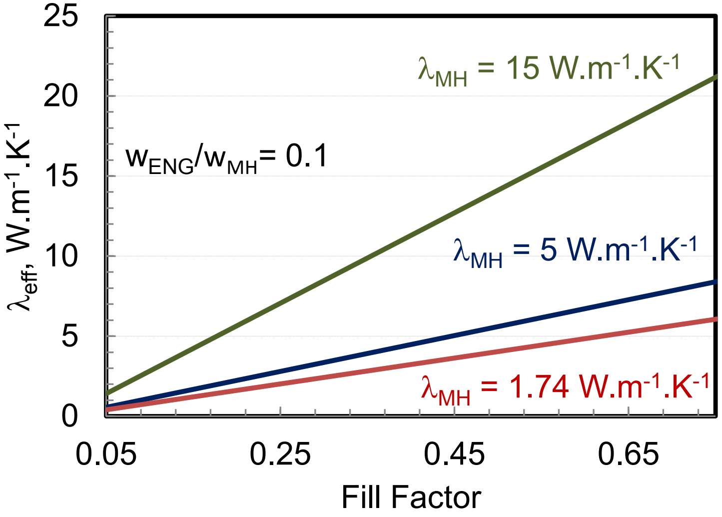


Heat Transfer Requirement

Expanded natural graphite and metal hydride compacts for conductivity enhancement and bulk density improvement

- Thermal conductivity (λ_{eff}) is a function of the graphite to MH powder weight ratio and the fill factor (ε), IJHE 2003
- Target ε determined by MH bulk density needed to satisfy the volumetric capacity
- Tube spacing determined by the required rate of heat removal during refueling (25 g/s) rather than heat supply during discharge (1.6 g/s)
- Charge/discharge kinetics also affected by λ_{eff} and ε


Data from Pasini and van Hassel (UTRC)

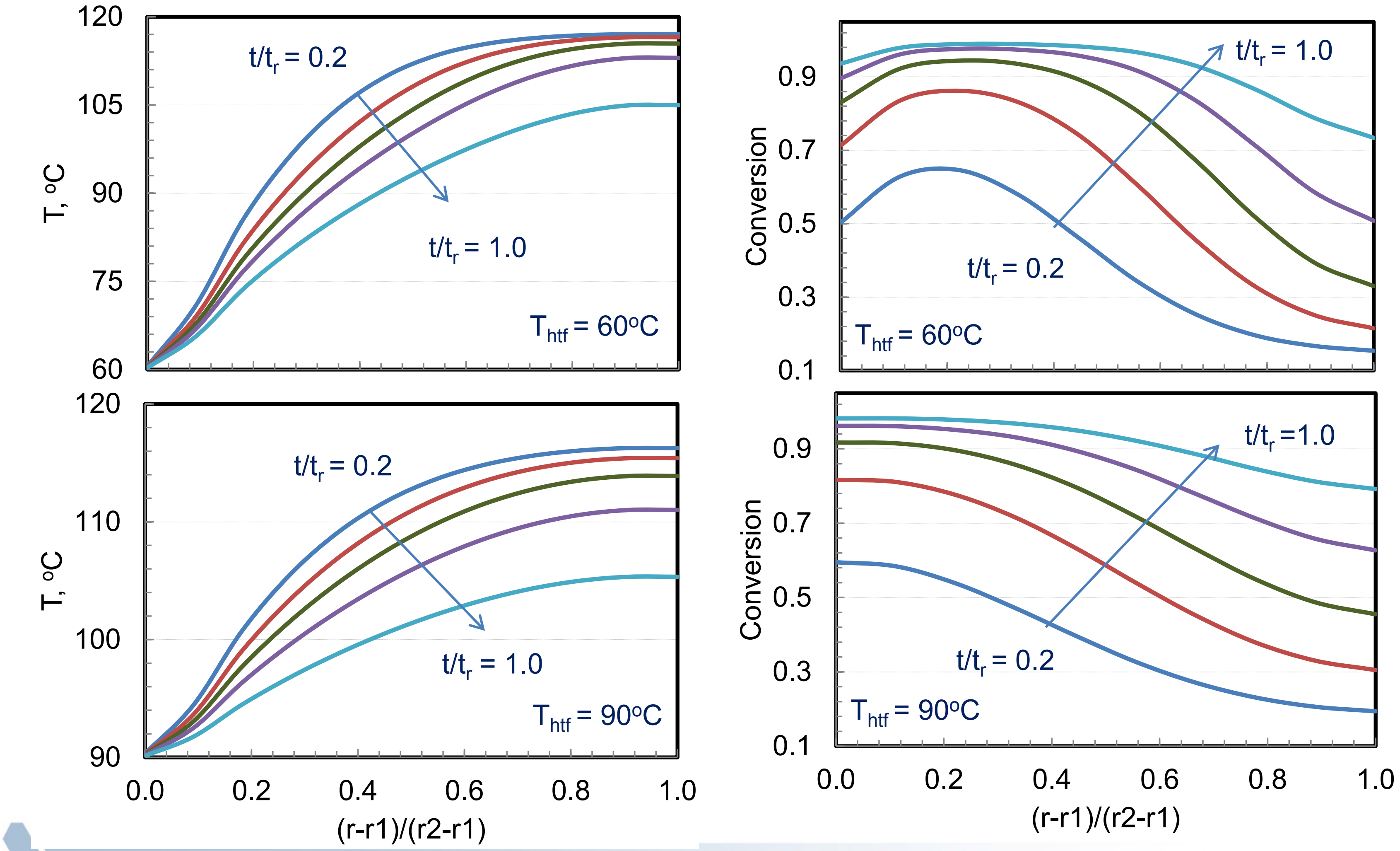


AR Sanchez, HP Klein, and M Groll, Int. J. Hydrogen Energy 28 (2003) 313-327

MH Refueling: Temperature Profiles and Conversion

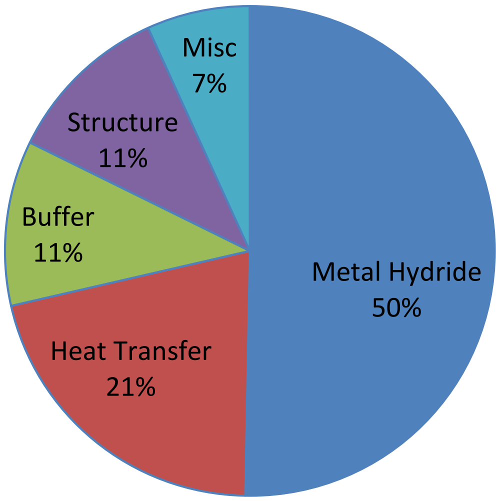
Dynamic finite-difference model for bed temperature and conversion

- MH outer periphery heats rapidly, approaches equilibrium T, then cools
- Highest conversion at or near the HX tubes

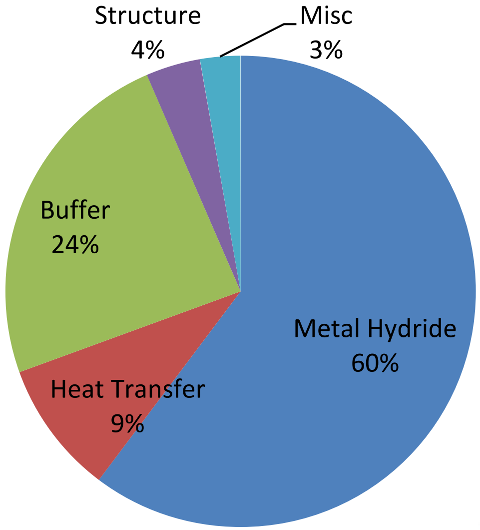


Reference MH Targets

Independent Variables	**Related Variables**	**Reference Values**	**Constraints**
MH Intrinsic Capacity		13.6% H capacity	5.5 wt% gravimetric capacity
Fill Ratio	Bulk Density	24.7% bed porosity	40 g/L volumetric capacity
	Thermal Conductivity	589 kg/m^3 MH bulk density	
		8.4 W/m.K bed conductivity	
Discharge Kinetics	X_{min} = 10%	τ_d = 16.8 min	1.6 g/s min full flow rate at 60°C, 5-atm back pressure
		τ_d = 67.2 min	25% of full flow rate at 20°C, 5-atm back pressure - Startup from -40°C
Charge Kinetics	X_{max} = 90%	k_c = 4.2 g/kg$_{MH}$/min/atm	Complete refueling in 3.7 mins - X_{min} to X_{max} in 1.85 min at T_{opt}, 100 atm
HX Tube Spacing	Number of HX Tubes	r_2/r_1 = 3.1	1.5 kg/min refueling rate
		85 U tubes	
Mass of MH	Mass of Expanded	51.2 kg MH	5.6 kg usable H_2
	Natural Graphite	5.1 kg ENG	
Buffer Tank Capacity	Weight of Al tank	11.1 kg buffer tank weight	Startup from -40°C
		33.7 L buffer tank volume	



Weight Distribution



Volume Distribution

FY2013 Collaborations

Compressed H_2	Applied Nanotech, Ford, Lincoln Composites, PNNL, SA
Metal Hydrides	HSECoE: SRNL, UTRC
Sorbents	HSECoE
Chemical Hydrogen	University of Orgeon (UO)
GHG Emissions	ANL (GREET)
Off-Board Spent Fuel Regeneration	SRNL, UH, UO
Off-Board Cost	ANL (H2A Group), ANL (HDSAM), SA
On-Board Cost	SA
SSAWG	DOE, HSECoE (PNNL, SRNL, UTRC), OEMs,Tank Manufactures, SA

– Argonne develops the storage system configuration, determines performance, identifies and sizes components, and provides this information to SA for manufacturing cost studies

Future Work

Physical Storage

- Propose and analyze methods of reducing carbon fiber (CF) content (doilies, end caps, winding angle) and cost of 700-bar storage tanks (SA collaboration)
- Validate results on CF reduction methods with laboratory data on coupons (advanced materials, Applied Nanotech collaboration)
- Validate finite element model against experimental and field data (collaboration with PNNL led project)

Material Based Storage

- Reverse engineering to establish material targets for higher-temperature metal hydrides that need on-board burner
- Reverse engineering to develop material targets for low-temperature sorbents that need off-board refrigeration
- Reverse engineering to develop material targets for chemical storage systems that require off-board regeneration
- Provide system analysis support (catalytic activity, reactor, operating conditions) to U Oregon effort to develop CBN heterocycle materials

Project Summary

Relevance:	Independent analysis to evaluate on-board and off-board performance of materials and systems
Approach:	Develop and validate physical, thermodynamic and kinetic models of processes in physical and material-based systems Address all aspects of on-board and off-board targets including capacities, rates and efficiencies
Progress:	Established baseline performance of 700 bar Type-4 storage tanks and systems: CF requirements, BOP components and layout, and gravimetric and volume capacities Analyzed methods to achieve 10-20% reduction in carbon fiber requirement: doilies, variable hoop angles, integrated end caps, increased stress ratio Developed a dynamic model for charge, discharge and start-up of a metal hydride bed and coupled it to a system analysis code Performed reverse engineering to determine material targets for metal hydrides: thermodynamics, intrinsic capacities, heat transfer, and charge and discharge kinetics
Collaborations:	SSAWG, HSECoE, Ford, PNNL, SA, U. Oregon
Future Work:	Propose, analyze and validate methods of reducing cost of CF wound storage tanks Reverse engineering to establish material targets for metal hydrides, sorbents, and chemical storage