

Systems Engineering of Chemical Hydrogen, Pressure Vessel, and Balance of Plant for On-Board Hydrogen Storage

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> DOE Fuel Cell Technology Program Annual Merit Review

Washington, DC May 15, 2012 Technology Development Managers: Ned Stetson and Jesse Adams



U.S. Department of Energy Energy Efficiency and Renewable Energy Bringing you a prosperous future where energy is clean, abundant, reliable, and affordable



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Project ID: ST005

Overview

Timeline

- Start: Feb. 2009
- Project End: Jan. 2014
 - End Phase 1: 2011
 - End Phase 2: 2013
 - End Phase 3: 2014
- Percent complete: 55%

Budget

- \$5.8M Total (PNNL) Program
 - DOE direct funded
 - No cost-share required for National Lab

United Technologies

Research Center

- FY12: \$895k
- FY11: \$960k



Barriers

- A. System Weight and Volume
- B. System Cost
- C. Efficiency
- D. Durability

Partners

GΜ

mber of Hexagon Composites G

- E. Charging / Discharging Rates
- G. Materials of Construction
- H. Balance of Plant (BOP) Components
- J. Thermal Management
- O. Hydrogen Boil-Off

BAS

S. By-Product/Spent Material Removal

National Renewable

HSM

Pacific No

Energy Laboratory Innovation for Our Energy Future

Relevance: Hydrogen Storage

Impact to FCT Program

- Demonstrate hydrogen storage system that meets DOE 2015 targets for light duty vehicles using chemical hydrogen storage
- Apply materials discoveries from the Materials Centers of Excellence
- Discover/develop engineering solutions to overcome material's deficiencies
- Identify minimal performance for materials to be applicable in engineered H₂ storage systems for light duty vehicles.
- Hydrogen Storage Community at Large
 - Develop and/or advance modeling and simulation tools for the optimum design and engineering of on-board storage systems
 - Provide functional prototype systems available to OEMs
 - Provide engineering methodologies, analysis tools, and designs applicable to stationary storage and portable power applications
 - Demonstrate on-board storage to advance state of the art.
 - Identify, develop and validate critical components either for performance, mass, volume, or cost.

Approach:

PNNL's Roles Supporting Engineering Center Structure

- Lead Technology Area (TAL) for Materials Operating Requirements
- Coordinate activities as the Technology Team Lead (TTL)
 - Bulk Materials Handling (Transport Phenomena)
 - Pressure Vessels (Enabling Technologies)
 - Manufacturing and Cost Analysis (Performance Analysis)
- Liaison to VT Program projects and resources
- Technical Objectives of PNNL Scope:
- Chemical Design chemical hydrogen H₂ storage system & BOP components Develop system models to predict mass, volume, performance
 - Reduce system volume and mass while optimizing storage capability, fueling and block are formed as a storage capability.
 - fueling and H₂ supply performance
 Mitigate materials incompatibility issues associated with H₂
 - embrittlement, corrosion and permeability

All Systems

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- Demonstrate the performance of economical, compact lightweight vessels for hybridized storage
- Guide design and technology down selection via cost modeling and manufacturing analysis
 - Perform value engineering of BOP to minimize cost, volume and mass
- Phased/ gated progressions aligning with HSECoE go/no-go decisions

FY12 Objectives

- Pressure Vessel
 - Exercise model to assess materials and design options
 - Optimize vessel design in terms of cost
 - Assess chemical compatibility of polymer liners
 - Assess vessel cost as function of pressure
- Chemical Hydrogen Storage Design
 - Validate models and concepts via experiments
 - Assess feasibility of liquid-slurry chemical hydrogen storage
 - Assess feasibility of heat exchanger
 - Assess feasibility of slurry use with heat exchanger, pump, valves.

Balance of Plant

- Maintain BOP library
- Size components (heat exchangers, valves, pumps,...)
- Determine material compatibility
- Identify where improvements can be made
- Cost Modeling

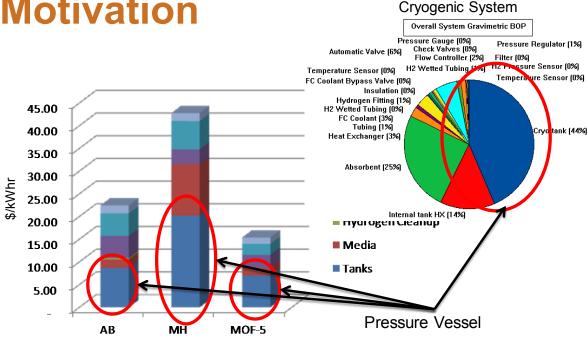


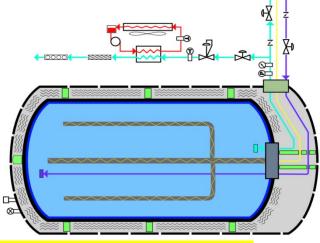
Accomplishments: Milestones FY12

Q3 🔵	Task 1	Complete Development of Simulink® AB Slurry Storage Model
Q4 🔘	Task 1	Report on sensitivity study to determine operating envelops for viscosity, heat of reaction, flocculation/setting.
Q4 •	Task 1	Report on feasibility to identify/develop a radiator/heat exchanger capable of cooling the effluent from ~525K to ~360K having a mass less than or equal to 1.15kg and a volume less than 10.9 liters
Q2 🔵	Task 2	Report on feasibility to achieve a 40 wt% AB slurry with viscosity <1500cp pre and post dehydrogenation with comparable kinetics.
Q3 🔵	Task 4	Report on feasibility to identify BoP materials suitable for the Chemical Hydrogen system to have a system mass no more than 41kg and a system volume no more than 57 liters
Q4 🔵	Task 4	Report on ability to identify Type IV tank liner materials suitable for 40K operation having a mass less than or equal to 8kg and a volume less than 3 liters (2.55mm thickness)
Q4 🔵	Task 4	Report on ability to identify BoP materials (excluding internal HX, external HX, and combustor) suitable for 60 bar cryogenic adsorbent system having mass less than 17 kg and a volume less than 18.5 liters.
Q1 🔵	Task 5	Update Cost Analysis for F2F8 Meeting.
Q2 🔵		Go/No-go assessment of endothermic vs exothermic materials (for the Engineering Center, not DOE)
Q3 🔵		Go/No-go assessment of liquid vs slurry

Pressure Vessel Motivation

- Vessel is high cost, high mass
- Initial work (FY10-11) based on 200-250 bar pressure vessel
 - Limited to Type III
- Partners found lower pressure options
- New work (FY12) examine trade-off in pressure and volume for optimized gravimetrics
 - Expand tank types to include Type I and Type IV





Pressure vessel improvement needed to Achieve Mass and Cost Targets

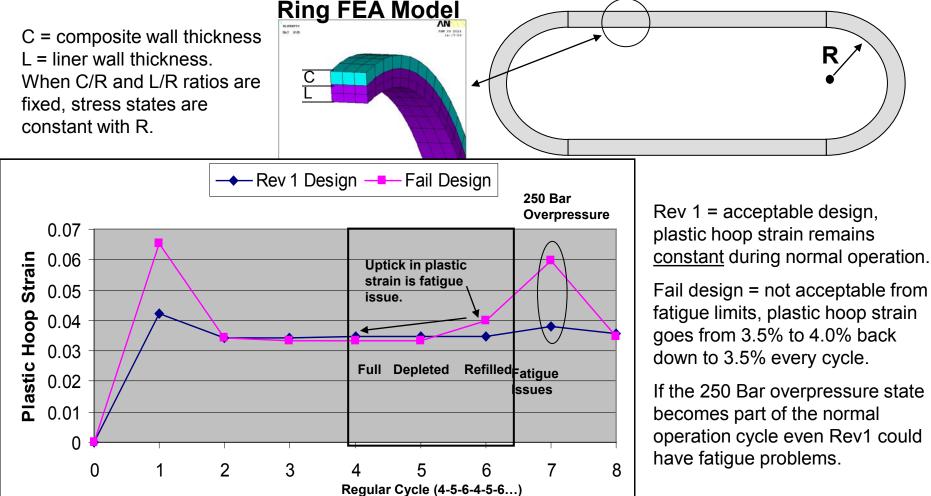


Different Pressure Vessel Types

	Pro	Challenges
Type I - all metal pressure vessel	 Low outgassing (Limited to hydrogen) Lower cost 	 Higher mass compared to Type IV Tank fabrication limitations with aluminum
Type II - metal with overwrap cylinder section	 Reduced liner thickness at low pressures 	 Large mass penalties at high pressure
Type III - metal lined, composite overwrap	 Previously demonstrated 	Fatigue life challenges
Type IV – polymer lined composite overwrap	 Lightweight 	Not demonstratedHigher Cost



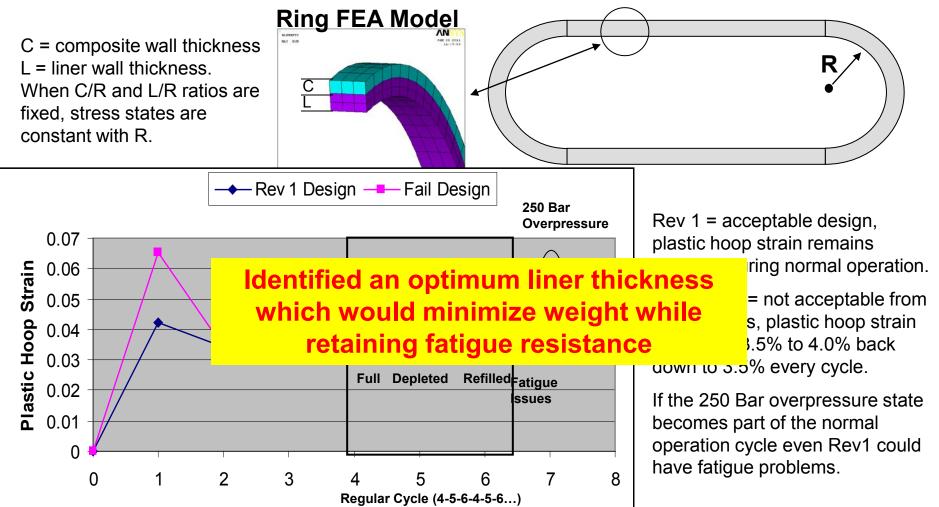
Accomplishments: Type III Wall Cylinder FEA for Tank Thickness



200L, 200 Bar Cryo (77-120K) Fail design 7.5mm liner, 7.2 mm shell Rev 1 design 9.0mm liner, 7.2mm shell



Accomplishments: Type III Wall Cylinder FEA for Tank Thickness



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200L, 200 Bar Cryo (77-120K) Fail design 7.5mm liner, 7.2 mm shell Rev 1 design 9.0mm liner, 7.2mm shell

Accomplishments: Cryogenic Test Plan for Polymer Liner Material (Type IV Vessel)

Can we use a type IV tank in cryogenic conditions?

- Cryogenic dewar setup on large load frame
 - Grip design changes
- > H₂ Permeation (Lincoln)
- Fensile
- Fatigue
- Weld strength (Lincoln to weld)
- Impact (Lincoln)
- Coefficient of Thermal Expansion
- Dynamic Mechanical Analysis

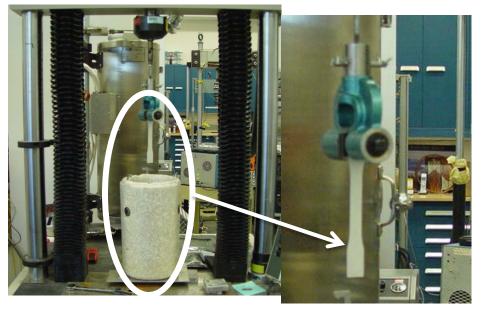
Materials

- HDPE Completed
- ≻ Kynar[®] Completed
 - Homopolymer
 - Copolymer
- > Halar[®] Completed,
- ➢ Kel F[®]
- Polytetrafluoroethylene
- > Nylon
- Ethylene Vinyl alcohol

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- Others
- Wound composite

Accomplishments: Cryogenic Test of Liner Materials

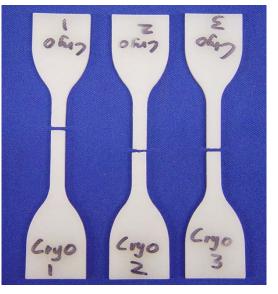




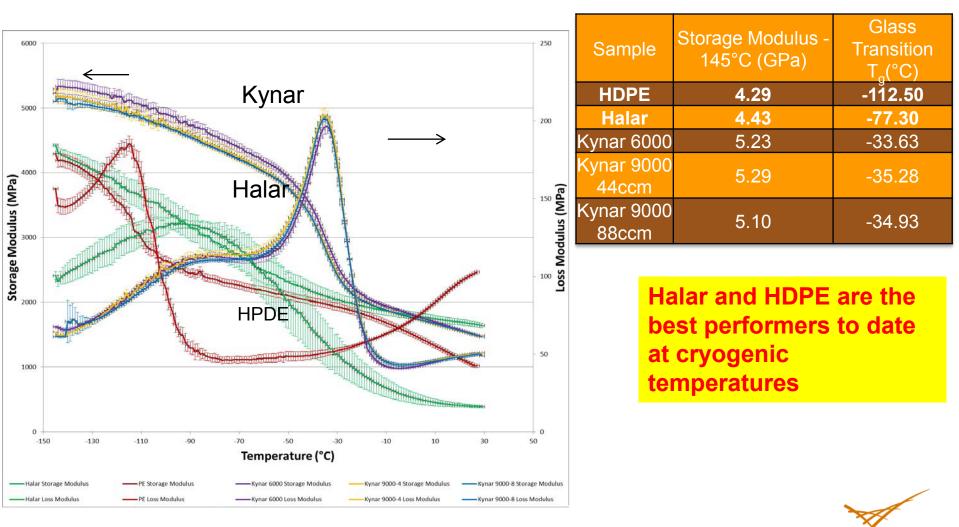
Halar Room Temp. TS: 42 MPa Modulus: 1.6 GPa Elongation: 20%



Halar in Liquid N₂ TS: 143 MPa Modulus: 4.4 GPa Elongation: 4.5%



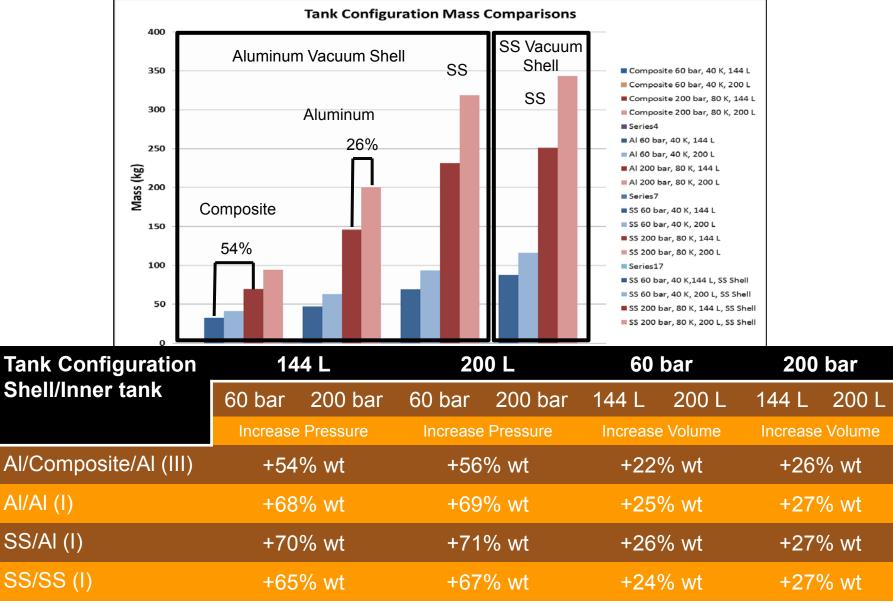
Accomplishments: Dynamic Mechanical Analysis for Type IV Liner Materials



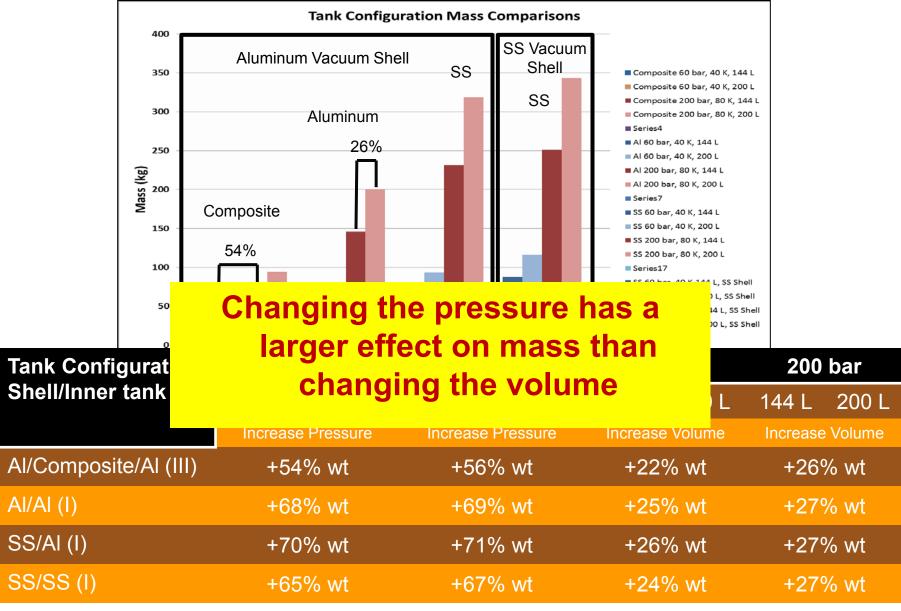
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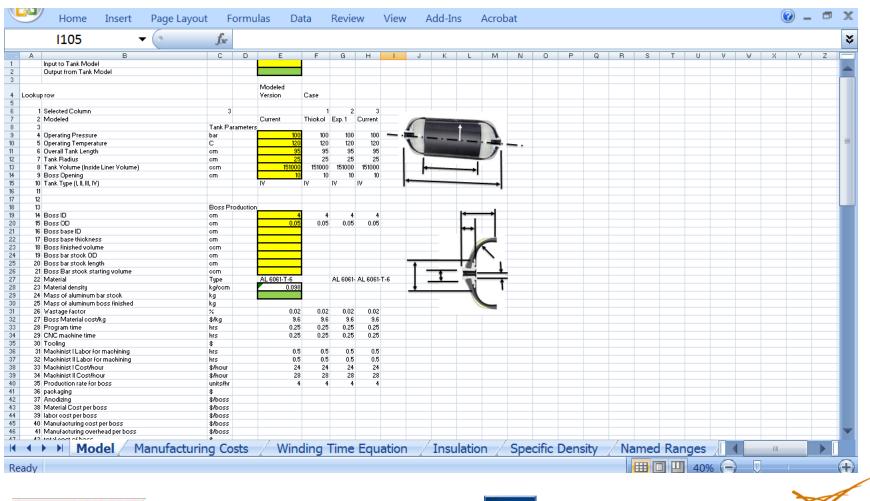
Accomplishments: Sensitivity of Tank Type Mass <u>Relative to Pressure and Volum</u>e



Accomplishments: Sensitivity of Tank Type Mass <u>Relative to Pressure and Volum</u>e



Pressure Vessel Next Step- Combine predictive models with cost models













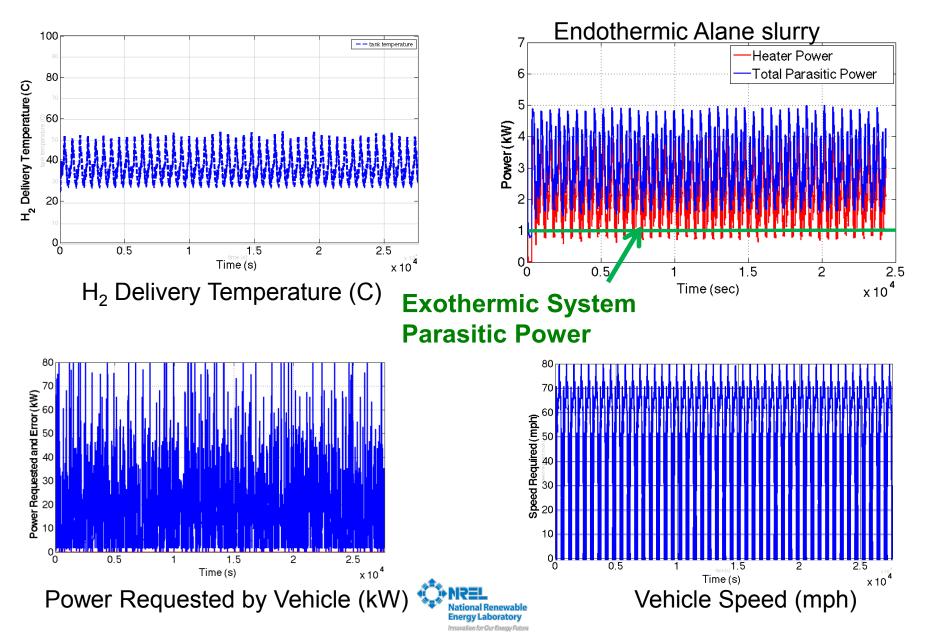
Chemical Hydrogen Storage Development

Modeling and Validation

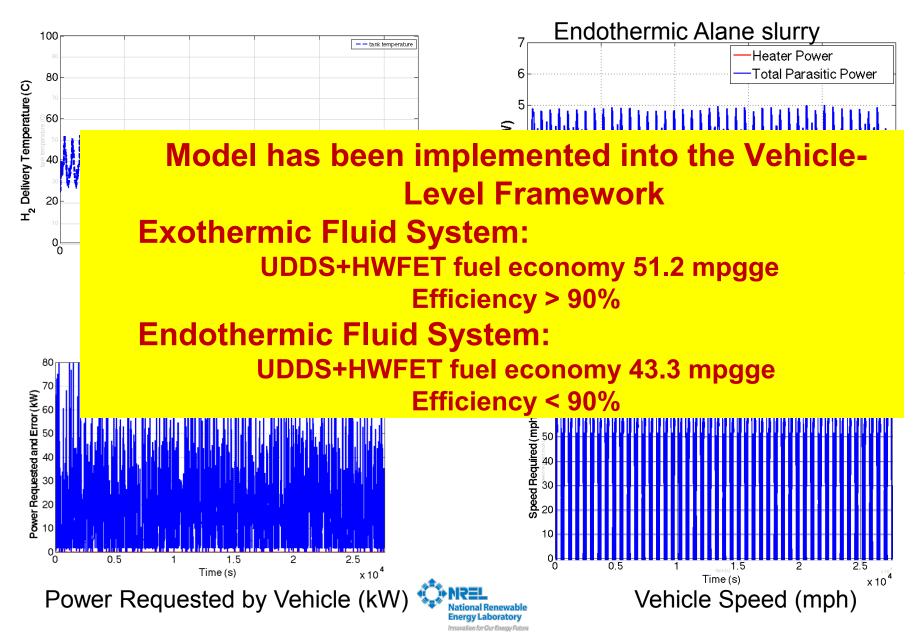
- Operational envelope
- Validation (Reviewer section)
 - Radiator/Heat Exchanger
 - 50% reduction in mass/volume from baseline
 - Validation underway
 - Pump
 - 44% reduction in mass from baseline
 - Validation underway
 - Displacement volume tank FY13
- Liquid-Slurry development
 - Endothermic liquid-slurry: Alane surrogate leverage BNL's work
 - Exothermic liquid-slurry: Ammonia borane surrogate



Accomplishments: Chemical Hydrogen Storage Results of US06 Drive Cycle in Framework

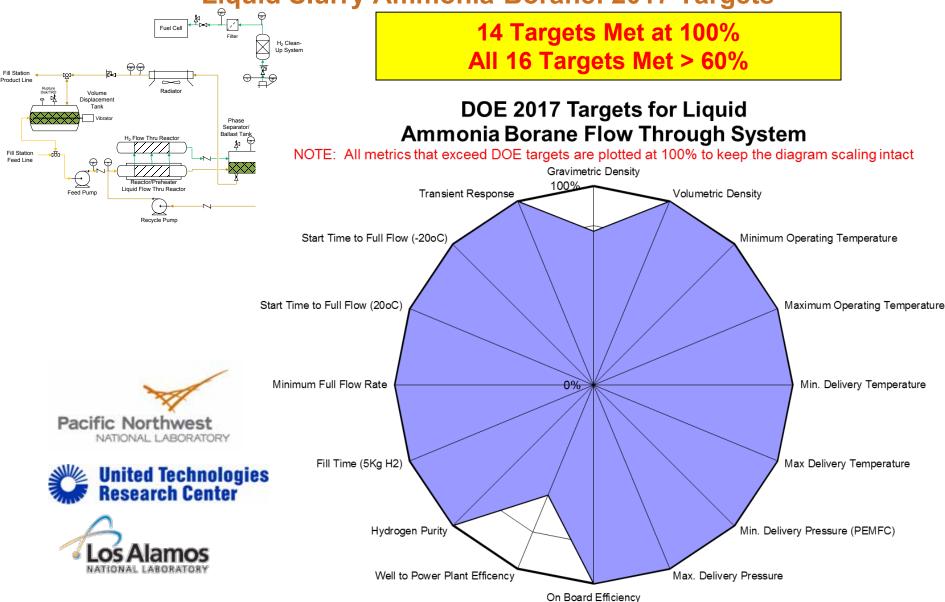


Accomplishments: Chemical Hydrogen Storage Results of US06 Drive Cycle in Framework



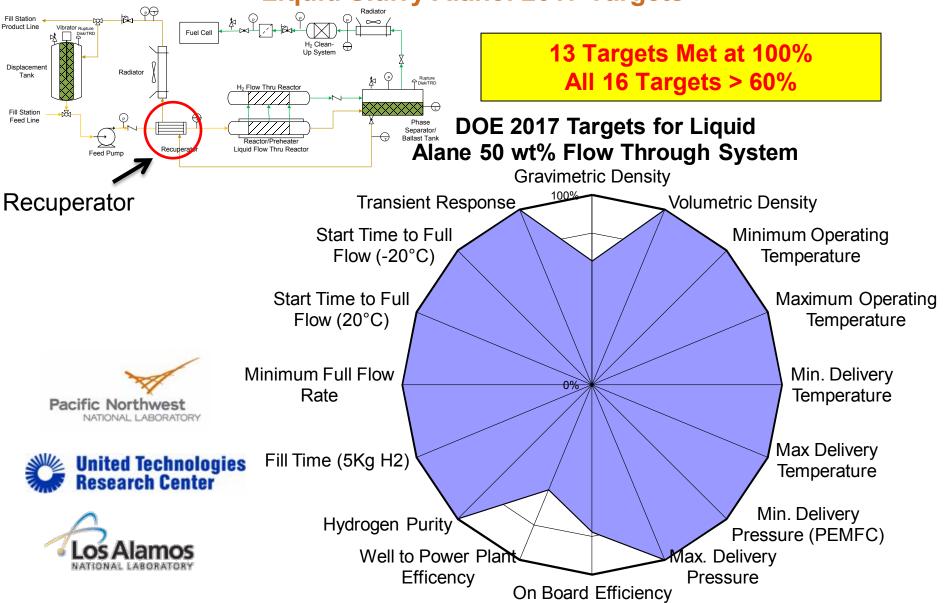
Accomplishments: Exothermic Chemical Hydrogen System

Liquid Slurry Ammonia-Borane: 2017 Targets

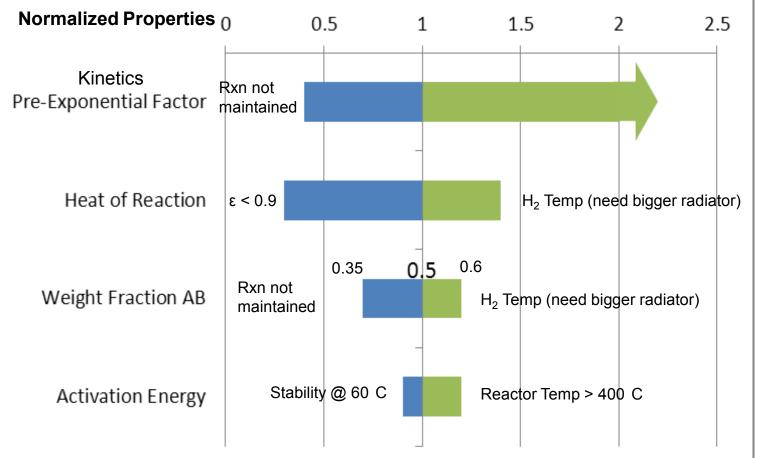


Accomplishments: Endothermic Chemical Hydrogen System (Alane)

Liquid Slurry Alane: 2017 Targets



Accomplishment: Sensitivity Analysis Tornado Chart "Operability Envelope"-Example Exothermic Chemical Hydrogen



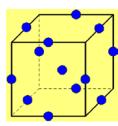
Assumes no changes to the design







Accomplishments: Box-Behnken Type Sensitivity Analysis Example Endothermic CH (Alane)



Normalized to Alane Properities			Reactor	US06 On-Board	Fraction of DOE
Kinetics	Heat of Reaction	Alane Wt%	Length (m)	Efficiency	Mass Target
1	0.5	70	1.83	91%	78%
1	0.5	50	1.83	91%	63%
1	0.75	70	1.83	89%	78%
1	0.75	50	1.83	89%	63%
1	1	50	1.83	87%	63%
1	1	70	1.83	87%	78%
10	0.5	70	1.83	92%	78%
10	0.5	50	1.83	92%	63%
10	0.75	70	1.83	89%	78%
10	0.75	50	1.83	89%	63%
10	1	50	1.83	87%	63%
10	1	70	1.83	87%	78%

 \wedge Alane Wt% $\rightarrow \downarrow$ System Mass

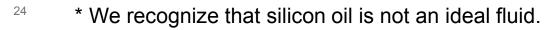


 $\downarrow \Delta Hrxn \rightarrow \uparrow Efficiency$



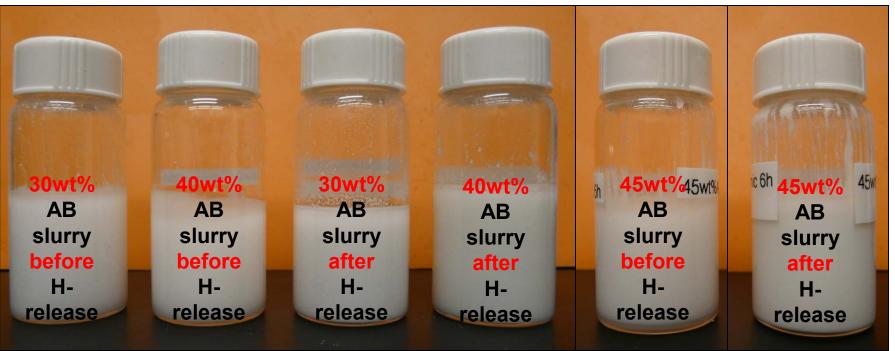
Accomplishments: Exothermic Liquid-Slurry Development (AB Slurry)

- Evaluated
 - 4 candidate carrier liquids
 - 6 additives
 - 7 synthesis techniques
- Results
 - Achieved 45 wt% AB in silicon oil¹ (>7 wt% H₂)
 - Synthesis Sieve followed by sonication
 - Settling/flocculation evaluated
 - Viscosity measurements completed
 - Kinetics verified
 - Discontinued
 - 3 carrier liquids
 - 3 additives
 - 6 synthesis technique





Accomplishments: Liquid Slurry



Material remains a liquid-slurry before and after release Fresh slurry no settling/flocculation for 3+ months Spent slurry settling within several hours



~600cP Viscosity of AB Slurry (45wt%) Before & After H-release



Anton Paar MCR301 rheometer with a bob/cup set-up

	AB slurry before H-release	AB slurry after H-release	Measured Temp. (°C)
Plastic viscosity (cP)	~ 617	~ 442	25
Yield stress (Pa)	~ 48	~ 3.7	25

Experimental conditions & Key results:

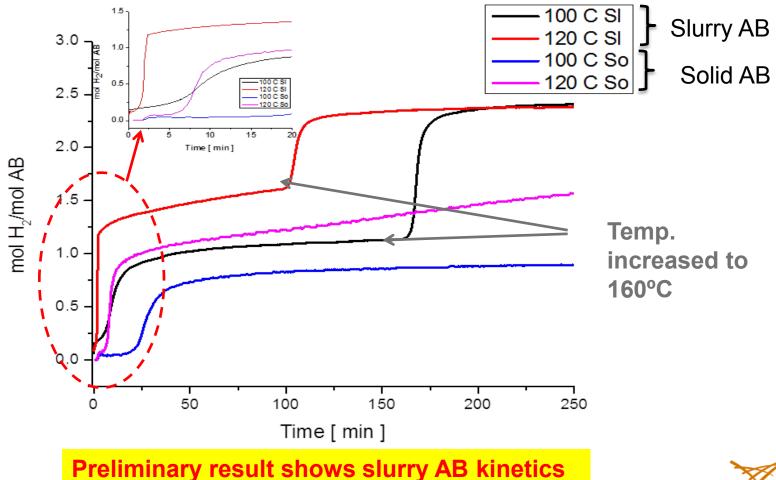
- Measuring the shear stress (τ) in the range of 0-1000 1/sec shear rate ($\dot{\gamma}$)
- Basic rheological model

 $au = au_y + \eta_p \dot{\gamma}$ (Bingham model with a yield stress au_y and plastic viscosity η_p)

- AB slurry (40wt%) before H-release & decomposed AB slurry (settled down → re-stirring) used for viscometer
- Decomposed AB less viscous (~442 cP) than fresh AB slurry (~617 cP)

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Accomplishments: Dehydrogenation Kinetics of Slurry AB Comparable to Solid AB



similar to solid AB with 2.5 equivalent of hydrogen release, but, no induction period



Collaborative Activities

Hydrogen Storage Engineering Center of Excellence	 Lincoln Composites - study of CF cost and pressure vessel design modeling GM - design of structured media bed for MH Ford - characterization of absorbent materials UQTR - design and materials characterization of carbon absorbent OSU - microarchetecture device concept development and thermodynamic analysis UTRC - develop solutions for H₂ impurities filtering LANL - AB system design and measure H₂ impurities NREL - input for tank to wheels analysis and system cost models SRNL - study AB reactivity and kinetics model development
SSAWG	Participate in group discussions and analysis
Materials 'Reactivity' Program	 Khalil (UTRC) and Anton (SRNL) - understand reactivity properties of AB Van Hassel (UTRC) - study impurities in H₂
Independent Analysis	 TIAX - provide design details for AB refueling cost and feasibility assessment, plus share cost parameters for system cost modeling

Future Work: FY13

Chemical Hydrogen System

- Detailed Design, Engineering
 and Analysis
 - Complete sensitivity analysis
 - Viscosity
 - Settling/flocculation
 - Vapor pressure
 - Thermal stability...
- Validate Critical Components
- Complete Solid-Liquid Slurry Development
 - Composition
 - Additives

BOP, Pressure Vessel and Cost Analysis

- Value Engineering
 - Examine BOP volume/mass tradeoffs
- Pressure Vessel Engineering
 - Reduce cost, mass
 - Maintain safety
 - Materials Compatibility/ Reactivity
 - Finalize H₂ wetted material compatibility in components
 - Determine BOP and pressure vessel materials compatibility
- Cost Analysis
 - Work with partners, vendors on reducing cost
 - Update analysis with detailed design

Summary

Pressure Vessels

- Completed the HSECoE tank needs survey for bench top tank production
- Modeled various cases of type I, III, and IV tanks of pressure and temperature
- Fested of type IV liner materials at cryogenic temperatures
- Evaluated mass comparisons between type I, III, and IV
- Cost Analysis

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- > Updated MOF 5
- Cost analysis being combined with vessel design models
- Chemical Hydrogen System BOP
 - Identified key components to reduce mass / volume for pump, radiator (Heat exchanger)
 - Validation of performance initiated
- Chemical Hydrogen System Modeling and Validation Exothermic Slurry (Ammonia Borane as surrogate)
 - Modeled fraction AB critical to meeting DOE mass target
 - > 45 wt% AB slurry demonstrated- Slurry pre and post H₂ release

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Summarv

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- Chemical Hydrogen System Modeling and Validation Exothermic Slurry (Ammonia Borane as surrogate – cont.)
 - Increased ΔH_{rxn} or fraction AB results in T_{H2} outlet excesses (with current design)
 - > 150% of ΔH_{rxn} and 70 wt% AB system T_{H2} > 85°C
 - > 50 wt% AB and a range of kinetics met all targets
 - On-Board Efficiency target can be met with > 8 cold-starts/day
- Chemical Hydrogen System Modeling and Validation Endothermic Slurry (Alane as surrogate)
 - Alane cannot meet DOE targets for mass for the system specified and conditions evaluated
 - Performed regression analysis on results
 - > System Mass is dominated by weight fraction alane
 - Can meet DOE target with current BOP at 0.82 weight fraction alane
 - System Efficiency improved with reduced heat of reaction
 - System On-Board Efficiency of 90% possible with US06 if $\Delta H_{rxn}/2$
 - System On-Board Efficiency of 90% possible with Cold FTP if $\Delta H_{rxn} = 0$
 - Kinetics has little effect on the system efficiency or mass (reactor small fraction of total system mass—most is alane itself)

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With multiple start-ups the DOE on-board efficiency target difficult to achieve



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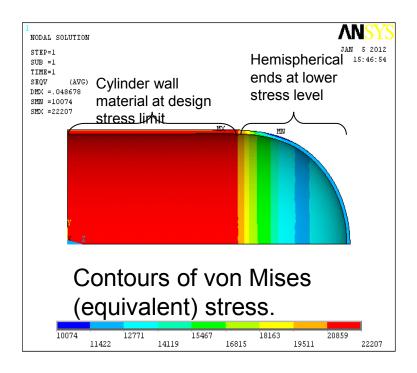
Don Anton – HSECoE, Director Ned Stetson – DOE EERE, Technology Development Manager Jesse Adams – DOE EERE, Technology Development Manager



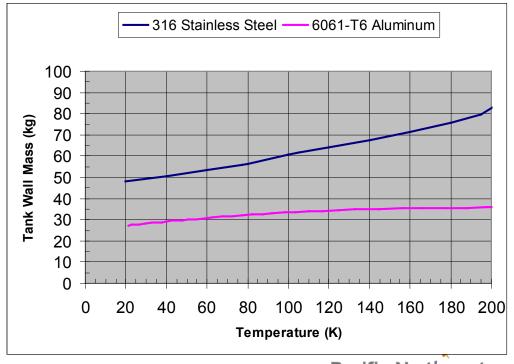
Technical Back-up Slides



Accomplishments: Modeling of Type I Pressure Vessel



Pressure 60 bar Temperature = 40K – 120K R=202.3mm (internal) L/D=3 (external) Storage Capacity = ~144L (varies slightly, 142.6-144.8L) Wall Thickness = 0.15-0.24" (steel), 0.25-0.34" (aluminum)



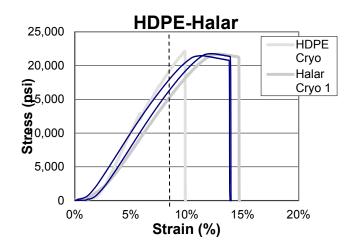
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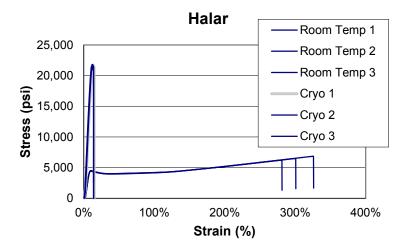
Accomplishments: Type IV Pressure Vessel Data

- 200L Capacity, 200 Bar 80K-160K
 - Comparable to Type III designs
 - 180K, 250 Bar overpressure is peak stress/strain state
- 144L Capacity, 60 Bar, 40-120K Temperature Range
 - All cases hit the minimum 3 layer composite limit
 - Larger diameter would be a more effective use of material
 - HDPE liner (assume no load carry)

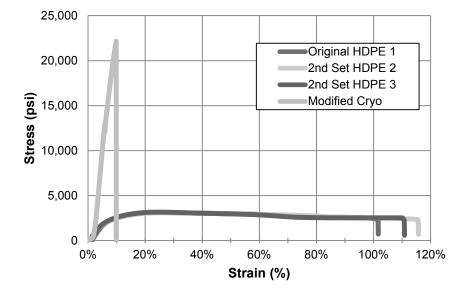
60 Bar	, 144 L	60 Bar	; 144 L	200 Ba	r, 200 L
300		4(00	50	00
3 mm	6 mm	3 mm	6 mm	3 mm	6 mm
14.9	21.1	11.8	16.6	26.5	32.2
5.7	11.5	4.5	9.1	5.1	10.3
9.2	9.6	7.3	7.5	21.5	21.9
	3(3 mm 14.9 5.7	3 mm6 mm14.921.15.711.5	300 40 3 mm 6 mm 3 mm 14.9 21.1 11.8 5.7 11.5 4.5	300 400 3 mm 6 mm 3 mm 6 mm 14.9 21.1 11.8 16.6 5.7 11.5 4.5 9.1	300 400 50 3 mm 6 mm 3 mm 6 mm 3 mm 14.9 21.1 11.8 16.6 26.5 5.7 11.5 4.5 9.1 5.1

Accomplishments: Cryogenic Material Testing for Type IV Pressure Vessels



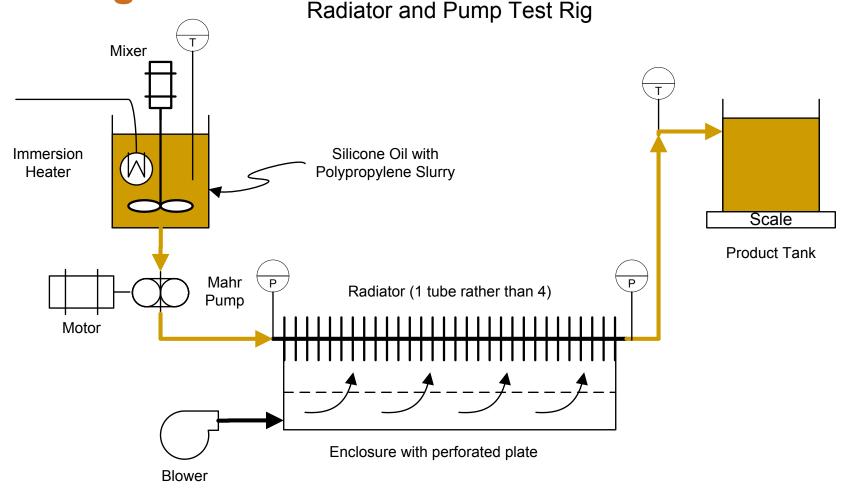


High Density Polyethylene





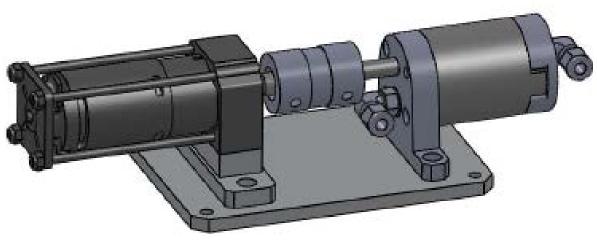
Chemical Hydrogen Component Validation Testing Plan





Accomplishments: Chemical Hydrogen System Identified Components (Pump)

Feed Pump	Requirements	Actual Mahr TC-1251 Round Pump
Viscosity	≤1500 cp	≤ 50,000 cp
Pressure	20 bar	≤ 65 bar
Flow rate	1 Liter/minute	1.2 Liter/minute
Weight	≤ 3 kg	2.5 kg (includes pump, motor, couplings etc).
Volume	≤ 0.77 Liter	1.5 Liter



This is a ~44% reduction in mass from baseline



Accomplishments: Chemical Hydrogen System Identified Components (HX)

HX	Requirements	Actual Energy Transfer MDE
Outlet temperature For US06 and SC03 Hot Cycle	< 60°C	
Fluid: AB/IL 50/50 or AB slurry in silicone oil		
Weight	≤ 1.15 kg	1.32 kg + 1.0 kg for fan
Volume	≤ 10.9 Liter	1.3 Liter+ 5.9 Liter for fan



This is a ~60% reduction in mass and ~50% reduction in volume from baseline

