Hydrogen Storage Engineering
CENTER OF EXCELLENCE

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

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Technology Development Managers: Ned Stetson and Jesse Adams

U.S. Department of Energy
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Project ID: ST005

Overview

- **Timeline**
  - Start: Feb. 2009
  - Project End: Sept. 2015
    - End Phase 1: 2011
    - End Phase 2: 2013
    - End Phase 3: 2015
  - Percent complete: 80%

- **Budget**
  - FY13 DOE Funding: $700k
  - Planned FY14 DOE Funding: $600k
  - Total DOE Project Funding: $5.5M
    - DOE direct funded
    - No cost-share required for National Lab

- **Barriers**
  - A. System Weight and Volume
  - B. System Cost
  - C. Efficiency
  - D. Durability
  - E. Charging / Discharging Rates
  - G. Materials of Construction
  - H. Balance of Plant (BOP) Components
  - J. Thermal Management
  - O. Hydrogen Boil-Off
  - S. By-Product/Spent Material Removal

- **Partners**

Relevance: Overall Impacts

- Impact to FCT Program
  - Apply materials discoveries from the Materials Centers of Excellence
  - Develop engineering solutions to overcome material's deficiencies
  - Identify, develop and validate critical components either for performance, mass, volume, or cost.
  - Develop hydrogen storage systems that meets DOE 2017 targets for light duty vehicles based on adsorbents and chemical hydrogen storage materials
- Impact to Hydrogen Storage Community at Large
  - Develop models and simulation tools to predict the performance of materials that would be acceptable in engineered H_2 storage systems for light duty vehicles.
  - Provide engineering methodologies, analysis tools, and designs applicable to stationary storage and portable power applications
  - Advance state of the art by demonstrating on-board storage.

Relevance: Barriers Addressed This Reporting Period

- **A. System Weight and Volume**
  - Updated system models to calculate the system mass and volume for trade-off studies
- **B. System Cost**
  - Developed cost model for alane storage system and performed a sensitivity analysis to determine critical costs
  - Laid out a manufacturing approach for elevated design consolidated component in preparation for developing a cost model
- **C. Efficiency**
  - Designed and modeled a recuperator for the alane system to improve on-board efficiency
- **E. Charging / Discharging Rates**
  - Developed and performed testing on thermos bottle concept to increase charging rate
- **H. Balance of Plant (BOP) Components**
  - Designed consolidated BOP component for adsorbent system to minimize its mass and volume
- **J. Thermal Management**
  - Performed validation testing of the ammonia borane reactor to determine the temperature rise from the exothermic reaction

Approach:

- PNNL's Roles Supporting Engineering Center Structure
  - Technology Area Lead (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 Hydrogen
  - **Design** chemical hydrogen H_2 storage **system**
  - Develop **system models** to predict mass, volume, performance

Adsorbents
  - Perform value engineering of BOP to minimize cost, volume and mass
  - Develop creative approaches to **refueling and dormancy**
  - Demonstrate the performance of economical, compact, and lightweight **vessels** for hybridized storage

Both Systems
  - Mitigate materials incompatibility issues associated with H_2 embrittlement, corrosion and permeability
  - Guide design and technology down selection via **cost modeling** and **manufacturing analysis**
  - **Reduce system volume and mass** while optimizing storage capability, fueling and H_2 supply performance

Approach for Previous Work (FY12-13)

- Chemical Hydrogen Storage Design
  - Develop system models
  - Scale-up slurry production
  - Assess feasibility of liquid-slurry chemical hydrogen storage
  - Assess feasibility of volume-exchange tank
  - Assess feasibility of slurry use with heat exchanger, pump, valves.
- Pressure Vessel for Cryo-Adsorbent Hydrogen Storage
  - Exercise “tankinator” model to assess materials and design options for type I, III, and IV vessels
  - Optimize vessel design in terms of cost
  - Assess vessel cost as function of pressure and temperature
- Balance of Plant
  - Maintain BOP library
  - Size components (heat exchangers, valves, pumps,…)
  - Determine material compatibility
  - Identify where improvements can be made
- Cost Modeling

Changes in Approach for Chemical Hydrogen in FY13

- No-Go Decision made for Chemical Hydrogen Storage Materials in June 2013
  - No near term material that can meet the off-board efficiency and cost targets
  - Difficulty in handling slurries
  - Chemical Hydrogen materials not to continue into Phase 3
- New Scope for Chemical Hydrogen Storage Materials
  - Complete remaining experimental work to validate reactor model
  - Finish cost modeling for alane
  - Finalize and publish system models
  - Prepare final chemical hydrogen storage report
- Continued Scope for Adsorbent Storage Materials

Accomplishments: Milestones

FY13 Q3	**Task 3**	Complete the materials database from components in the SA designs
FY13 Q4	**Task 5**	Update Cost Analysis for Chemical Hydrogen Storage Materials (Alane)
FY14 Q1	**Task 1**	Deliver up to 2L of slurry AB (1 L 50 wt% AB, 1 L 35 wt% AB slurry)
FY14 Q2	**Task 4**	Complete experimental work to validate the thermos bottle concept and provide input into the design of the 2 liter thermos bottle prototype.
FY14 Q3	**Task 2**	Document and provide to SRNL for posting one exothermic and one endothermic chemical hydrogen storage model.
FY14 Q3	**Task 4**	Submit Chemical Hydrogen Storage Engineering Center of Excellence Report to DOE.
FY14 Q4	**Task 4**	Design a 2L scale thermos bottle concept tank with the LN2 cooling that meets the DoE technical targets for refilling
FY14 Q4	**Task 5**	Update Cost Analysis for Adsorbent Materials

= complete
= on schedule
= at risk
= behind

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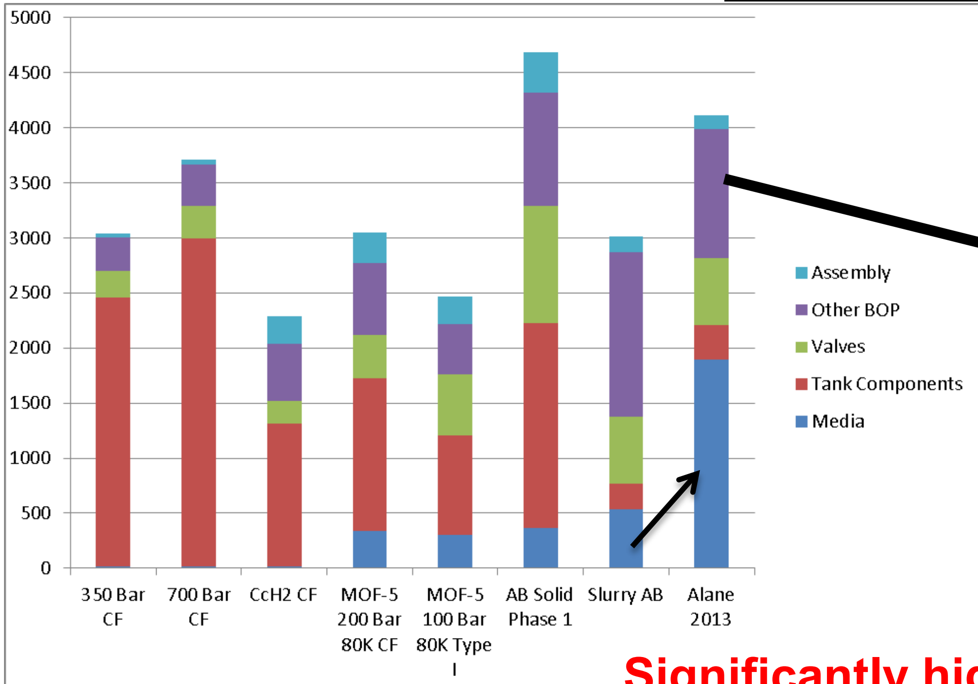
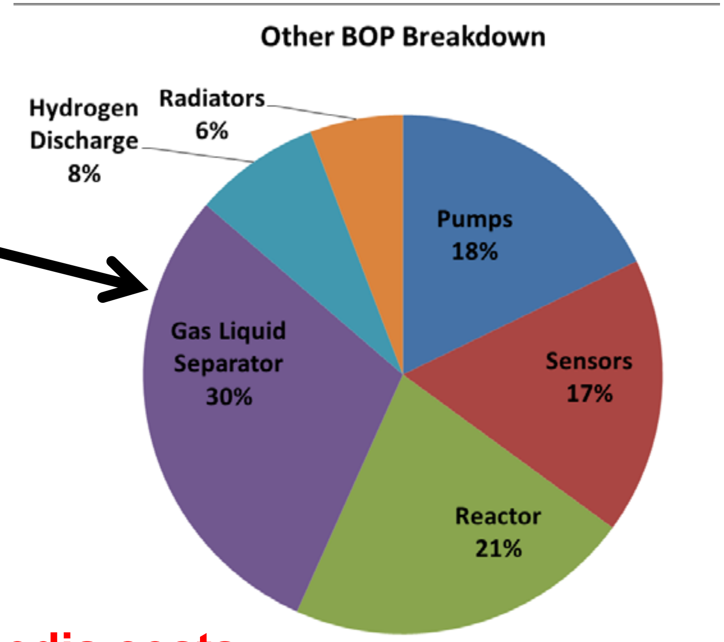
Cost Analysis of Alane-Based System

- Approach based on AB system costs
  - Removed ammonia and borazine clean up
  - More silicon oil and media than AB
  - Added recuperator
- Scale up number of units

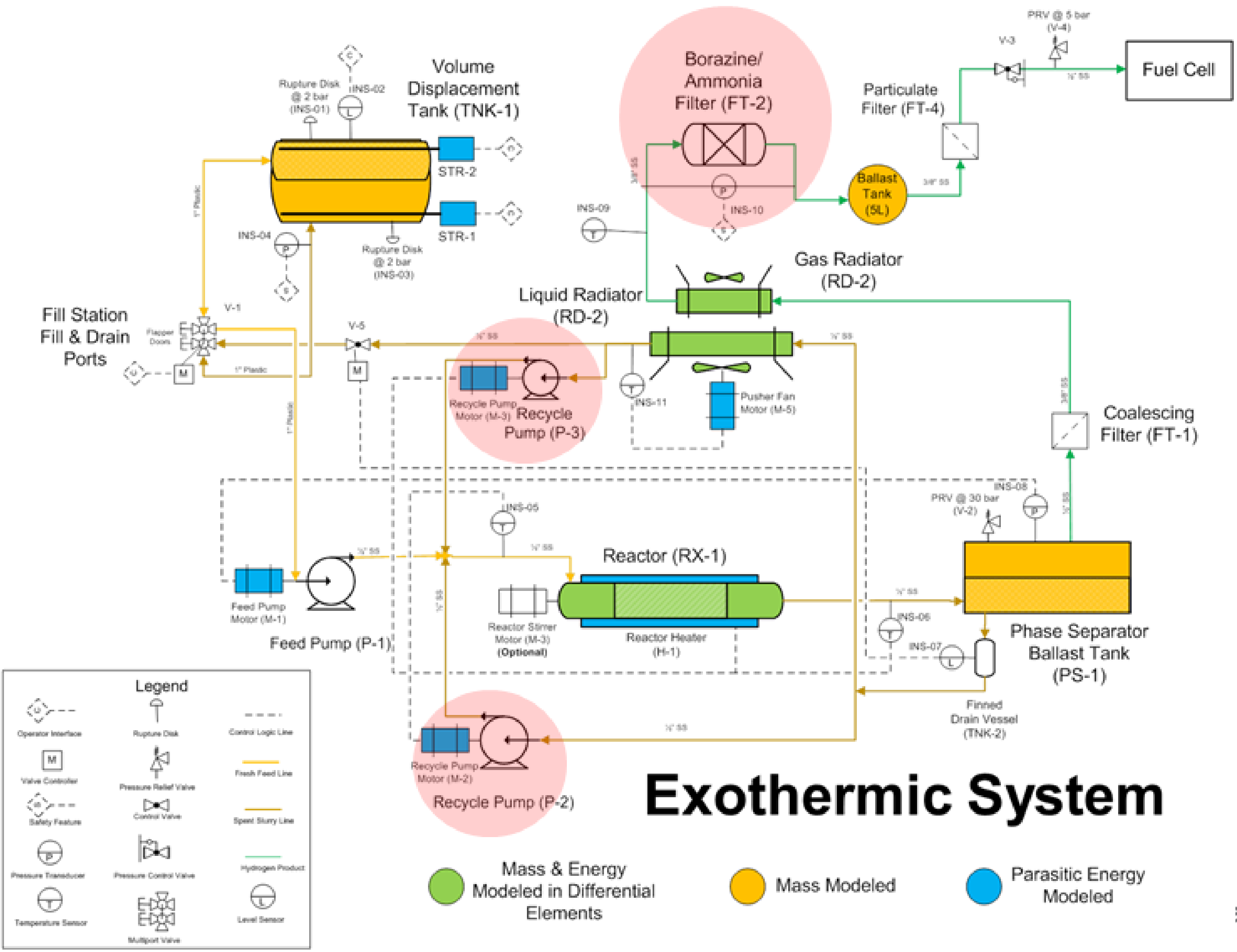
Item \ # of units	10,000	30,000	80,000	130,000	500,000
	$/Systems				
Media	11,732	6,989	4,424	3,535	1,909
Tank	472	412	370	352	311
Feed Loop	1,399	1,127	951	879	721
Return Loop	1,396	1,057	829	736	534
Recycle Loop	-	-	-	-	-
Hydrogen Discharge	1,032	794	664	617	522
Manufacturing And Assembly	326	251	199	178	129
System Cost	**16,357**	**10,631**	**7,436**	**6,297**	**4,127**
$/kWh	**87.72**	**57.01**	**39.88**	**33.77**	**22.13**





Significantly higher media costs

Combined Exothermic/Endothermic Model



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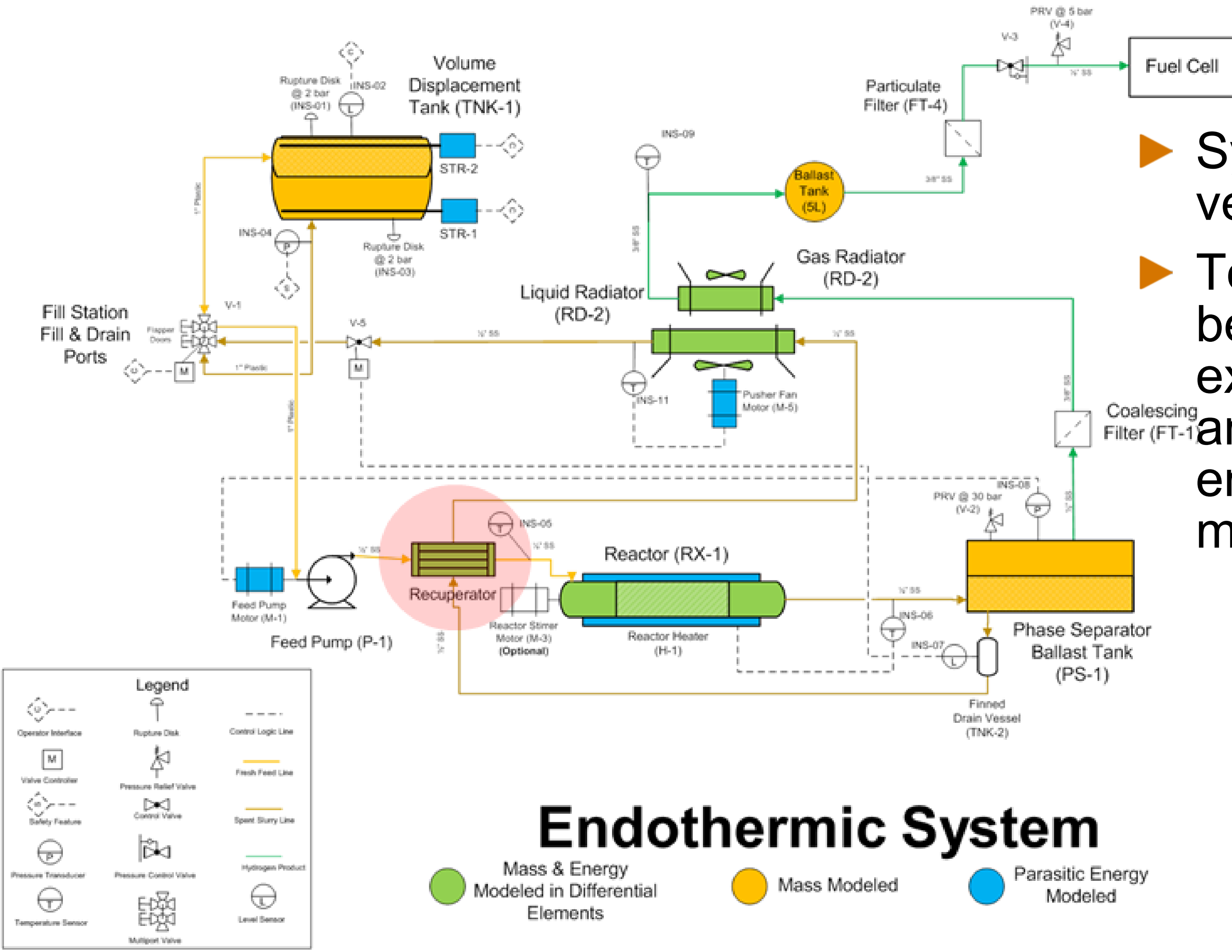
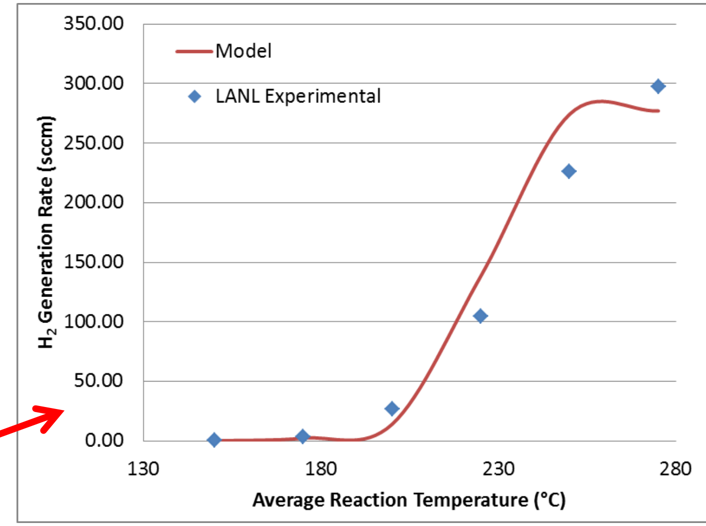
Combined Exothermic/Endothermic Model



- Systems are very similar
- Toggle between exothermic and endothermic models

Model Fit of LANL Reactor Alane Data

- Used kinetic data from Graetz*
- Modeled 2014 experimental data from LANL
- One parameter adjusted to fit the data: final foam density
- Coefficient of Determination
  - $R^2 = 90\%$
- Good fit when then compared model to 2013 LANL data



Solids Loading	Reactor Residence Time	Auger Speed	Average Reaction Temperature	Measured Alane Conversion	Model Conversion Values
(wt%)	(min)	(rpm)	(°C)	(mol/mol)	(mol/mol)
50%	7.6	12	185	16%	11%
50%	7.6	40	185	11%	4.6%
50%	4.2	12	187	7%	6.6%
50%	7.6	12	214	88%	80%
50%	7.6	40	214	74%	53%
50%	4.2	12	214	38%	49%
20%	6.8	40	188	10%	7.1%
20%	6.8	40	212	38%	50%
20%	6.8	40	235	84%	100%
60%	7.2	12	180	5%	6.5%
60%	7.2	12	194	20%	21%
60%	7.2	12	208	48%	55%

Model does a reasonably good job of fitting alane data

* Graetz J and JJ Reilly. *JChemPhysB 109* (2005) 22181-85

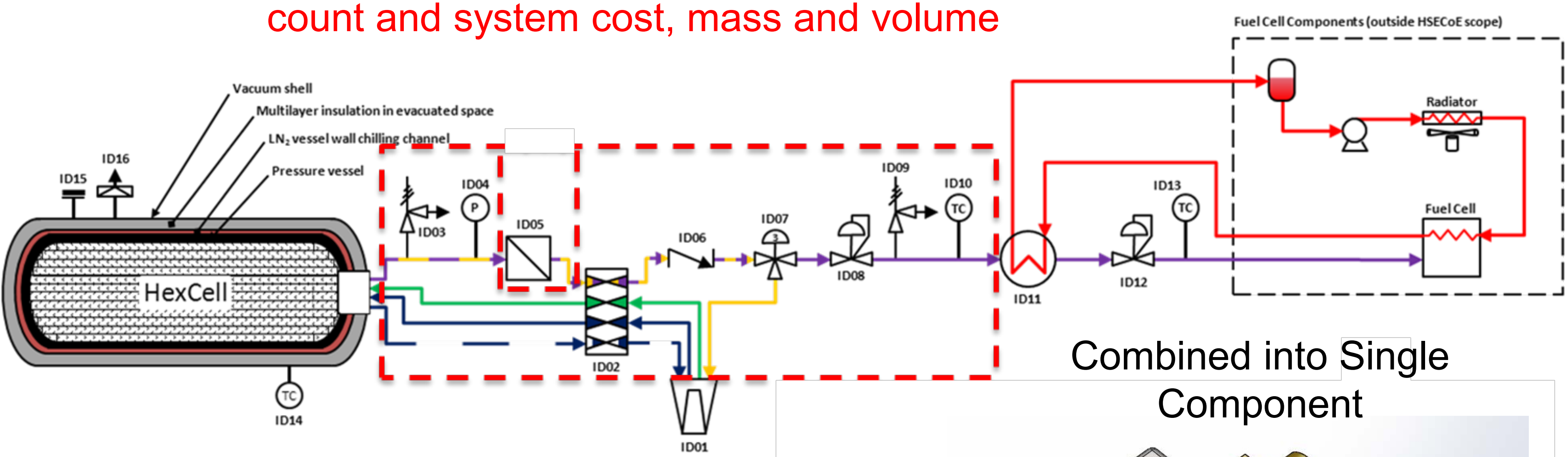
Accomplishments: Adsorbent Materials

- Reduce the mass and volume of the consolidated BOP component
  - "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." **FY13 Q2**

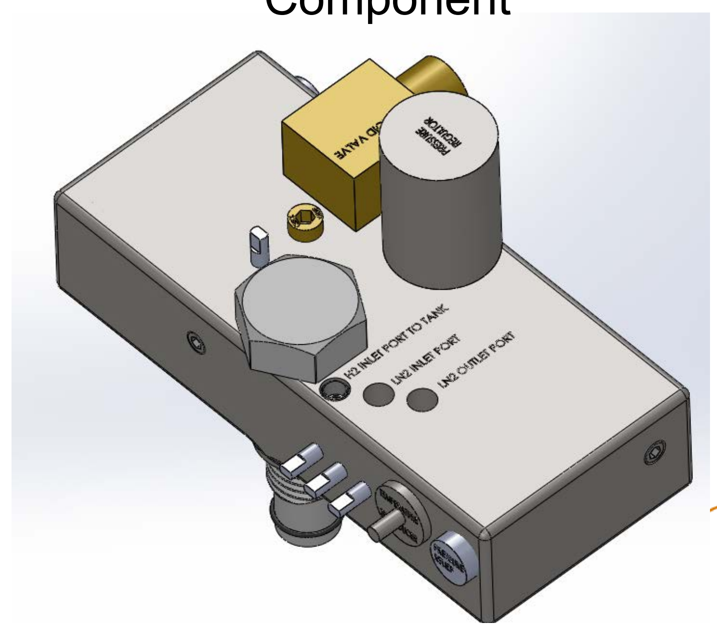
- Proof-of-Concept Testing of Thermos® Bottle Concept
  - "Complete experimental work to validate the thermos bottle concept and provide input into the design of the 2 liter thermos bottle prototype." **FY14 Q2**

BOP Component Consolidation

Looking for approaches to reduce part count and system cost, mass and volume



Combined into Single Component



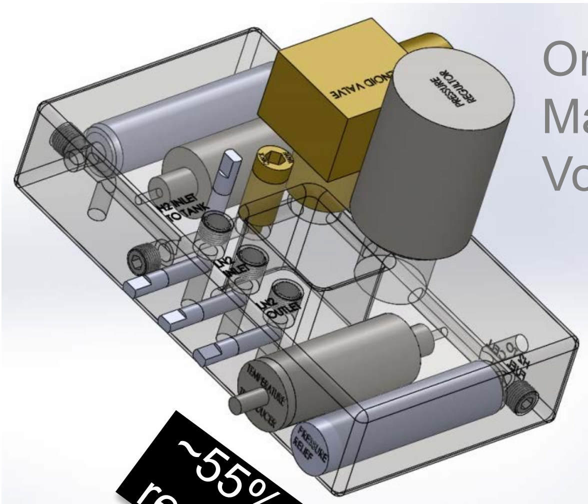
Mass = 9.6 kg, Volume = 1.3 L

Original Component Mass/Volume

Location	Name	Mass (kg)	Volume (L)
ID02	Isolation Valve	2.02	1.575
ID03	Pressure Relief/Gauges	0.11	0.025
ID04	H2 Pressure Sensor	0.04	0.04
ID06	Check Valve	0.13	0.48
ID07	3-Way Solenoid Valve	2.02	1.575
ID08	Pressure Regulator	1.09	0.41
ID09	Pressure Relief/Gauges	0.11	0.025
ID10	Temperature Sensor	0.2	0.02
Total		5.72	4.15

Reduce BOP Mass and Volume

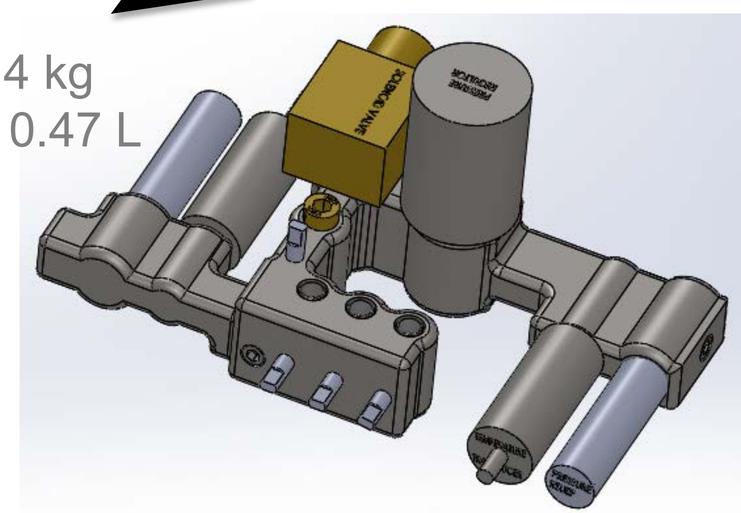
Alternative #1: Stand-Alone Component



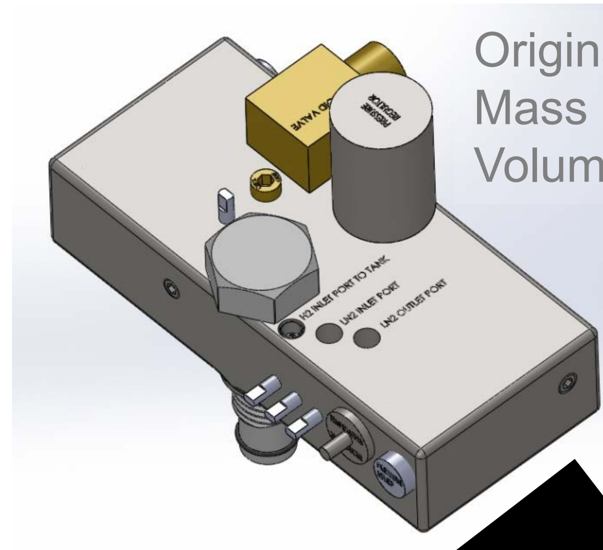
Original
Mass = 7.5 kg
Volume = .97 L

~55% reduction

Reduced
Mass = 3.4 kg
Volume = 0.47 L



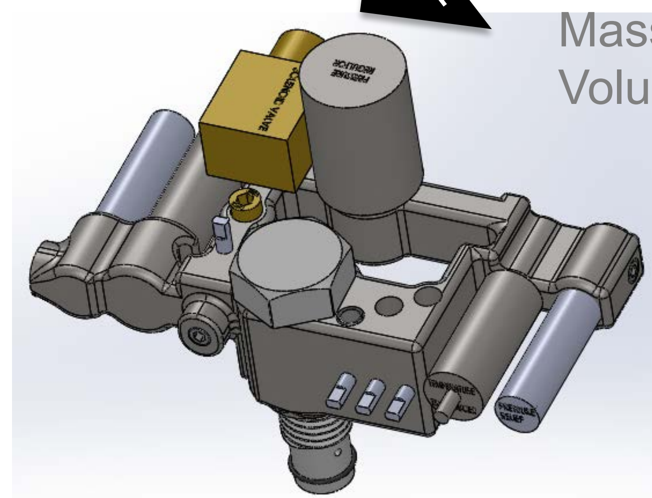
Alternative #2: Installed on Top of Tank



Original
Mass = 9.6 kg
Volume = 1.3 L

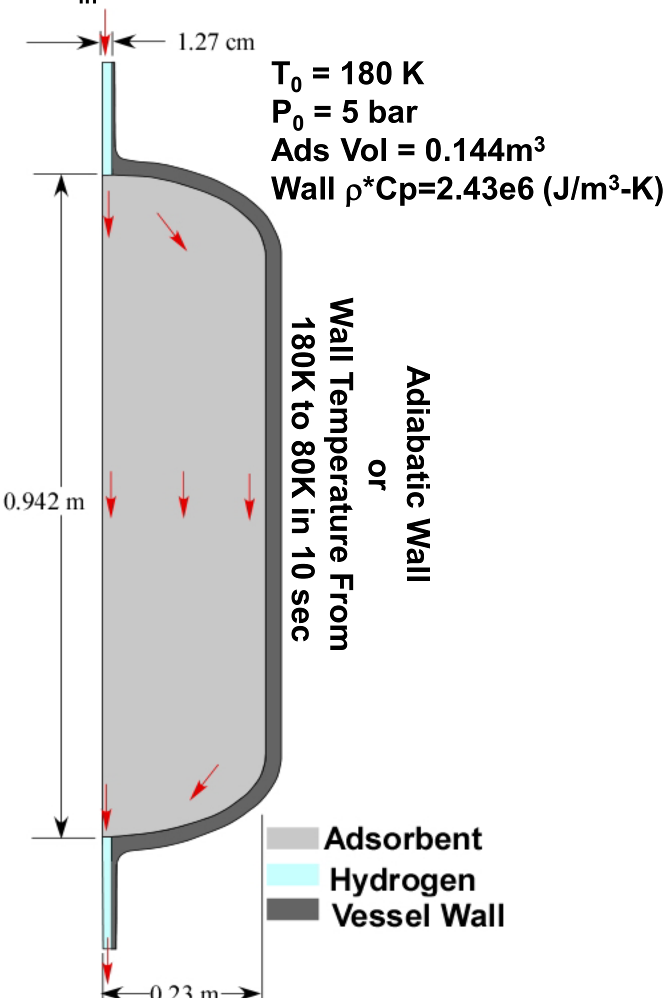
~60% reduction

Reduced
Mass = 3.9 kg
Volume = 0.61 L

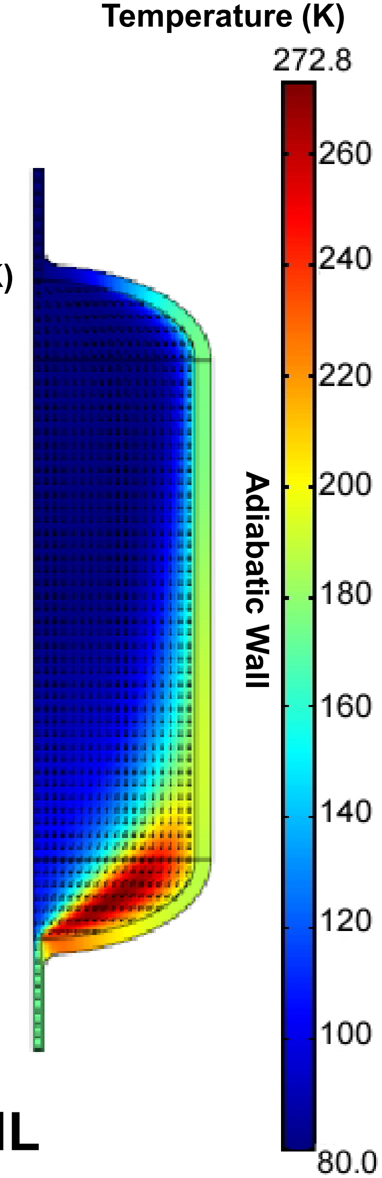


Flow-Through Cooling Analysis Suggests Supplemental Cooling is Needed

T_{in}=80K
P_{in} from 5 to 60 or 200 bar in 8 sec



Avg exit velocity from 0 to 7 m/s from 4 to 10 sec

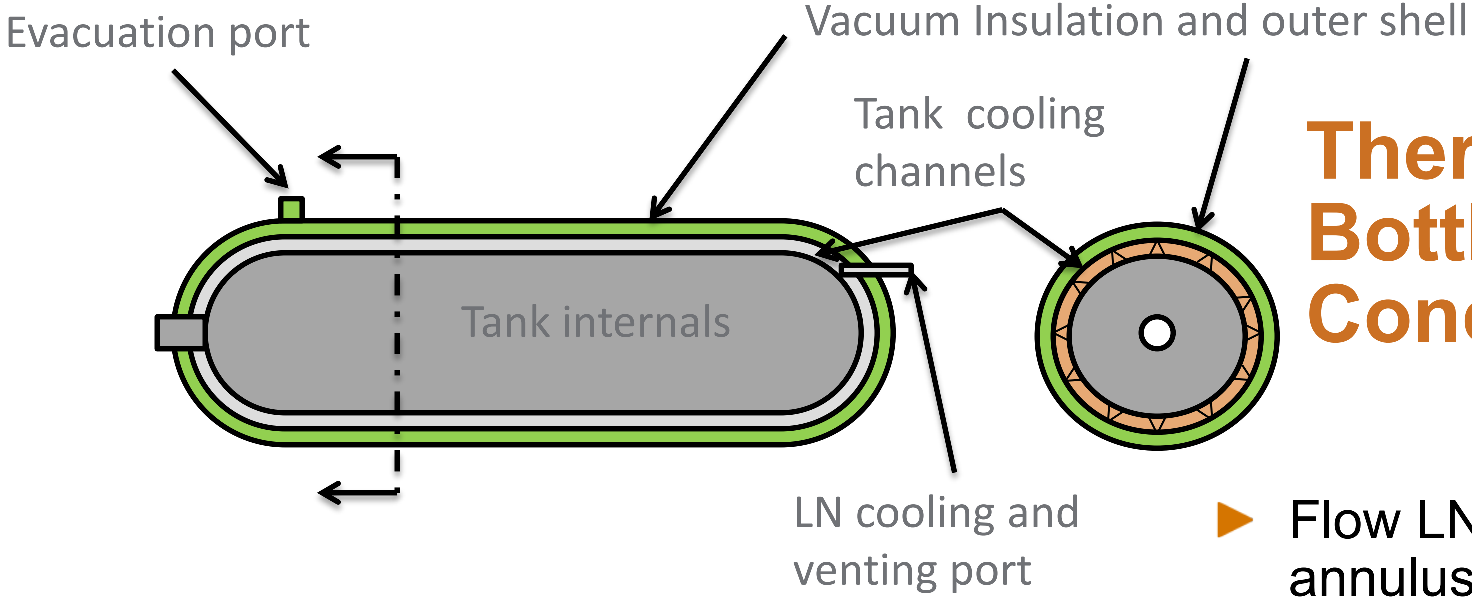


SRNL

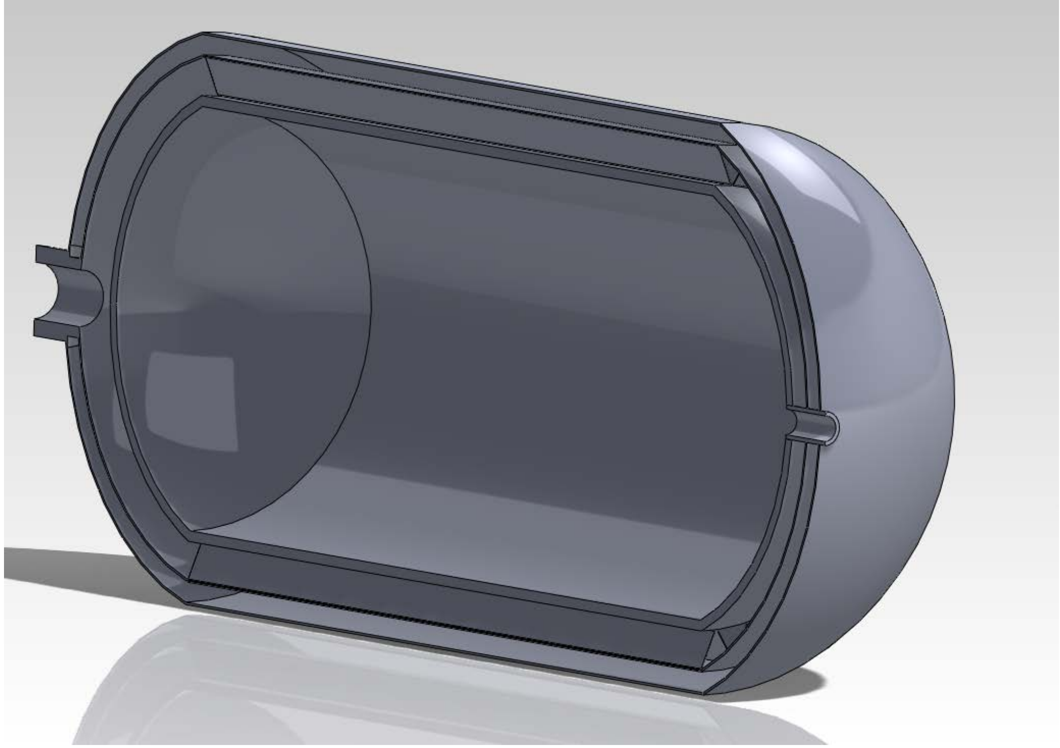
6.32kg of Available Hydrogen is Stored At Full Charge

	Time to Charge (sec)	Total Mass of Exhaust H_2 (kg)	Total Exhaust H_2 Enthalpy (J)
200 Bar	25	1.1	3.597×10^{6}
200 Bar Adiabatic	101	11.4	1.641×10^{7}
60 Bar	108	2.4	6.477×10^{6}
60 Bar Adiabatic	>300	>11.8	>1.836×10^{7}

A Preliminary JPL Test Indicated that the Time Required to Cool the Outer Wall is Longer than Assumed in the Model (~1.5 minutes from 180 K to 80K)

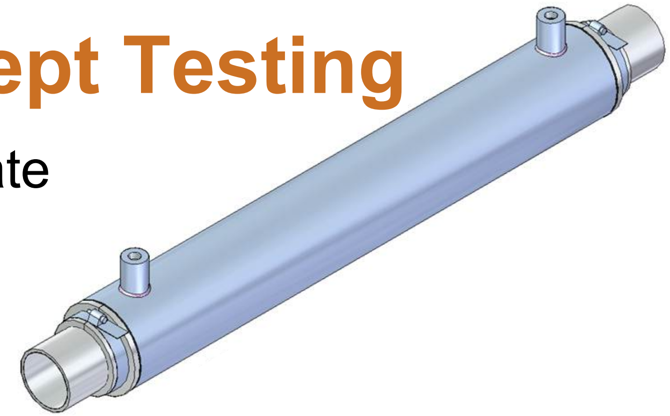


Thermos Bottle Concept

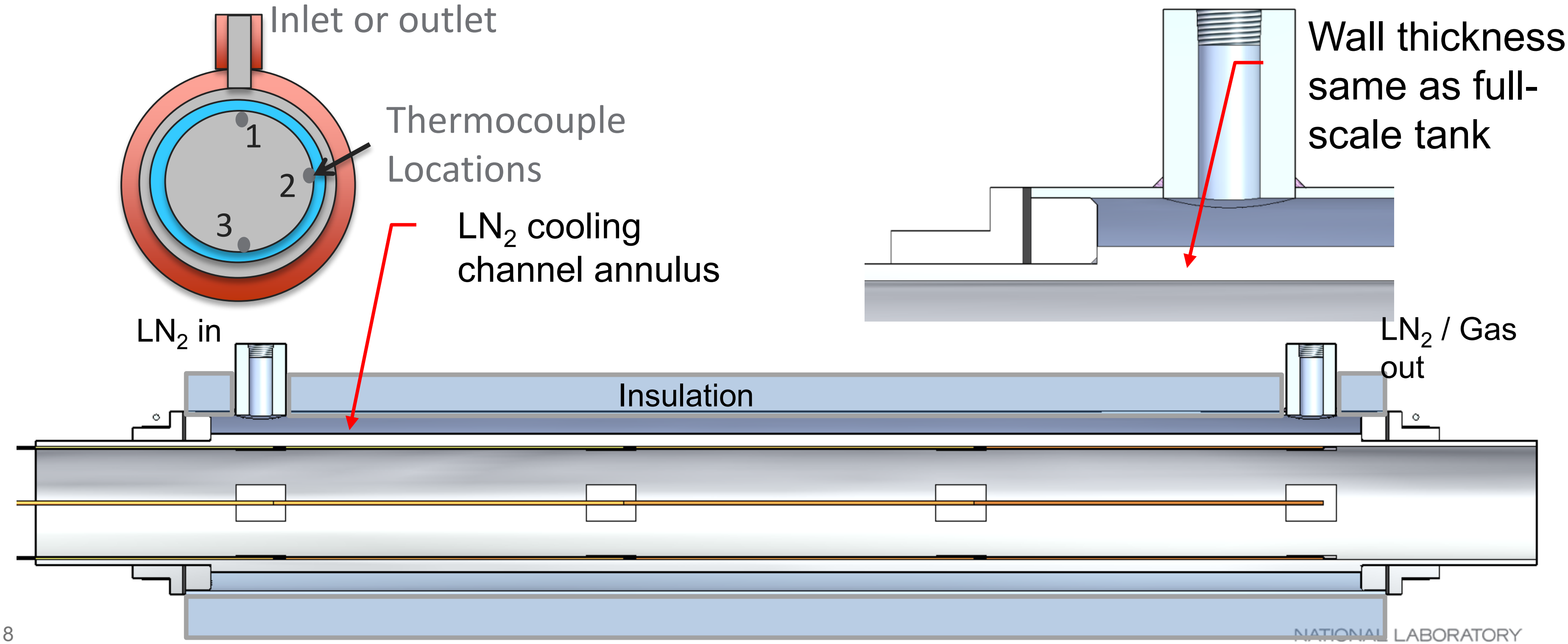


- Flow LN_2 in an annulus between insulation and tank to cool tank wall during H_2 filling
  - Reduces the amount of H_2 required
  - Accelerates system cooling

Thermos Bottle Proof-of-Concept Testing

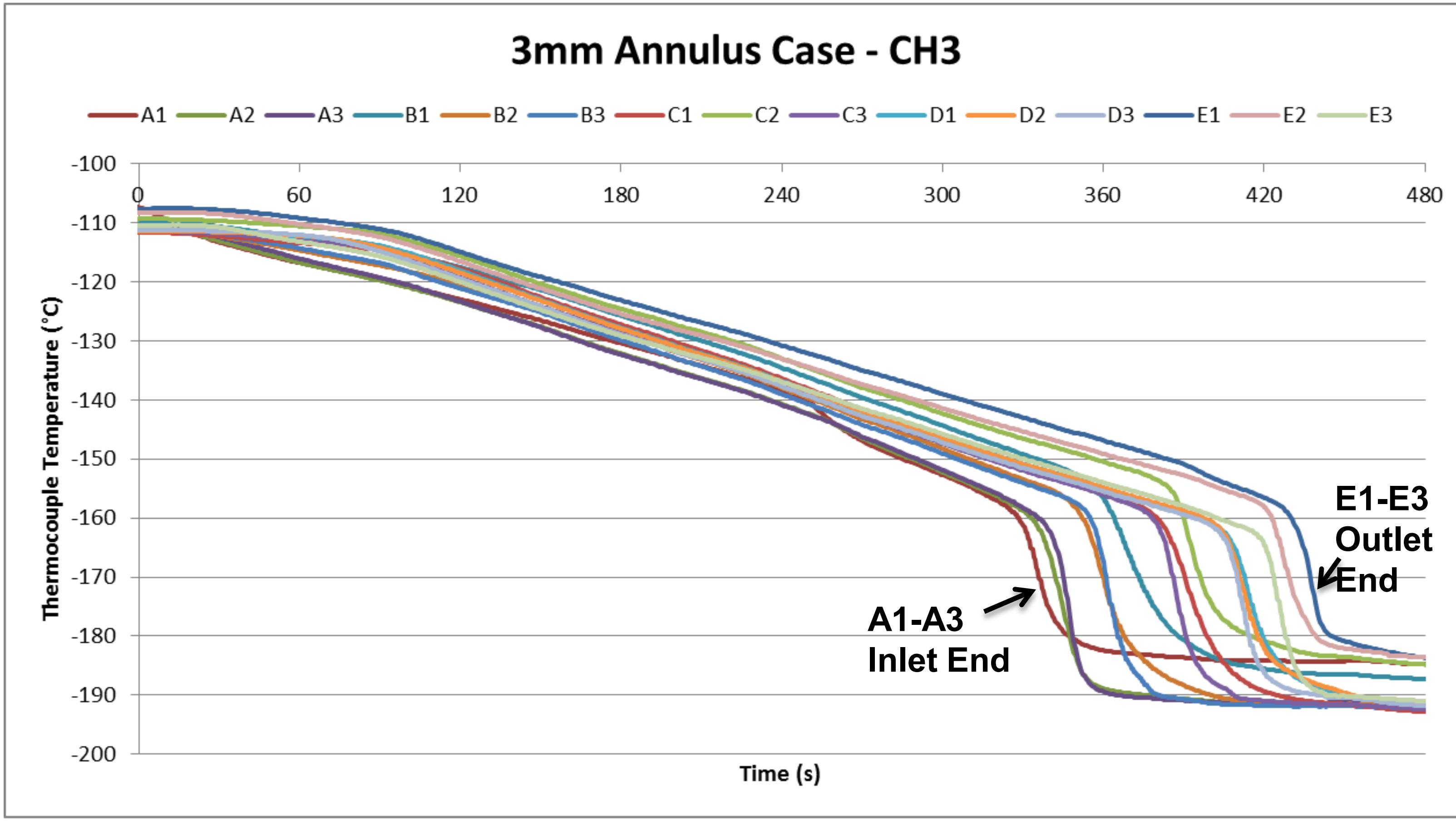


- Flow LN_2 in annulus and measure cooling rate
- Vary parameters:
  - Starting temperature
  - Mass flow rate of LN_2
  - Cooling annulus opening thickness
  - Insulation properties on exterior wall



Experimental Set up for Proof-of-Concept Testing

Typical Thermocouple Data Set



Cooling trend is roughly uniform until a rapid cooling front advances along the length of the pipe.

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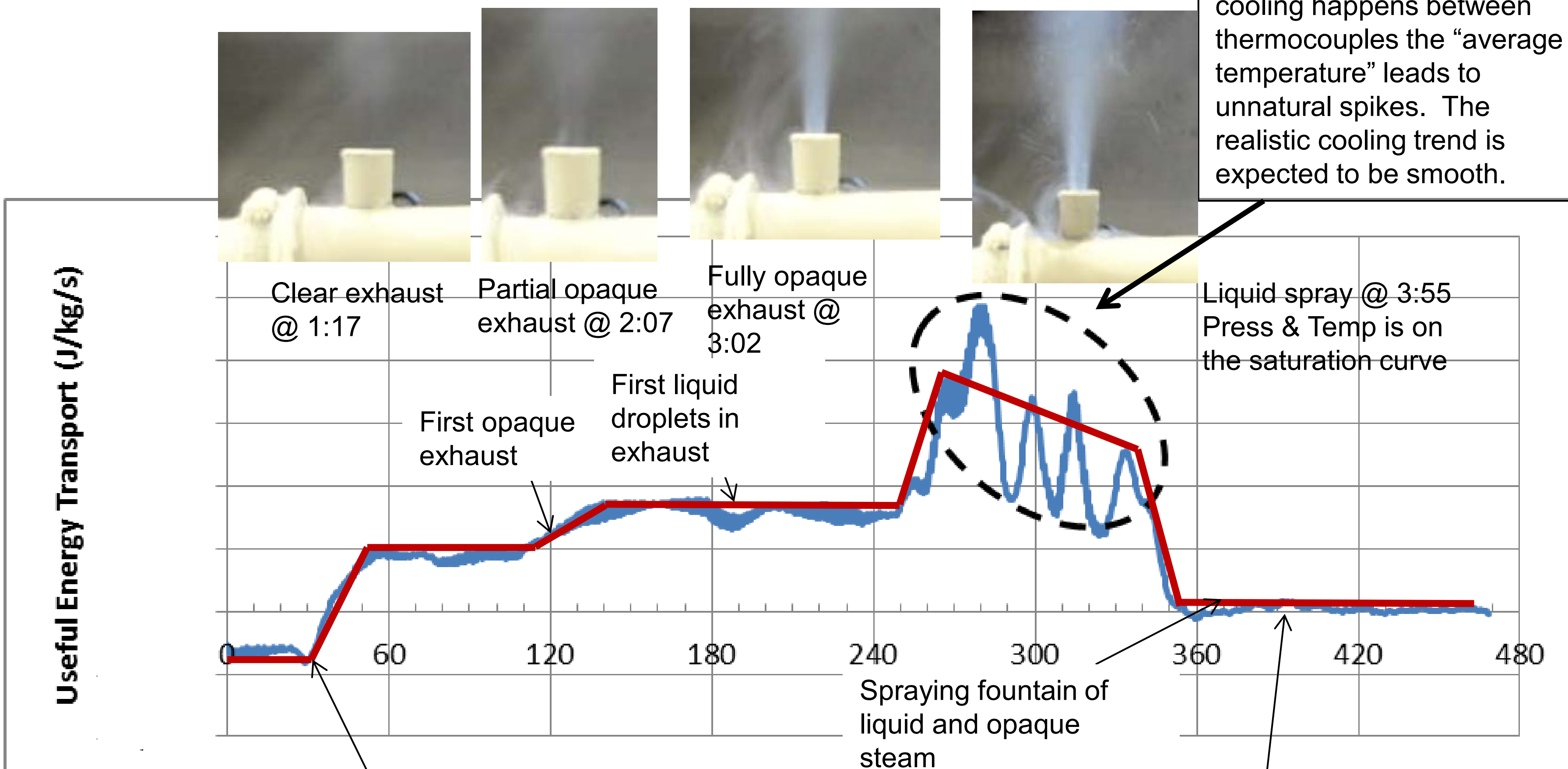
Useful Energy Transport Capacity

This is the rapid cooling front region. Because cooling happens between thermocouples the "average temperature" leads to unnatural spikes. The realistic cooling trend is expected to be smooth.

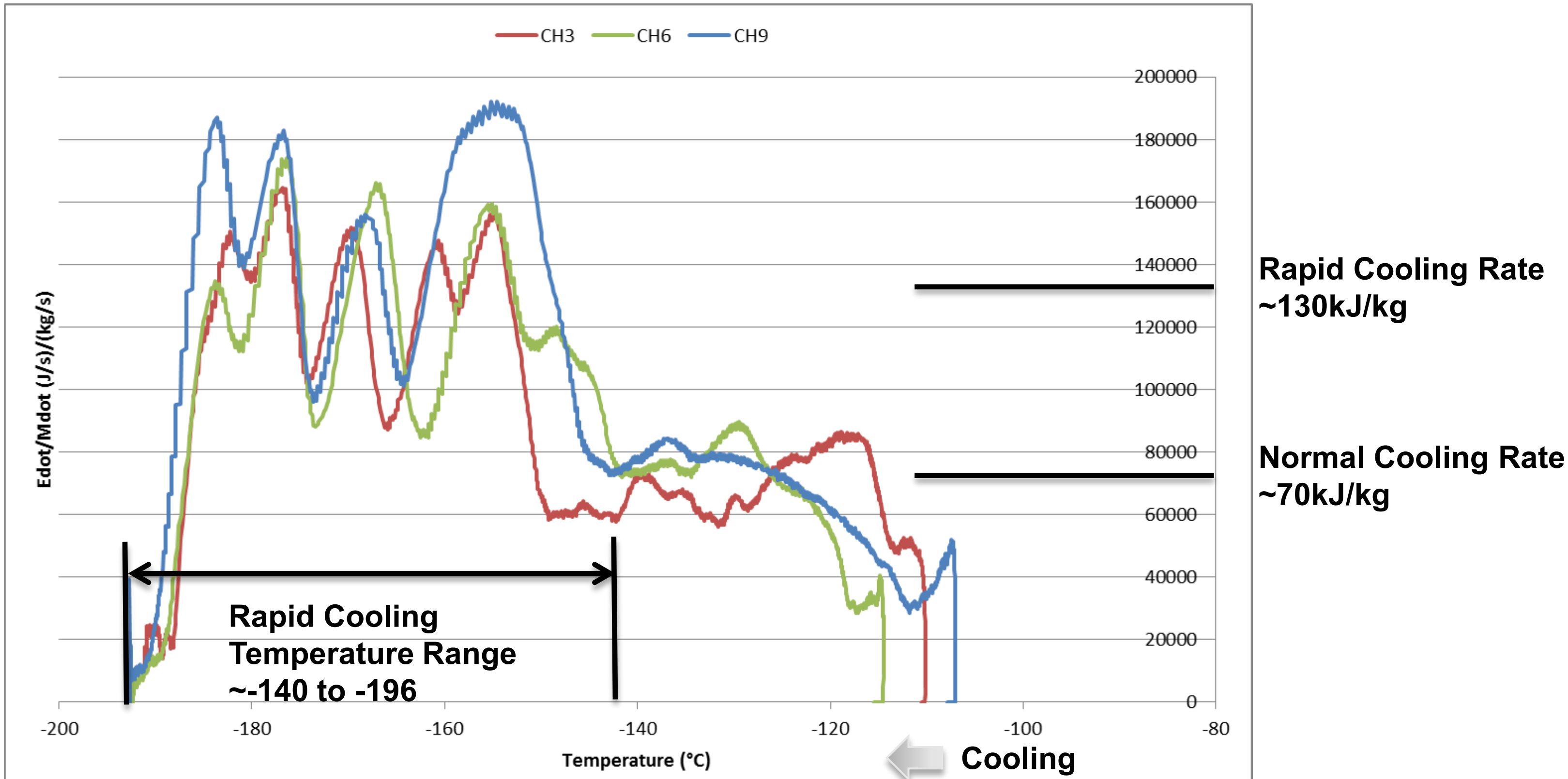


Negative values mean heat is actually being added to the pipe instead of removed.

Near-zero values means the added LN2 is not having much of an effect on the temperature. This is a cooling saturation point.

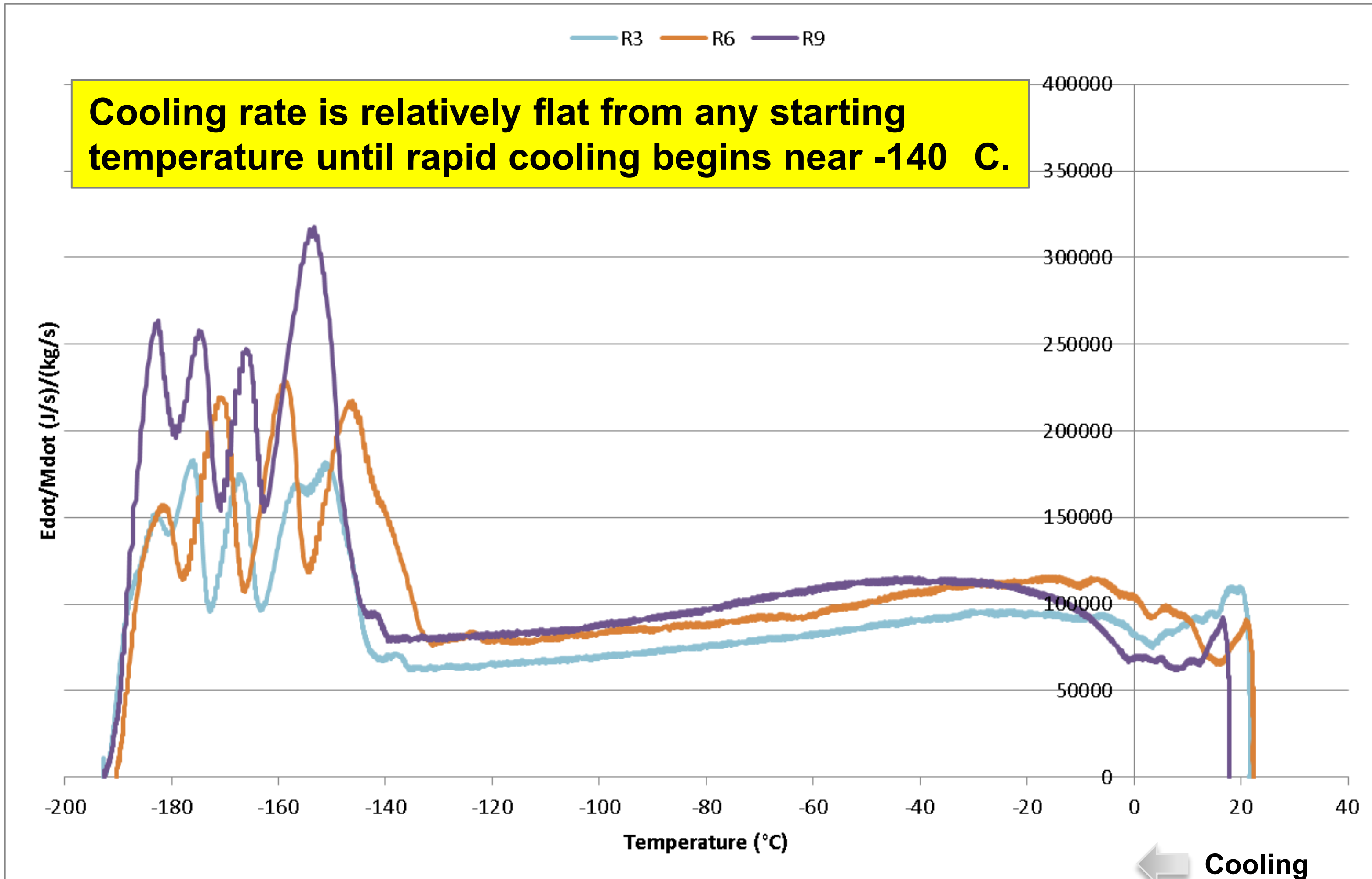
Exhaust provides insight into the cooling rate within the pipe

Pipe Cooling Rate by Temperature



Test data shows two distinct cooling phases with a transition temperature around -140 C average pipe temperature or -160 C local inlet temperature.

Pipe Cooling Rate from Room Temperature



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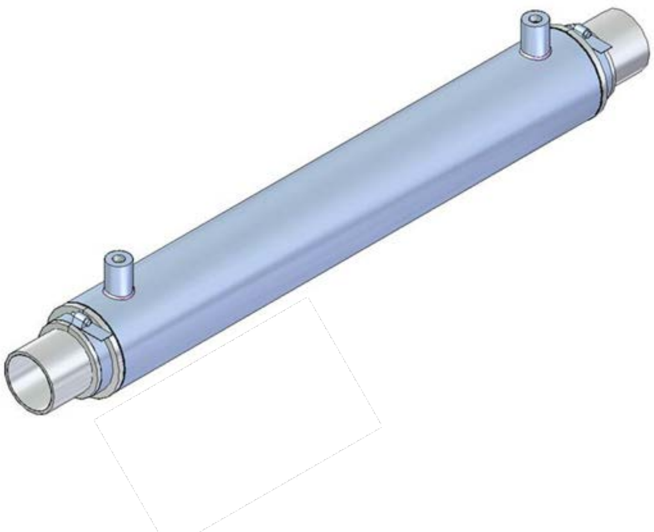
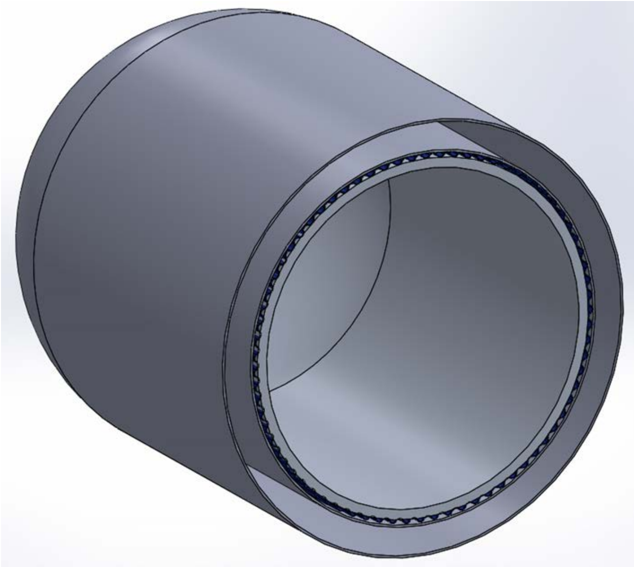
Applying Pipe Test Results to Tank Design

Proof-of-Concept Pipe Test System



Inner Aluminum Pipe
Mass: 5.55 kg
Surface Area: 0.13 m^2
Diameter: 70 mm OD
Wall Thickness: 17 mm

Full-Scale Thermos Bottle Concept



Thermos Bottle Concept (163L / 250L)
Mass: 75 kg / 108 kg
Surface Area: 1.73 m^2/2.47 m^2
Diameter: 500 mm ID
Wall Thickness: 17 mm

Key Assumption: Similar cooling rates can be achieved by increasing mass flow rate to account for greater material mass and surface area in realistic tank design.

Cool Down Estimates: 163 Liter Tank

163 L, 75 kg Tank, 500mm ID, requires 5.8 MJ to cool from -110 C to -196 C in 4 minutes requires average 24.1 kJ/s

Cooling Rate Assumptions	Cooling Rate (J/s)/(kg/s)	Required LN_2 Mass Flow Rate	Total LN_2 Consumed
Minimum	50k	0.48 kg/s	116 kg
Normal	70k	0.29 kg/s	69 kg
Average Test	**87.1k**	**0.28 kg/s**	**66 kg**
Rapid Cooling	130k	0.19 kg/s	45 kg
Maximum	200k	0.12 kg/s	29 kg
Perfect LN2 Boiling	200k	0.12 kg/s	29 kg
Ideal LN2 Boil + Gas	241k	0.10 kg/s	24 kg

Best Estimate: Cooling a 163 Liter capacity tank with a 75 kg aluminum vessel mass in four minutes will consume about 66 kg of liquid nitrogen.

Note: Estimates are for cooling the tank only, not the sorbent media or removing the heat of adsorption

Cool Down Estimates: 250 Liter Tank

250 L, 108 kg Tank, 500mm ID, requires 8.4 MJ to cool from -110 C to -196 C in 4 minutes requires average 35 kJ/s

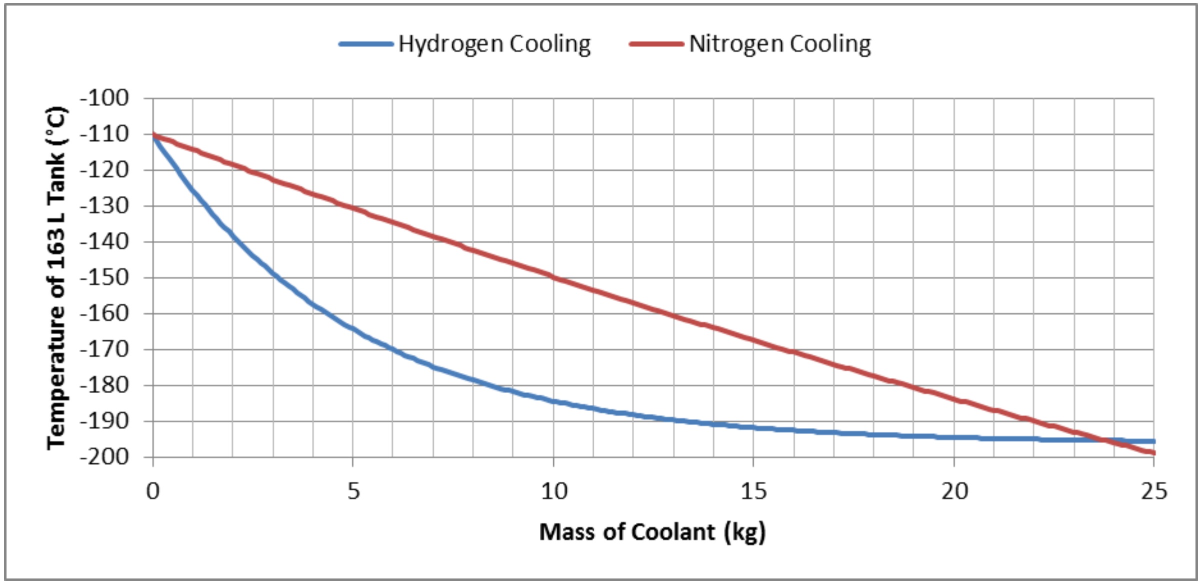
Cooling Rate Assumptions	Cooling Rate (J/s)/(kg/s)	Required LN_2 Mass Flow Rate	Total LN_2 Consumed
Minimum	50k	0.70 kg/s	168 kg
Normal	70k	0.50 kg/s	120 kg
Average Test	**87.1k**	**0.40 kg/s**	**96 kg**
Rapid Cooling	130k	0.27 kg/s	65 kg
Maximum	200k	0.175 kg/s	42 kg
Perfect LN_2 Boiling	200k	0.175 kg/s	42 kg
Ideal LN_2 Boil + Gas	241k	0.15 kg/s	35 kg

Best Estimate: Cooling a 250 Liter capacity tank with a 108 kg aluminum vessel mass in four minutes will consume about 96 kg of liquid nitrogen.

Note: Estimates are for cooling the tank only, not the sorbent media or removing the heat of adsorption

Ideal Cooling Capacity of LN_2 and H_2

	Heat of Vaporization	Specific Heat	Delta T = 86 °K	Delta T = 1 °K
Liquid Nitrogen	199 kJ/kg	-	-	-
Nitrogen Gas (T_{in} = -196°C)	-	1.04 kJ/(kg-K)	89 kJ/kg	1.04 kJ/kg
Hydrogen Gas (T_{in} = -196°C)	-	14.3 kJ/(kg-K)	1229 kJ/kg	14.3 kJ/kg



Note: 5.6 kg of H2 is target storage capacity.

Cooling Options:

a) 24 kg N2
b) 21 kg H2
c) 1 kg H2 + 20 kg N2
d) 2 kg H2 + 15 kg N2
e) 5 kg H2 + 10 kg N2
f) …

Cooling with a mix of H_2 and LN_2 is an attractive option.

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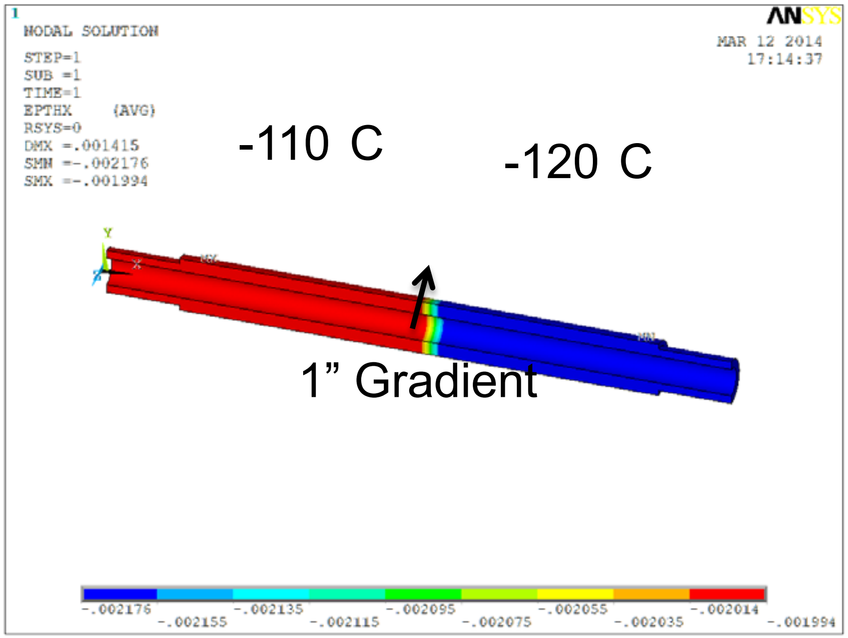
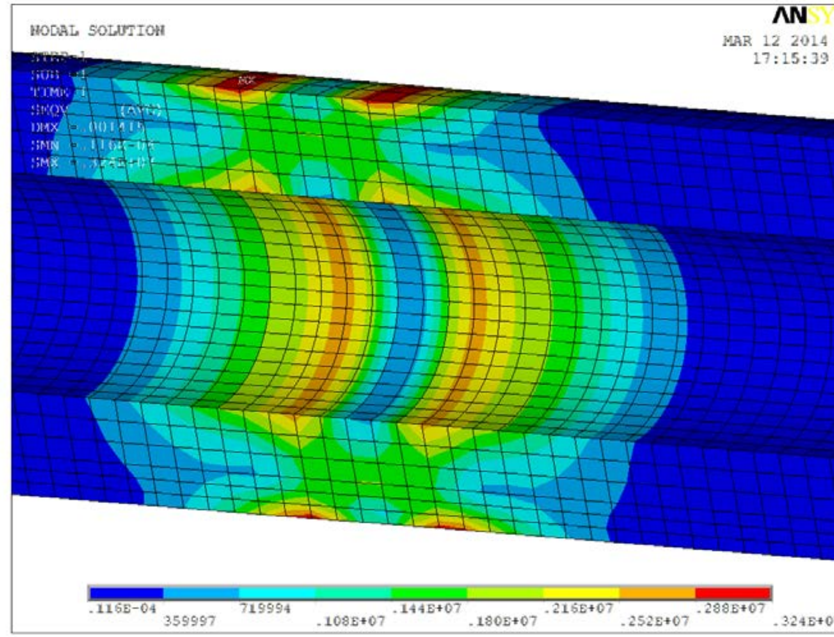
Fatigue Stress Calculation

A maximum of 5 C/inch axial and 10 C/inch radial was found experimentally.



10 C gradient applied to pipe model geometry to estimate peak thermal stress.



Peak thermal stress is 3.2 MPa (von Mises) or 3.4 MPa (stress intensity). Fatigue strength is expected to be much higher for 5000 cycles, 100 MPa* or more.

Significantly higher temperature gradients are needed to challenge the fatigue limit.

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* 100 MPa is fatigue strength at ambient. Strength increases at sub-ambient temperatures.

Response to Previous Year Reviewer's Comments

- Comment: Given the recent work on well-to-wheels efficiency of chemical hydrogen storage materials, the Program should consider stopping work on these systems until a more efficient material is found. . .. The project team should reduce its work on slurries and increase its work on sorbent and cryo tanks.

  Response: With the June 2013 No-Go decision for chemical hydrogen storage materials, the project's focus has changed to completing the model and final report and then begin addressing issues associated with the adsorbent system.

- Comment: Understanding heat exchange issues for sorbent-based materials is key to designing high-capacity systems and the knowledge is mostly transferrable to new sorbent materials as they become available.

  Response: The thermos bottle approach to tank cooling during refueling addresses a key heat exchange issue—that of removing heat from the tank from the outside. This approach would be transferrable to other sorbent materials and other system designs (both MATI and Hexcell).

- Comment: The "tankinator" model waterfall chart showing system improvements should be accompanied by credible strategies for achieving targeted improvements or some idea of how likely improvements are. The basis for the improvements should be explained and justified by preliminary experimental accomplishments.

  Response: The current focus of our work has shifted to proving the feasibility of the thermos bottle concept. This concept needs to be demonstrated. If successful, it will have a significant effect on system volumetric, gravimetric and cost targets. As a result, the mass and cost estimates in the "tankinator" and the potential for improvement needs to be tabled until the demonstration is complete.

Collaborative Activities

Hydrogen Storage Engineering Center of Excellence	• Hexagon Lincoln – fabricated and performed thermos bottle PoC testing, continued development of pressure vessels • UTRC - develop solutions for H_2 impurities filtering, and phase separator, framework model lead • LANL - AB and alane reactor testing and measure H_2 impurities, CH system design • NREL – Assist in the development, testing, and publishing of the system model • Ford – characterization of absorbent materials • UQTR – Phase 3 Hexcell testing • OSU – MATI design and fabrication • SRNL – Phase 3 MATI adsorbent testing and modeling
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 H_2
Independent Analysis	• SA - provide design details for AB and Alane regeneration cost, plus share cost parameters for system cost modeling

Remaining Challenges and Barriers

- Use results from Proof-of-Concept tests to design a 2 liter thermos bottle with Hexagon Lincoln
  - SMART Milestone: "Using thermal correlations, design a 2L scale thermos bottle concept tank with the LN2 cooling that is projected to be capable of meeting the DoE technical targets to enable a 5 minute fill of 5.6 kg H_2."
  - Thermos bottle design must provide insight into:
    - Cool-down rates during refueling
    - Provide an estimate of anticipated dormancy rates for a full-scale system
- Successfully validate and finalize CH storage system model
- Cost estimate needs to be developed for initial alane production
  - Regeneration costs have been estimated in some detail but not first fill

Proposed Future Work

- Adsorbents—Thermos Bottle
  - Develop 2L dormancy test with tank and vacuum thermos bottle design
  - Test 2L tank for cool down rates and dormancy
- Adsorbents—Cost Modeling
  - Update cost models and write up cost results for adsorbent systems: MATI and Hexcell
- Adsorbents—BOP
  - Perform stress and thermal modeling on consolidated component design and update designs as required

- Chemical Hydrogen Storage Materials
  - Final Report--Finalize final chemical hydrogen report that includes material characterization, system design, performance modeling, component validation testing and cost modeling
  - Storage Model--Document and publish exothermic/endothermic CH storage models

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Project Summary

Relevance	Address the engineering challenges for materials based hydrogen storage and provide feedback and recommendations on materials requirements.
Approach	• Design systems/validate the components in these systems • Develop system models/experimentally validate them. • Determine cost estimates of the system and material properties to guide future selections.
Technical Accomplishments and Progress	• Developed alane cost analysis • Updated CH storage model • Demonstrated proof-of-concept and estimated full-scale performance of the thermos bottle concept • Reduced the mass of the adsorbent system BOP
Collaborations	• Extensive collaboration with all of our HSECoE partners
Proposed Future Research	• Post CH storage model with vehicle framework • Finalize CH storage system final report • Design and test 2 liter prototype of thermos bottle • Develop cost estimates for adsorbent systems

Project ID# ST005

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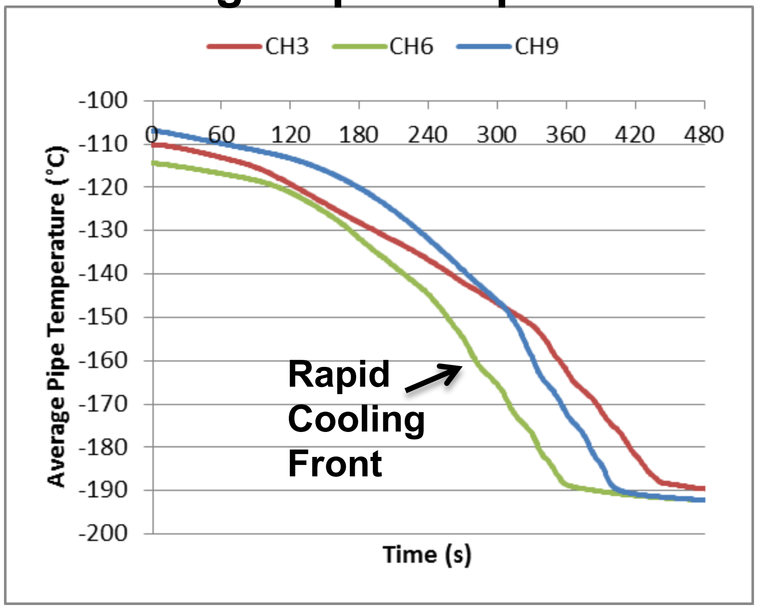
Technical Back-up Slides

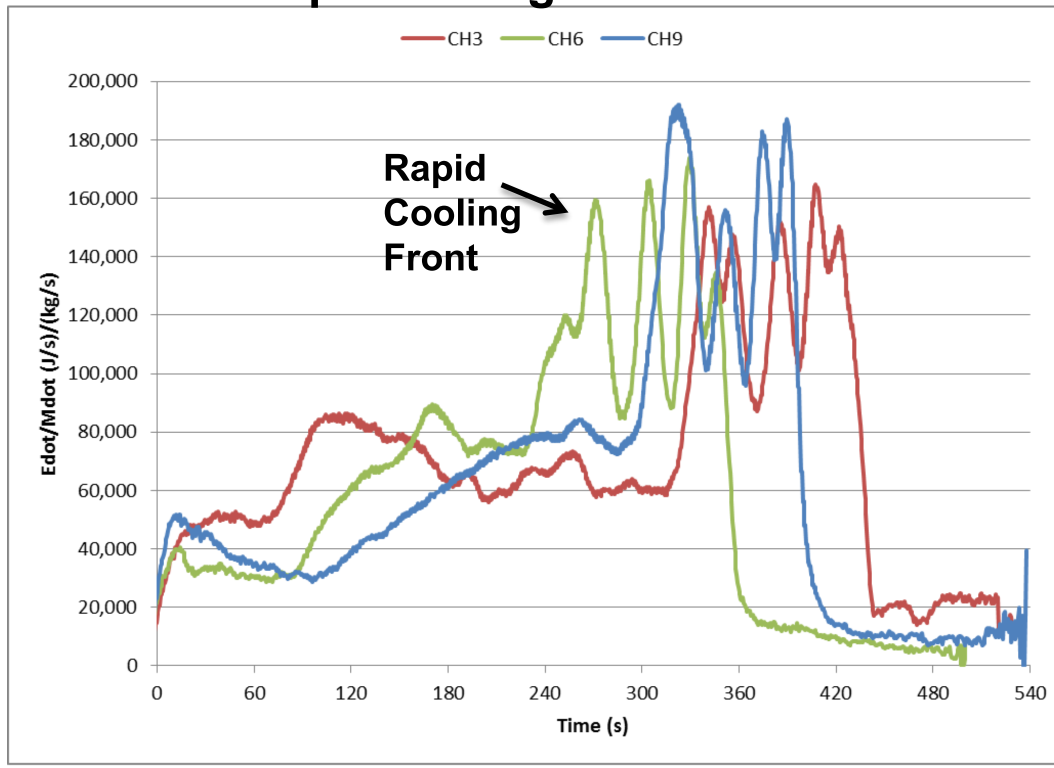
Estimating Pipe Cooling Rate from Testing

Average Pipe Temperature



The pipe requires 4973 Joules of energy removed for each degree Celsius cooled. This relates temperature change to energy. Note that the rapid cooling front causes noise in the average temperature trend because cooling happens between thermocouples.

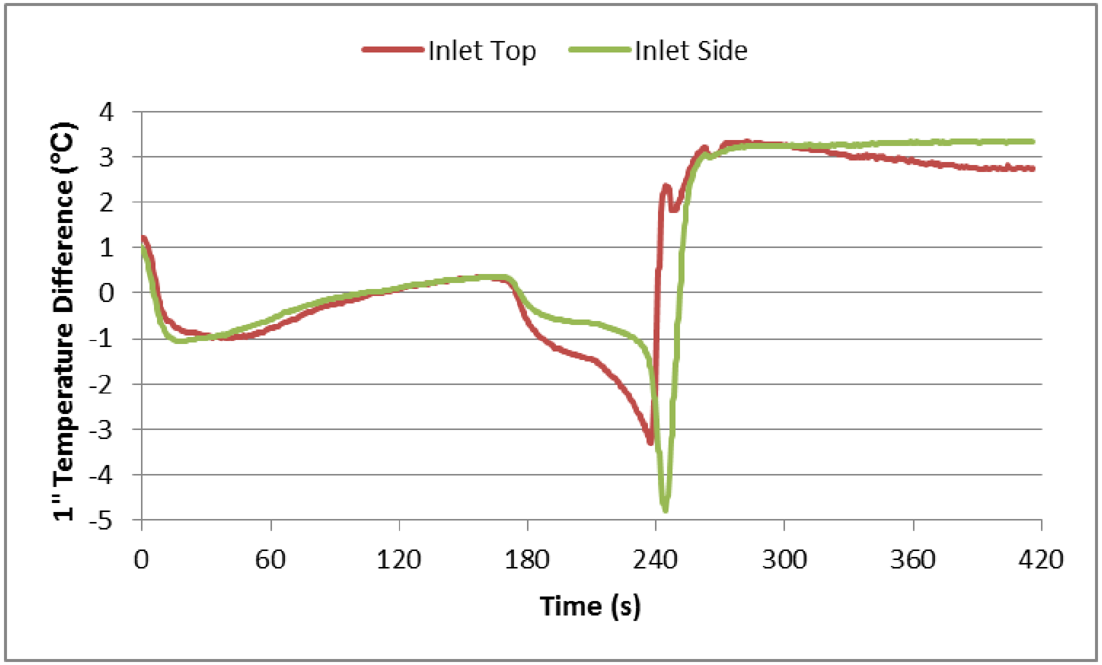
Pipe Cooling Rate



<u>Pipe Cooling Rate</u> is the energy removed per second, divided by the mass flow rate of liquid nitrogen. This is an indication of the cooling efficiency, normalized by the mass flow rate. Note that the rapid cooling front affects the calculation of Pipe Cooling Rate because it involves the time derivative of the average pipe temperature. The actual trend is expected to be smooth.

Thermal Gradient in 3mm Annulus Vertical Case

- Additional thermocouple situated 1 inch from A1 for maximum temperature gradient
- Large temperature gradients can increase thermal stresses during cooling
- A maximum of 5℃/inch was found
- Some cases had as high 10 ℃/inch on the circumference



This magnitude of temperature gradient is not expected to cause any significant thermal strains or necessitate changes to the design to avoid fatigue failure.