SRNL Technical Work Scope for the Hydrogen Storage Engineering Center of Excellence

Design and Testing of Metal Hydride and Adsorbent Systems

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Savannah River National Laboratory

May 15, 2012

Hydrogen Storage Engineering
CENTER OF EXCELLENCE

Project ID#ST044

This presentation does not contain any proprietary, confidential or otherwise restricted information

Overview

Timeline

- Start: February 1, 2009
- End: July 31, 2014
- 55% Complete (as of 3/1/12)

Barriers

- System Weight and Volume
- H_2 Flow Rate
- Energy Efficiency

Budget

- FY11 Funding: $1,040,000*
- FY12 Funding: $1,030,000*

* Includes $240,000/$240,000 for the University of Quebec Trois Rivieres (UQTR) as a subrecipient for FY11/FY12

Partners

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Pacific Northwest National Laboratory
Los Alamos National Laboratory
United Technologies Research Center
JPL
NREL National Renewable Energy Laboratory
BASF The Chemical Company
OSU Oregon State University
HRI UQTR
California Institute of Technology
Michigan
HSM Systems
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Relevance – Overall Project Objectives

Phase 1: 2009-2011

- Compile all relevant **metal hydride materials data** for candidate storage media and define future data requirements. **Complete**
- Develop engineering and design models to further the understanding of on-board storage **transport phenomena requirements**. **Complete**
- Apply **system architecture approach** to delete specific metal hydride systems not capable of meeting DOE storage targets. **Complete**

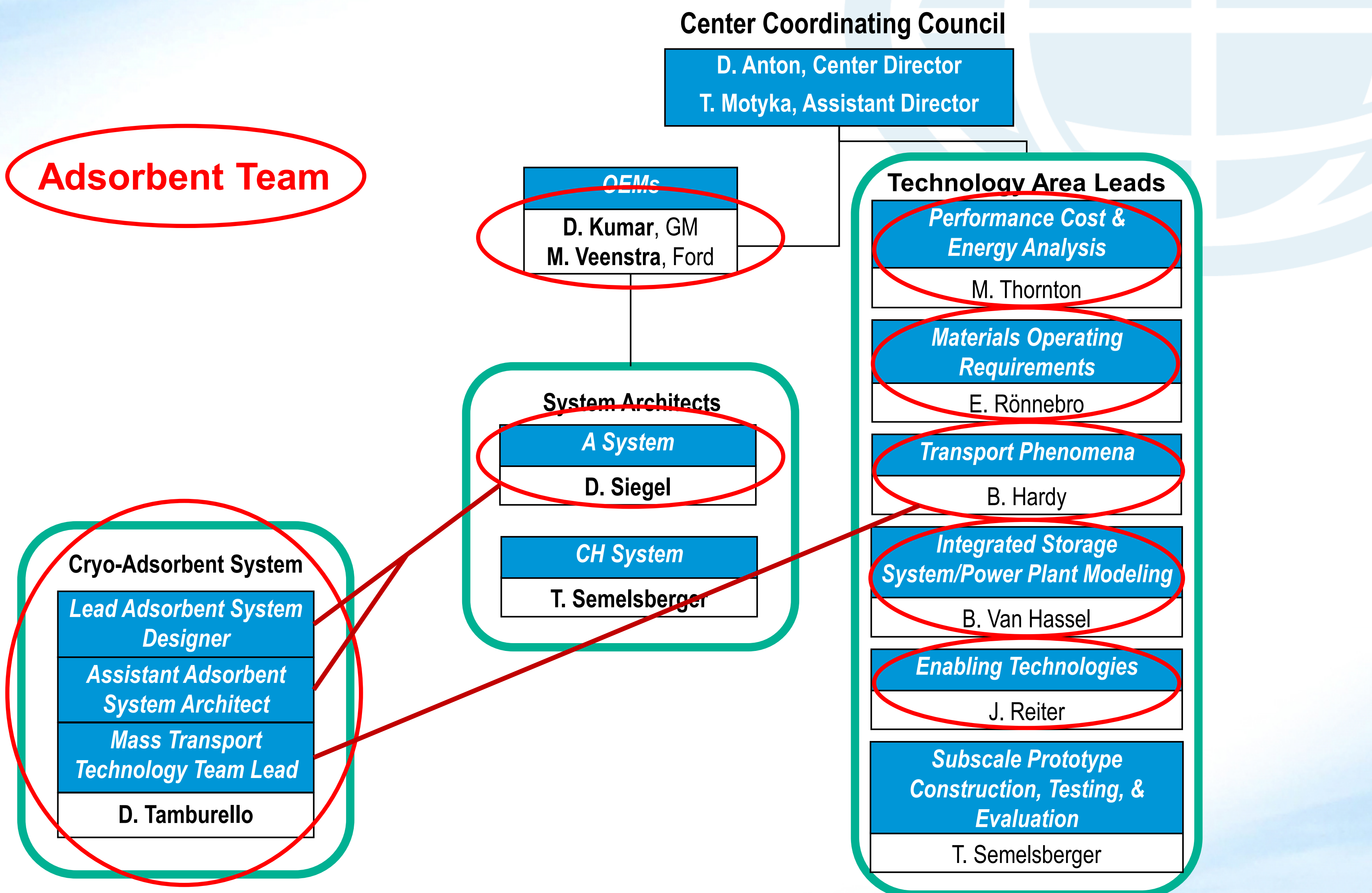
Phase 2: 2011-2013

- Develop **innovative on-board system concepts** for metal hydride and adsorption hydride materials-based storage technologies.
- Design components and experimental test fixtures to **evaluate the innovative storage devices** and subsystem design concepts, validate model predictions, and improve both component design and predictive capability.

Phase 3: 2013-2014

- Design, fabricate, test, and decommission the **subscale prototype systems** of each materials-based technology (adsorbents and metal hydrides storage materials).

Approach - HSECoE Organization



Approach – FY2012 / FY2013 Milestones

SMART Milestone

- Disseminate two of the HSECoE models (Metal Hydride Acceptability Envelope and Metal Hydride Heat Transfer Model) by making the models available for downloading on the HSECoE public website. 6/12
- Design (SRNL) and demonstrate (UQTR) flow-through cooling for adsorbent media, meeting the DOE 2017 hydrogen charging rate of 1.5 kg/min. 9/12

Tracking Milestones

1. Guide experimental validation of flow-through cooling concept for nominal form adsorbents with respect to model predictions. 4/12
2. Validate charging model utilizing modified UQTR experiments. 5/12
3. Complete one flow-through adsorbent storage vessel and system design for one adsorbent-cooling gas using available data. 7/12
4. Design, characterize, and experimentally evaluate a means for heating adsorbent beds to effect hydrogen discharge. 9/12

Additional Phase 2 SMART Milestone (SRNL/UQTR)

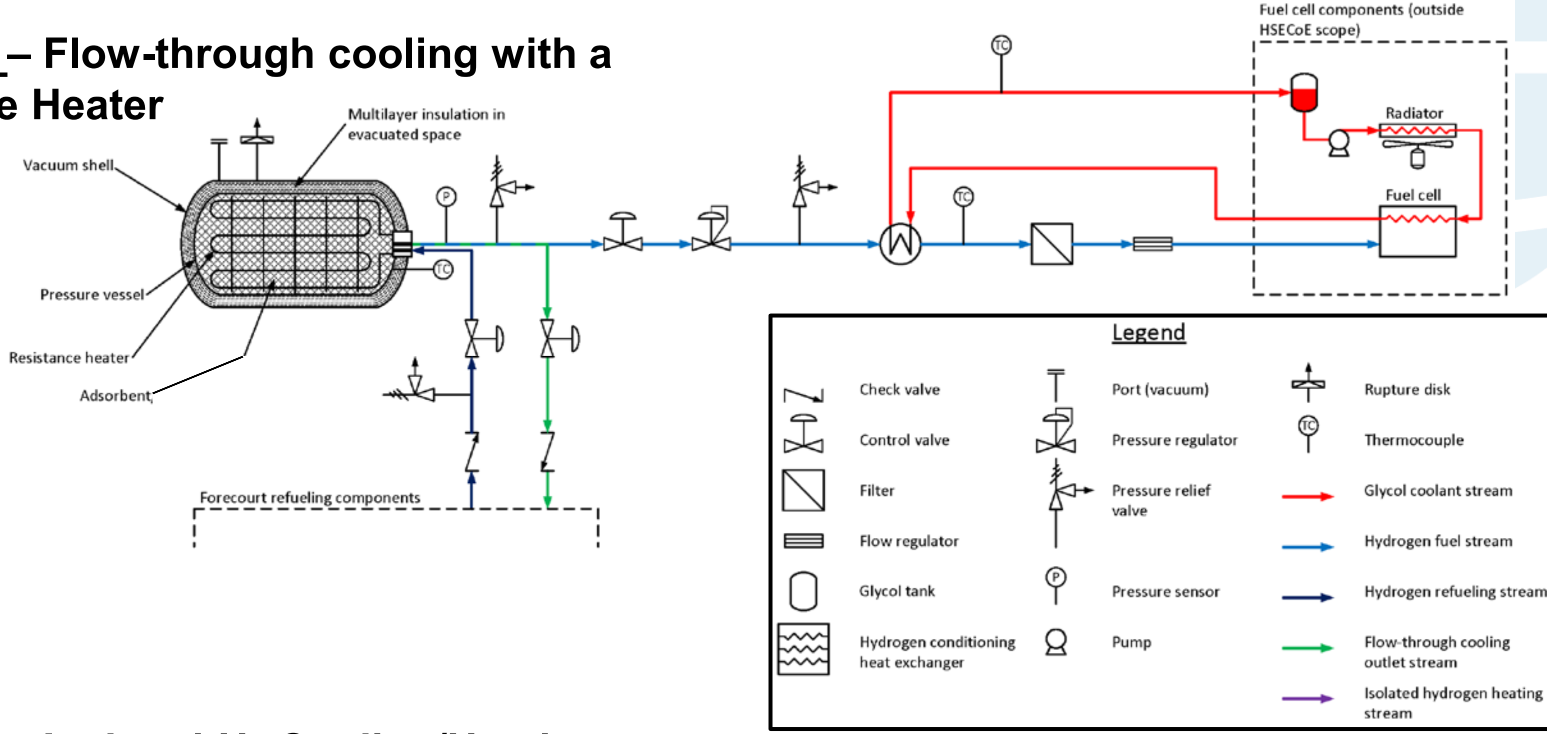
- Materials Development: Report on ability to develop a compacted MOF-5 adsorbent media bed having a total hydrogen density of 11 g_{H2}/g_{MOF} and 33 g_{H2}/L_{MOF} at P_{full} = 60 bar and T_{full} = 80 K. 3/13
- Internal Flow-through HX: Report on ability to develop and demonstrate an internal flow-through heat exchanger system based on compacted media capable of allowing less than 3 minutes scaled refueling time and hydrogen release rate of 0.02 g_{H2}/s-kW with a mass less than 6.5 kg and volume less than 6 Liters. 3/13

Accomplishments and Progress – Hydrogen Refueling and Desorption Schemes for Cryo-Adsorbent Systems

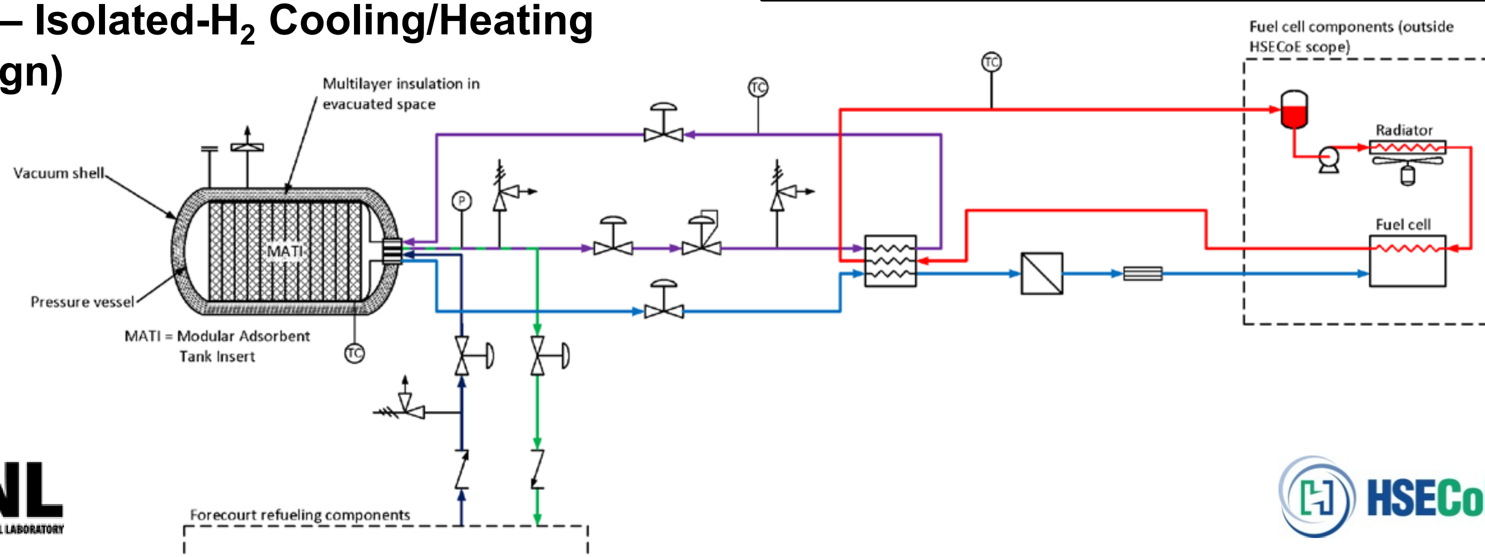
	Flow-through Cooling	Isolated LH_2 (or LN_2) Cooling
Resistance Heater	• Convection is most effective method of heat transfer • Models and initial testing shows great promise in powders • Very little permeability data • Resistance heaters are only 50% efficient • Thermal conductivity dominant	• Vaporization cooling is highly effective • Increased mass and volume • Resistance heaters are only 50% efficient • Thermal conductivity dominant
Isolated H_2 Heating	• Vaporization cooling is highly effective • Much higher efficiency than resistance heater • MATI • Very little permeability data • May have increased mass and volume • Thermal conductivity dominant	• Vaporization cooling is highly effective • Much higher efficiency than resistance heater • MATI • Very little permeability data • May have increased mass and volume • Thermal conductivity dominant

Accomplishments and Progress – Adsorbent System Designs

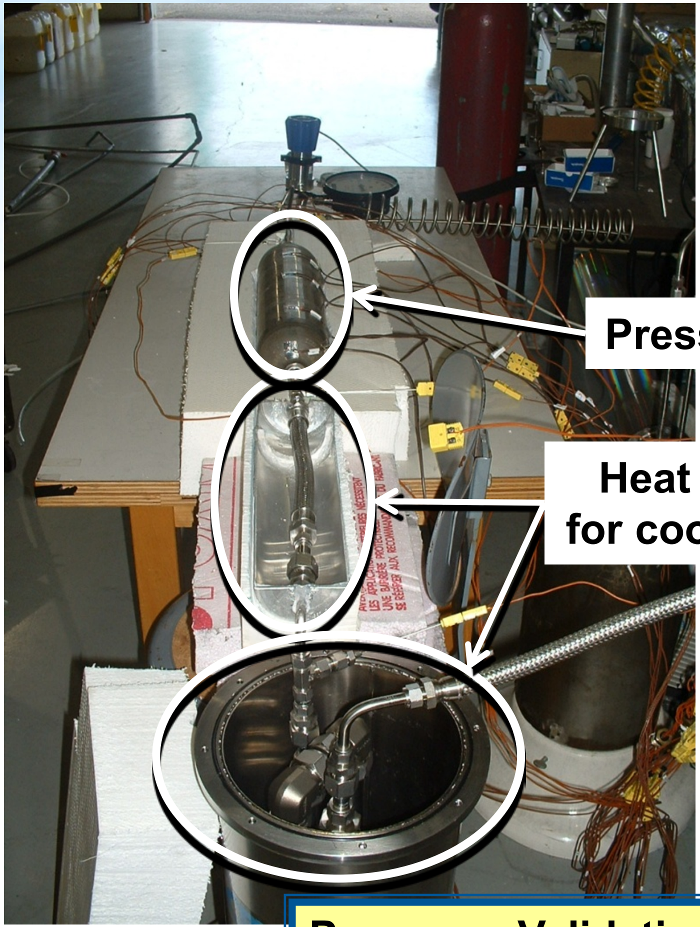
Design #1 – Flow-through cooling with a Resistance Heater

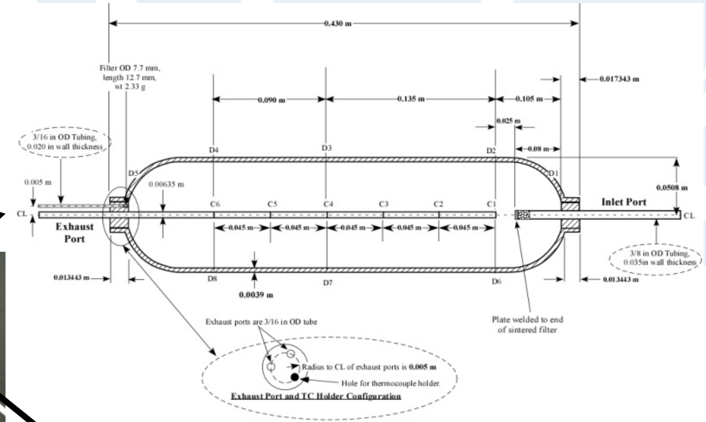


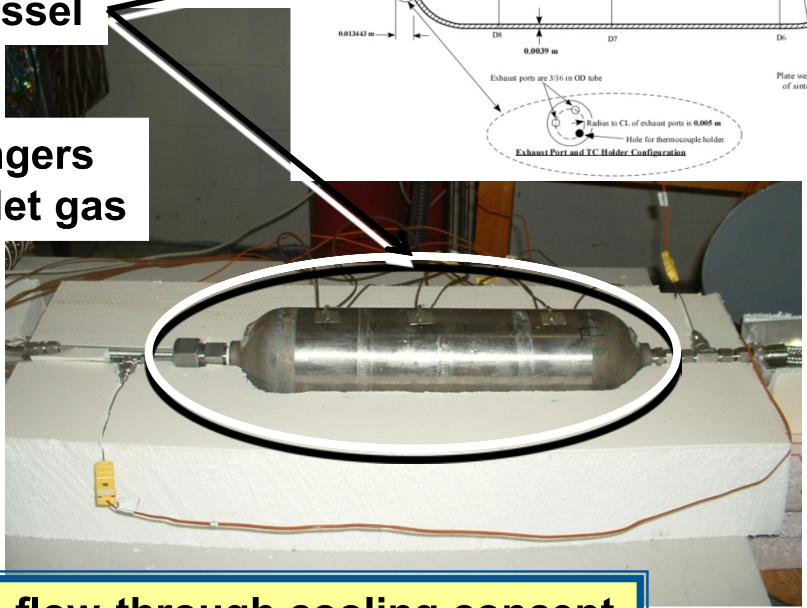
Design #2 – Isolated-H_2 Cooling/Heating (MATI design)



Accomplishments and Progress – Flow-Through Experiments







Purpose: Validation of the flow-through cooling concept

- ✓ Currently in preliminary stage
- ✓ Preliminary tests use same pressure vessel as for charging tests with granular activated carbon produced at UQTR
- ✓ Tests conducted with helium, nitrogen, and hydrogen

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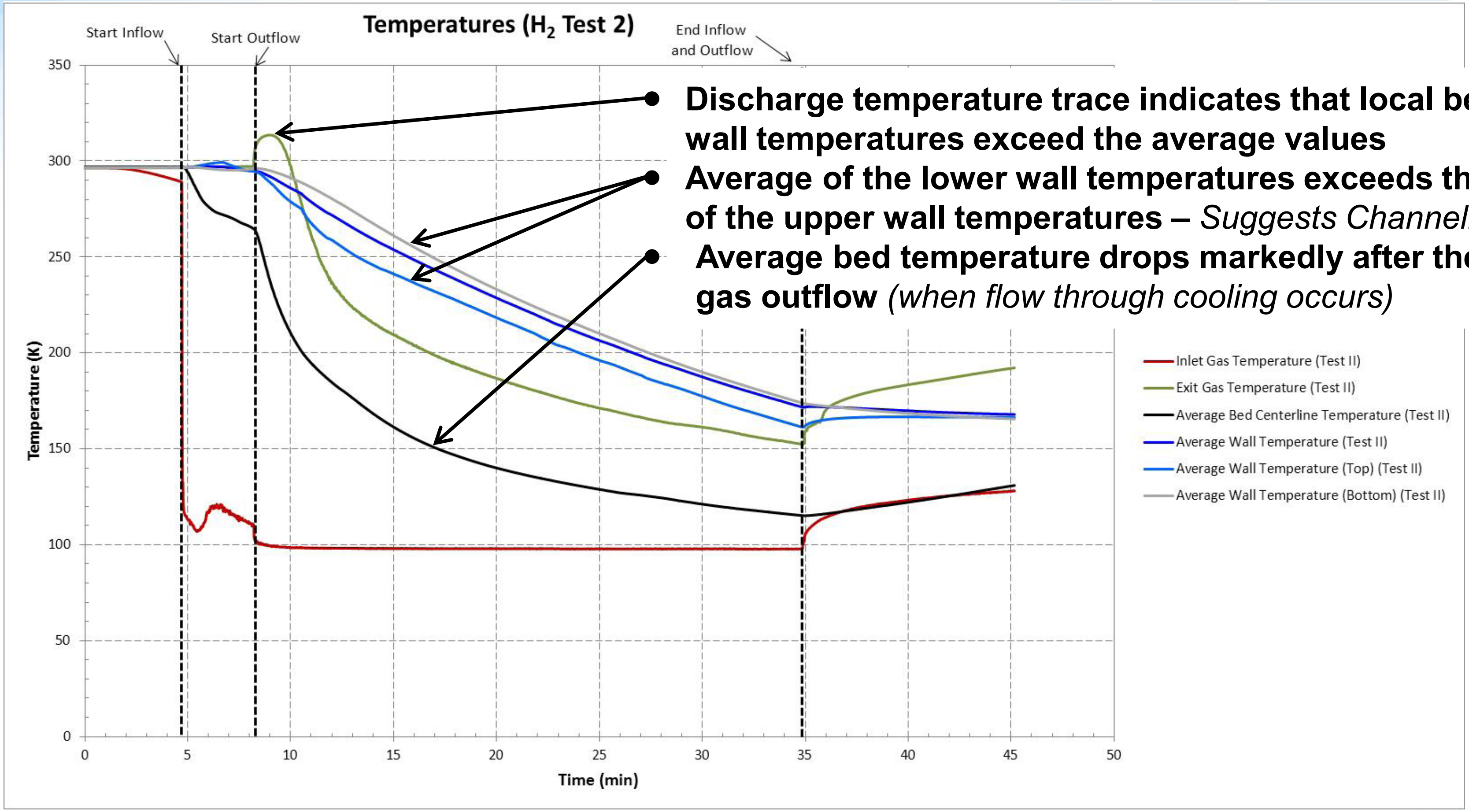
Accomplishments and Progress – Flow-Through Cooling Experimental Results: Averaged Temperatures



- **Discharge temperature trace indicates that local bed and/or wall temperatures exceed the average values**
- **Average of the lower wall temperatures exceeds the average of the upper wall temperatures –** *Suggests Channeling*
- **Average bed temperature drops markedly after the start of gas outflow** *(when flow through cooling occurs)*

Based on the average bed temperature, flow-through cooling has been experimentally shown to effectively cool a cryo-adsorbent hydrogen storage tank.

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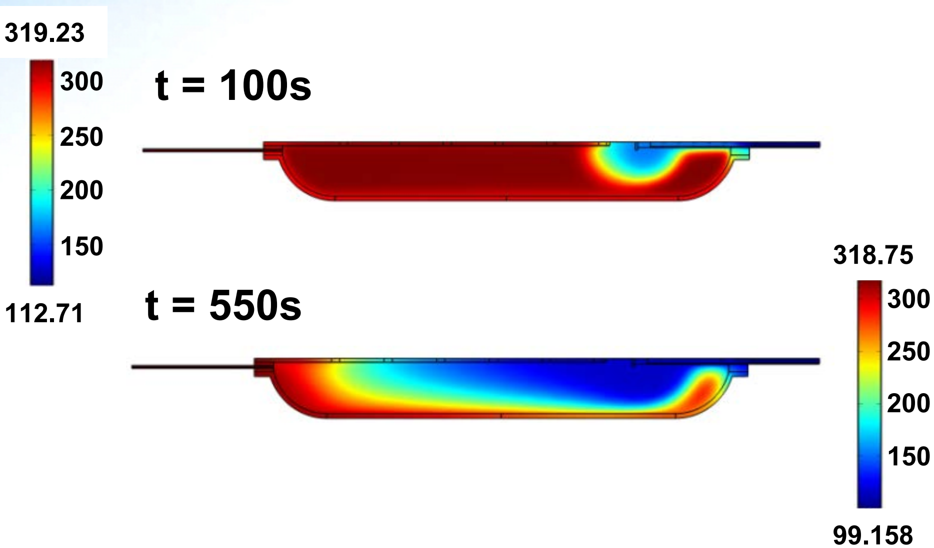
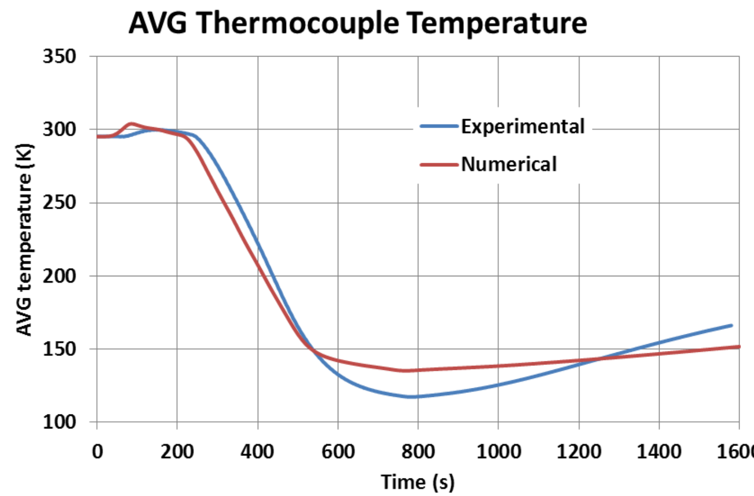
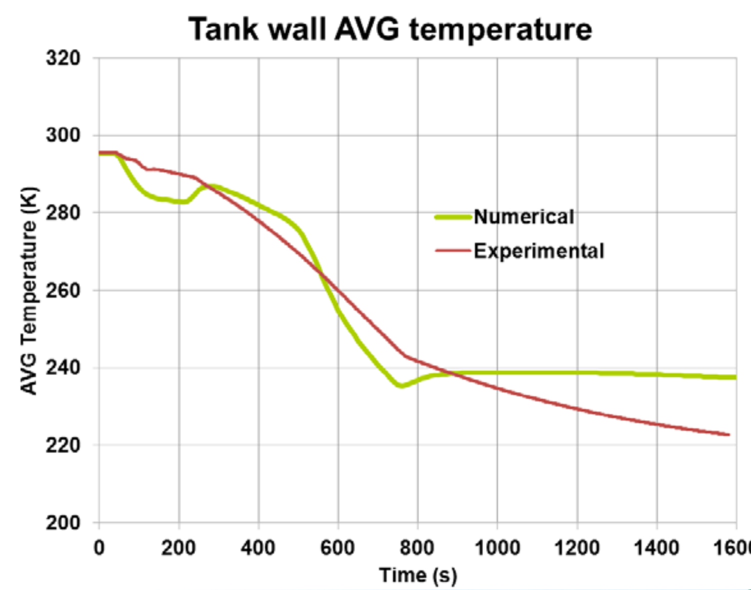
Accomplishments and Progress – Flow-Through Experiment Validation

Instantaneous Temperature Profiles





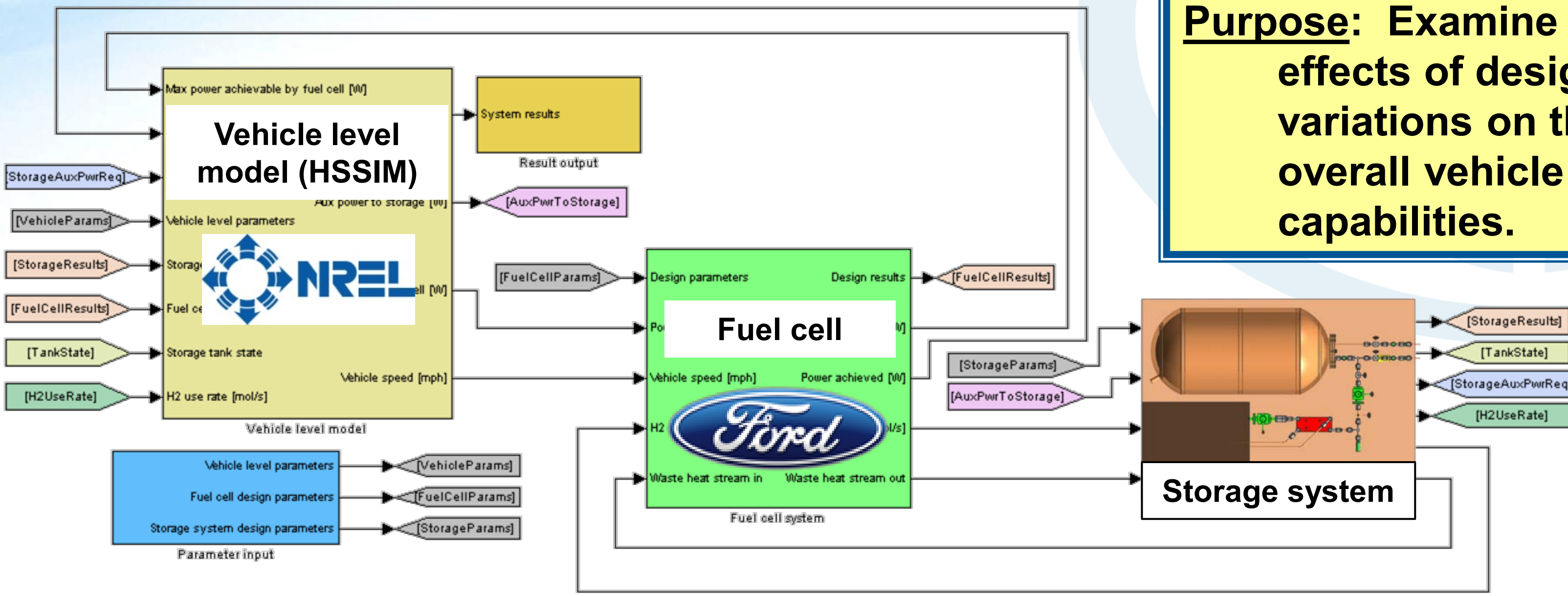


<u>Updated Platform to COMSOL 4.2a</u>

- **UQTR flow-thru models built**
  - **Aid in design of rig**
  - **Determination of flowrate and other operating parameters**
- **Extension to other designs / conditions**

- **Validation against measurements**

Accomplishments and Progress – Adsorbent System Models



Purpose: Examine the effects of design variations on the overall vehicle capabilities.

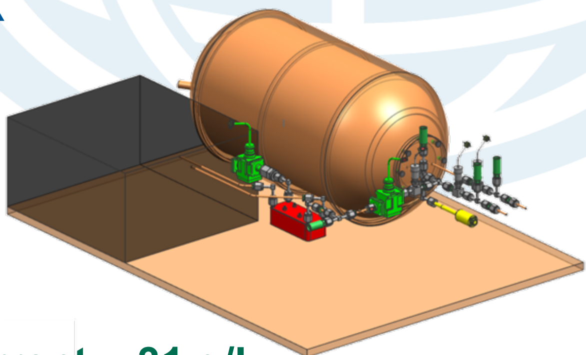
System Model Analysis Options:

- Operating Conditions:
  - ✓ 20 K < T < 450 K
  - ✓ 0.1 bar < P < 450 bar
- Cryo-adsorbent Media:
  - ✓ Activated Carbon / AX-21 / MaxSorb
  - ✓ MOF-5 Powder
  - ✓ Compacted MOF-5
  - ✓ Compacted MOF-5 with ENG
- Storage Vessel Options:
  - ✓ Type I Aluminum Tank
  - ✓ Type III Carbon Fiber Tank
- Internal Tank HX Designs:
  - ✓ Electric Resistance HX (Design #1 – Flow-Through cooling concept)
  - ✓ Isolated-H_2 HX (Design #2 –MATI)

Accomplishments and Progress – Cryo-Adsorbent System Model Results: Flow-Through Design Description

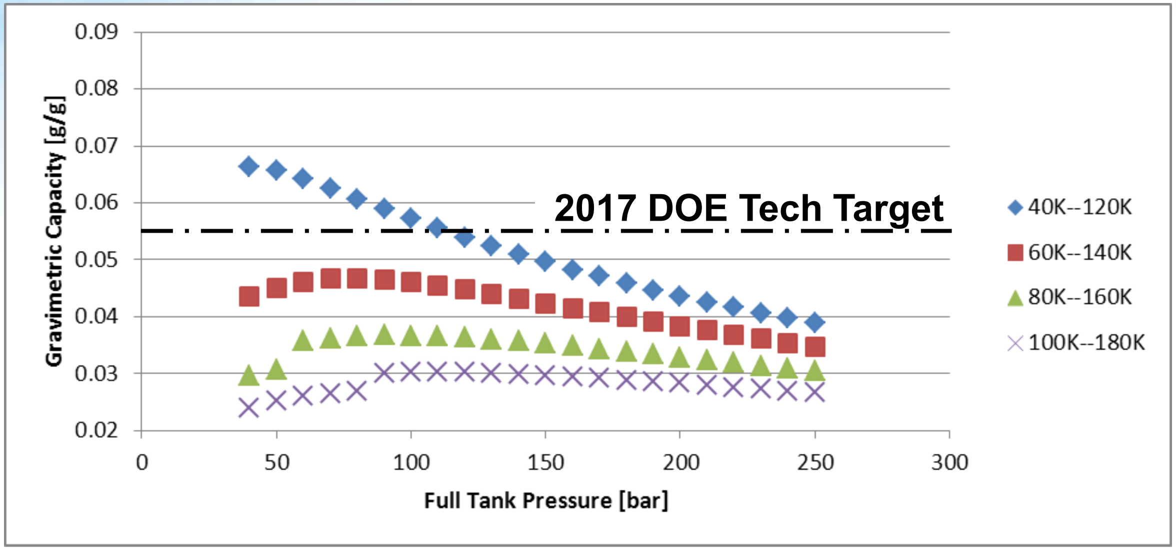
Design #1 – Flow-Through cooling with a Resistance Heater

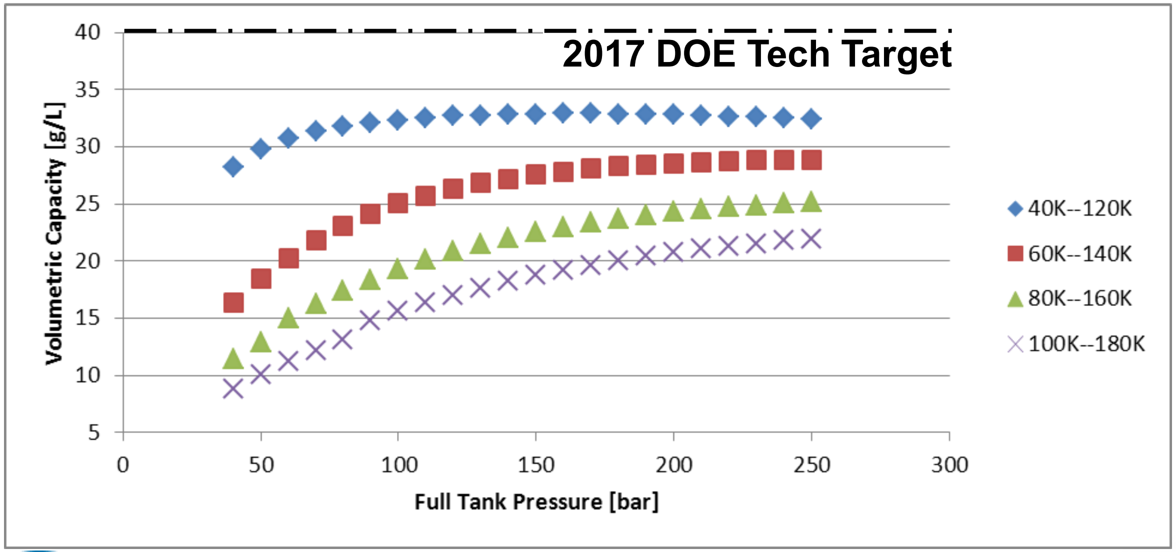
- Powder MOF-5 in a single, 2:1 (L to D) aluminum tank
- Flow-through cooling during refueling
- A resistance heater used during desorption (driving)
- Full tank conditions: 60 bar, 40 K
- Empty tank conditions: ~5 bar, 100 – 120 K
- Meets all 2017 DOE Technical Targets except:
  - Volumetric Capacity: Target = 40 g/L; Current = 31 g/L
  - WPP Efficiency: Target = 60%; Current = 40.1%
  - Loss of $H_{2,usable}$: Target = 0.05 g/hr/$kg_{H2stored}$ Current = 0.44 g/hr/kg
  - Cost: Target = "low cost" Current = "not low enough"



Adsorbent Media	System mass	System volume	Gravimetric Capacity	Volumetric Capacity
Powder MOF-5 (Composite Tank)	74.6 kg	180.6 L	0.0751 g_{H2}/g_{sys}	31.01 g_{H2}/L_{sys}
Powder MOF-5 (Aluminum Tank)	**87.3 kg**	**182.7 L**	**0.0641 g_{H2}/g_{sys}**	**30.66 g_{H2}/L_{sys}**
Powder MaxSorb / AX-21 / Activated Carbon	99.8 kg	206.6 L	0.0562 g_{H2}/g_{sys}	27.12 g_{H2}/L_{sys}

Accomplishments and Progress – Cryo-Adsorbent System Model Results: Variations in Operating Condition





- MOF-5 Powder
- Aluminum Type I Tank
- Temperature rise of ~80 K during operation
- Flow-through cooling during refueling
- Electric resistance heater for desorption

- Type I tanks are cost effective alternatives to Type III tanks at low pressure

- Lower temperature increases both gravimetric and volumetric capacities

- Higher pressures reduce* gravimetric capacity and increase volumetric capacity

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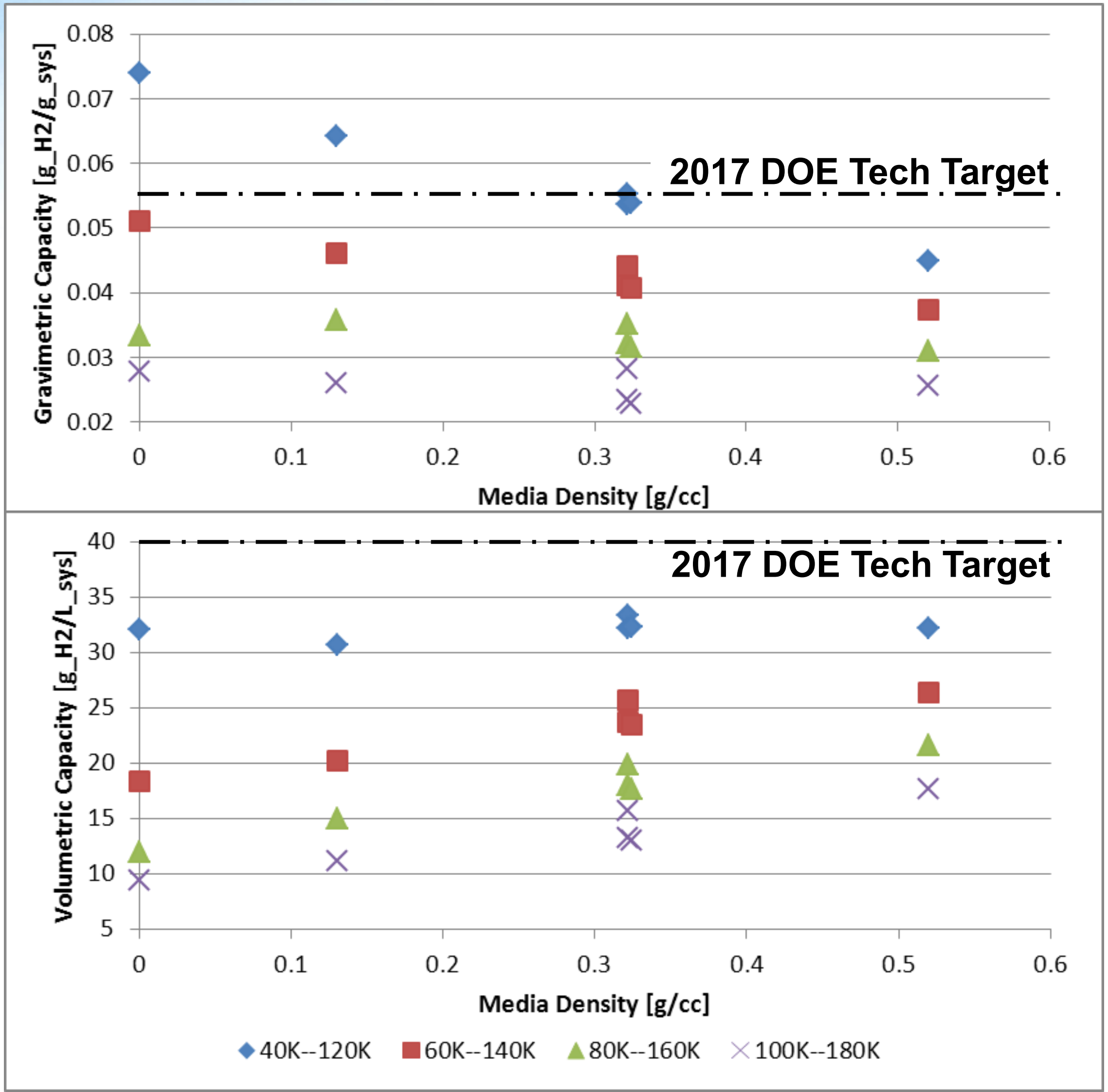
Accomplishments and Progress – Cryo-Adsorbent System Model Results: Variations in MOF-5 Density



- 60 bar full tank pressure
- Aluminum Type I Tank
- Temperature rise of ~80 K during operation
- Flow-through cooling during refueling
- Electric resistance heater for desorption
- "0" density corresponds to a comparable CcH_2 system

- Increasing density increases volumetric capacity and decreases gravimetric capacity
- All densified MOF-5 systems have better volumetric capacity than CcH_2
- Optimal level of compaction highly dependent on the design temperature and pressure of the vessel

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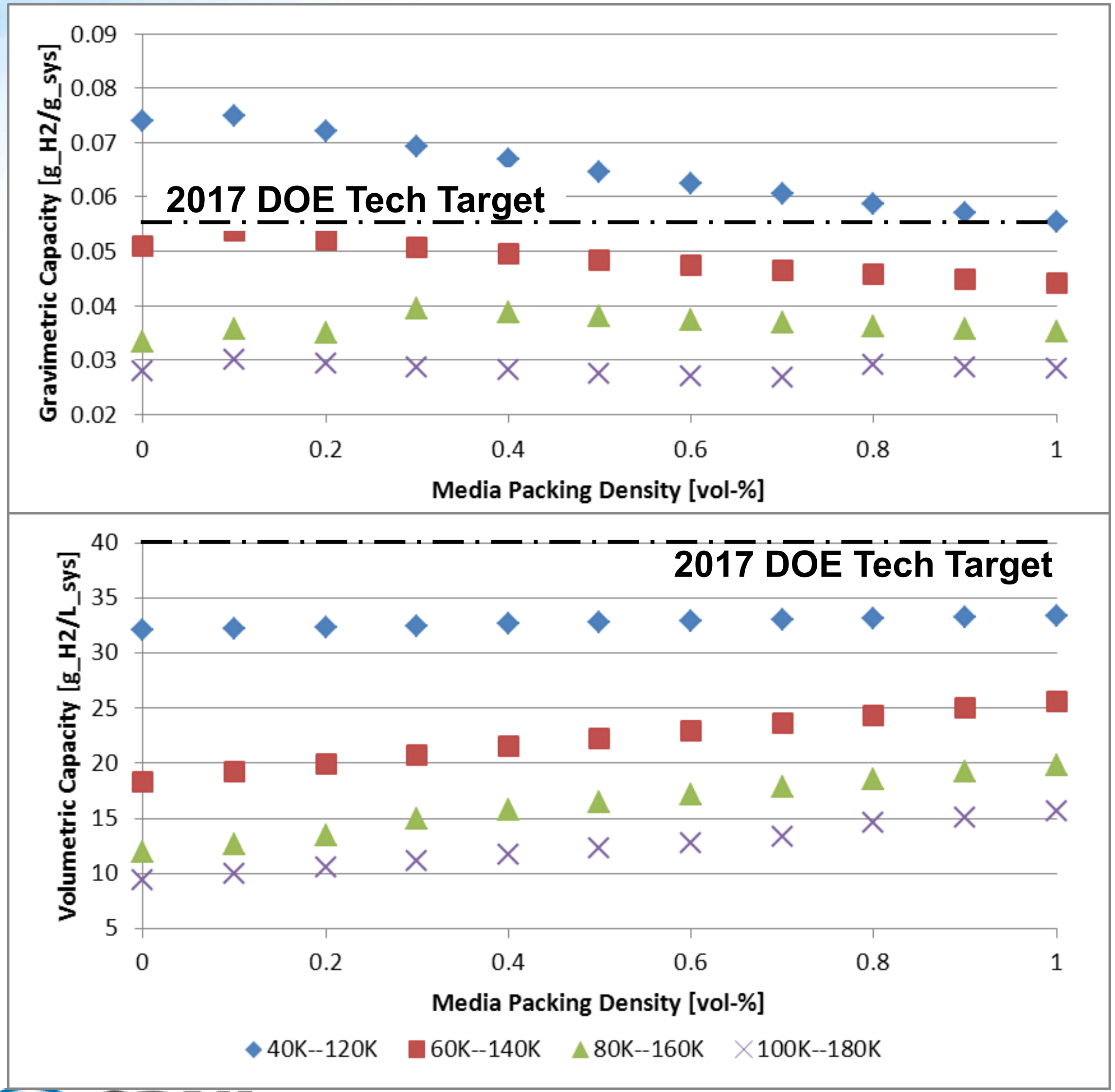
Accomplishments and Progress – Cryo-Adsorbent System Model Results: Variations in Media Packing Density

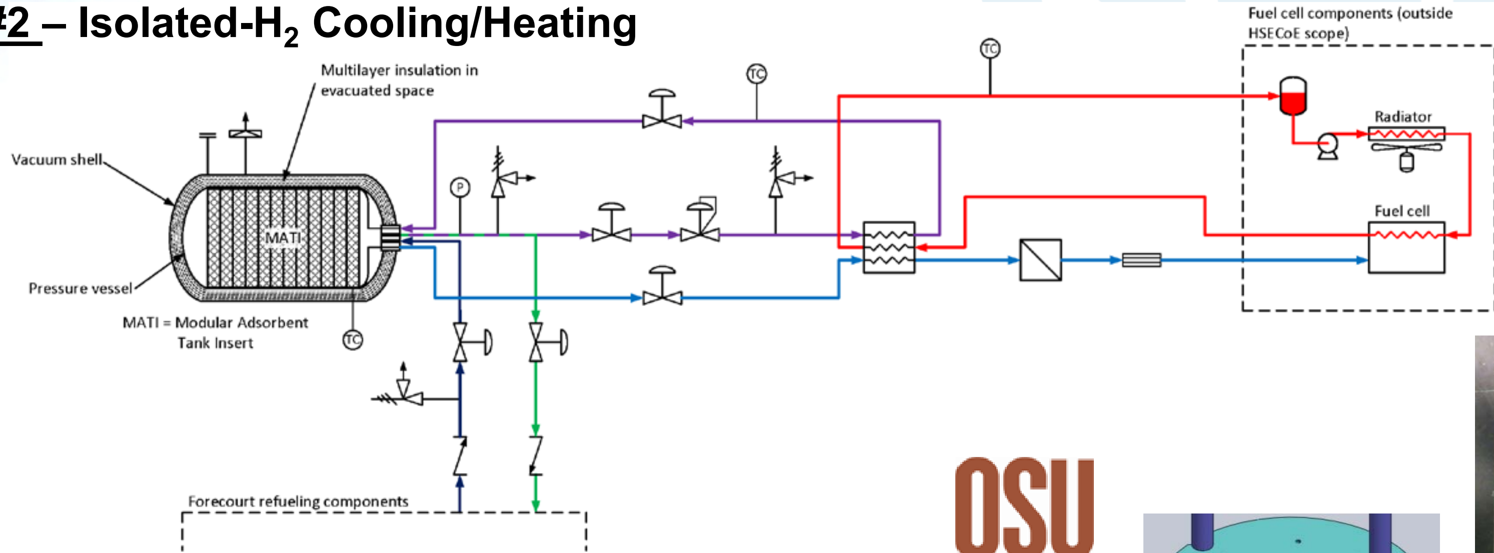


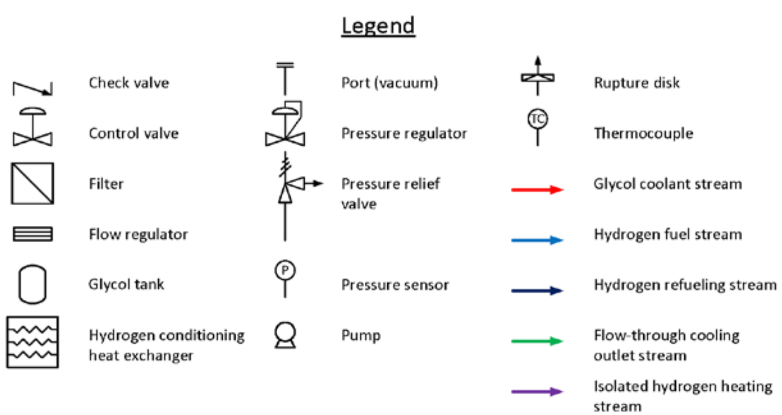
- 0.32 g/cc Compacted MOF-5
- 60 bar full tank pressure
- Aluminum Type I Tank
- Temperature rise of ~80 K during operation
- Flow-through cooling during refueling
- Electric resistance heater for desorption
- "0" density corresponds to a comparable CcH_2 system

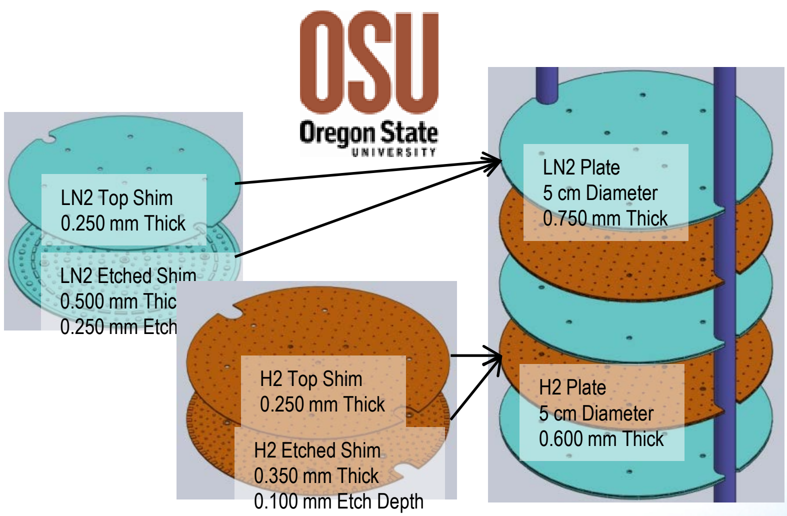
- **All compacted MOF-5 (0.32 g/cc) has higher volumetric capacity than the comparable CcH_2**
- **10% (volume) media packing density has higher gravimetric capacities than the comparable CcH_2**

Future Work – Cryo-Adsorbent System Designs: Modular Adsorption Tank Insert (MATI)

Design #2 – Isolated-H_2 Cooling/Heating







OSU's multi-module prototype will prove concept for system flow distribution, for separate hydrogen distribution and cooling plates, and determine if thermal stress induced failures occur.

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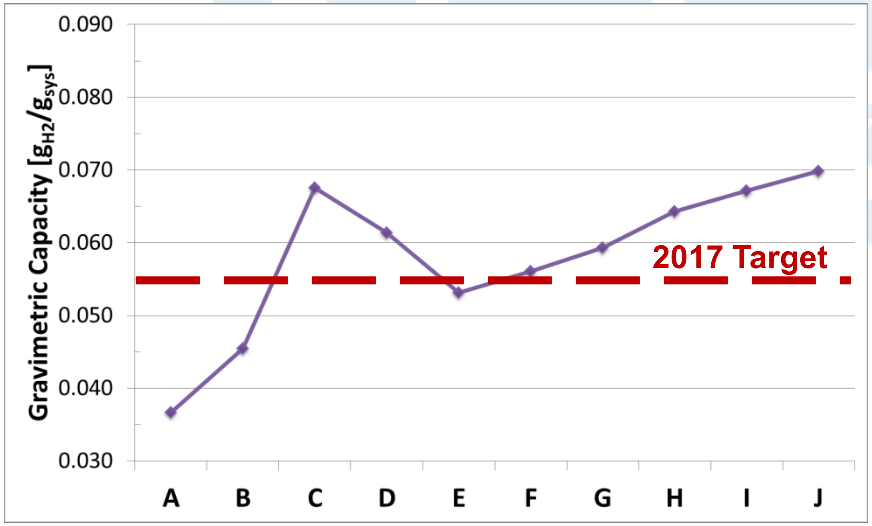
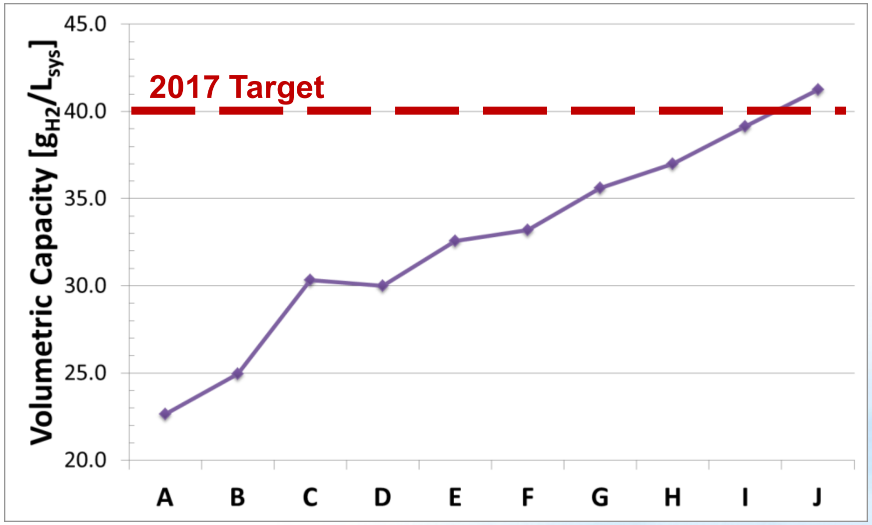
Future Work – Potential Improvements to Cryo-Adsorbent Systems

	Improvement Description	Grav. Cap.	Vol. Cap.
A	Phase 1 Baseline – Activated Carbon in a Composite Tank; Flow-Through Cooling with a Resistance Heater; Full Conditions of 80 K, 200 bar	0.03665 g_{H2}/g_{sys}	22.65 g_{H2}/L_{sys}
B	Material to Powdered MOF-5	24.0%	10.2%
C	Full Tank Conditions to 40 K, 60 bar	48.6%	21.5%
D	Tank to Type I Aluminum (lower cost)	-9.1%	-1.0%
E	Media to Compacted MOF5 (0.32g/cc)	-13.5%	8.6%
F	Increase Compacted MOF-5 thermal conductivity by an order of magnitude	5.5%	1.9%
G	Change from Flow-Through Cooling with a Resistance Heater to the MATI	5.8%	7.2%
H	Reduce mass and volume of BOP components by 25%	8.4%	3.9%
I	Improve material capacity by 10%	4.5%	5.8%
J	Improve material capacity by 20%	4.1%	5.4%





Future Work – Tasks

System Architect

- **SRNL Support for Adsorbent Based Systems**
  - Determine form of MOF-5 to be used in program
  - Assess new component and system designs
  - Select prototype configuration

UQTR preparing new test facilities for Phase 3 experiments

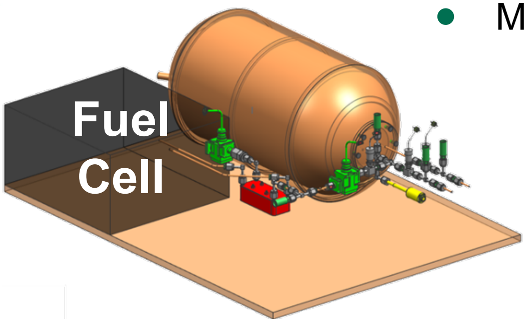
Experiments

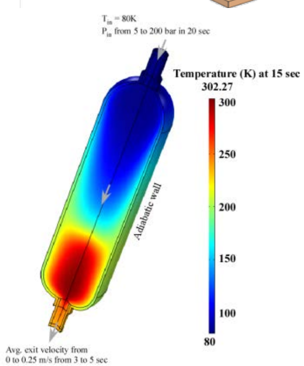
- **Small Scale Vessel**
  - Flow-through cooling
    - Apply to powder form and/or compacted MOF-5
      - *Level of compaction determined from models and small-scale experiments*
      - *Structured and random packing*
        - *Honeycomb lattice configuration proposed by UQTR*
    - Depending on material permeability a combination of novel heat exchanger concepts and flow through cooling my be required
    - Test heating concepts compatible with flow-through cooling design
      - *Resistance heating*
      - *Novel heat distribution concepts*
    - Conduct experiments specifically designed to aid in understanding physical behavior
  - MATI (performs heating and cooling function)
    - Concept validation
    - Possible addition of heat conduction enhancement to media
      - *Test selected heat transfer enhancement in actual charging experiment*
    - Application to both powder form and compacted MOF-5
      - *Decisions on tests are based on modeling work and small scale tests currently in progress*

Future Work – Tasks (continued)

Modeling

- **Validate, refine, and tune models based on experimental data**
  - Required for scale-up and prediction of performance (not possible to perform experiments for all operating scenarios
- **Optimize storage vessel with respect to the technical targets**
  - Operating efficiency
    - Minimize energy consumed during hydrogen & recycle process
      - *Minimize total enthalpy of discharge hydrogen for flow-through cooling*
        - *Requires control of total mass and average specific enthalpy of discharged hydrogen*
      - *Minimize heat generated by pressure work during charging*
      - *Use liquid nitrogen to pre-cool vessel wall during charging phase*
        - *Wall cooling is a major issue in cooling vessel*
      - *Reduce of effective thermal mass of the vessel wall*
    - Identify specific operational procedure to maximize dormancy
    - Develop suitable mechanism for heating adsorbent to effect hydrogen discharge
      - *Need to heat bed uniformly*
      - *Low thermal conductivity results in poor thermal penetration*
    - Determine thermal/depressurization scheme having minimal impact on dormancy
    - Address mass transfer resistance
      - *May be necessary for compacted media forms*
- **System model development**
  - Incorporate extended hydrogen property correlations
    - Supercritical and subcritical hydrogen
    - Include para-ortho conversion
  - Build model for cryo-compressed hydrogen storage for comparison





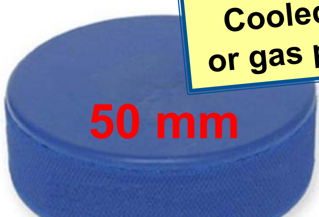
Future Work – Selection: MOF-5 Form, Tank, and Tank Internals / Heat Exchanger Design

Cooled by gas permeation or MATI

Powder Form

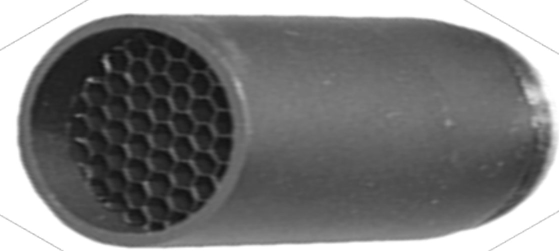
Cooled by gas flow over surface of pellets

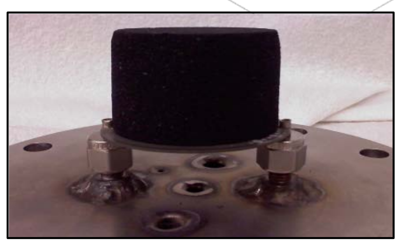
Pellet Form



Cooled by MATI or gas permeation

Large Compressed Form "Hockey Puck"





MOF-5 Form Selection:
- Powder Form
- Pelletized Form
- Large Compressed Form *(Hockey Puck)*
- ENG or other thermal enhancement

Tank Selection:
- Aluminum Type I
- Stainless Steel Type I
- Composite Fiber Type III
- Composite Fiber Type IV

Tank Internals / HX Selection:
- Resistance Heater
  - Fin and tube
  - Wire mesh
  - Hex-pack / Honeycomb
- MATI / Isolated-H_2 insert

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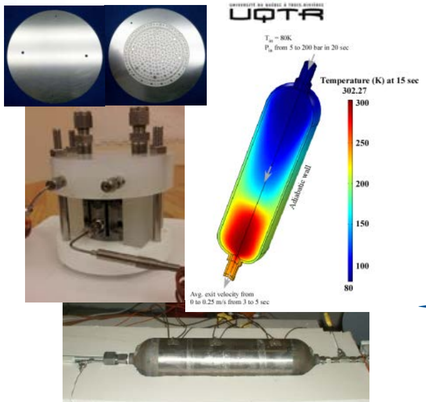
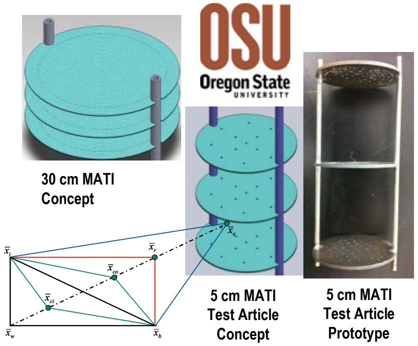
Collaborations

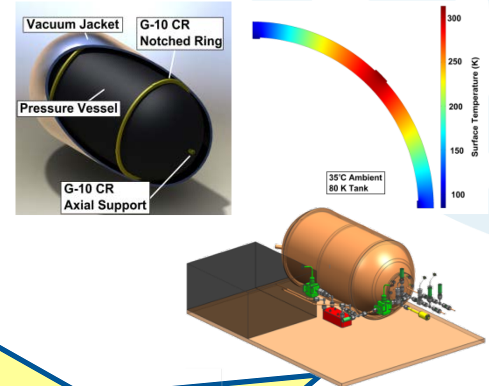
Adsorbent Prototypes: Design, Testing and Model Validation



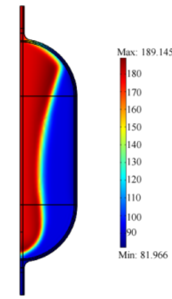
Modular Tank Insert: Optimization



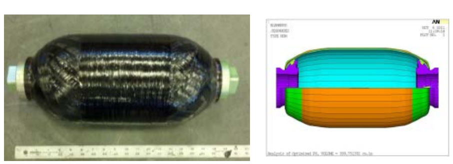
H_2 Flow and Heat Exchanger: Modeling and Analysis



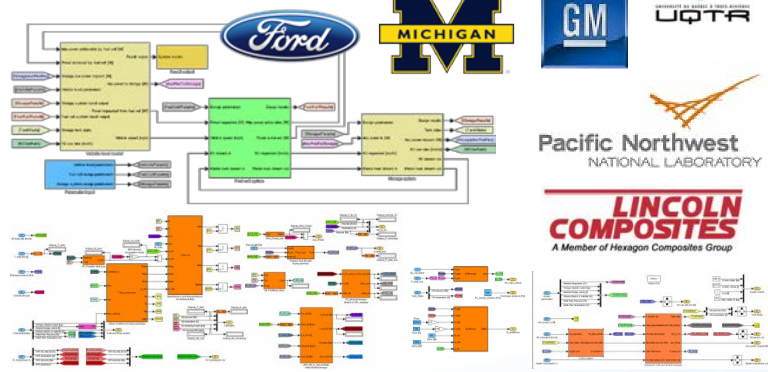
Flow-Through Heat Transfer Modeling



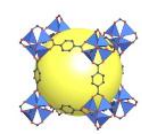
Pressure Vessel Properties and Wall Thicknesses



Metal Hydride and Adsorbent System Models



Compacted Media: Properties and Behavior



Project Summary

Relevance

As both the overall lead and a major technical contributor to the HSECoE project, SRNL is using its extensive expertise in thermodynamics, hydrogen materials compatibility, transport phenomena modeling & analysis, and hydrogen storage system & component design & fabrication to evaluate solid-state hydrogen storage systems for vehicle application that meet or exceed DOE's 2017 goals.

SRNL, through a subcontract grant, is also utilizing the expertise of the UQTR, which has been internationally recognized for its work in hydrogen adsorbent material and system development and testing.

Approach

In Phase II SRNL:

- Completed the MH System Architect analyses
- Provided analyses for the Phase 2 Go/No-Go decisions
- Investigated the viability of the flow-through cooling concept for adsorbent systems, from both modeling and experimental perspectives
- Developed and applied system models that determined hydrogen storage requirements and efficient media forms (compaction, structure, etc.

Technical Accomplishments and Progress (as of 3/12)

- UQTR, the subrecipient to SRNL, performed experiments to demonstrate flow-through cooling for adsorbent media
- SRNL validated detailed numerical models against UQTR flow-through data
- Developed external, publically accessible, web site and disseminated the metal hydride acceptability envelope and the metal hydride heat transfer model
- Used system models to identify suitable hydrogen refueling and desorption schemes for cryo-adsorbent systems
- Used system models to design adsorbent systems
- Identified optimal operation conditions for adsorbent system using MOF-5 or MaxSorb (including compacted forms)
- Evaluated media and gas thermodynamic properties required for modeling framework

Collaborations

HSECoE partners, Materials Centers, SSAWG, IPHE, IEA ; Griffith University, Brisbane, Australia

Proposed Future Work (remainder of Phase II and Phase III)

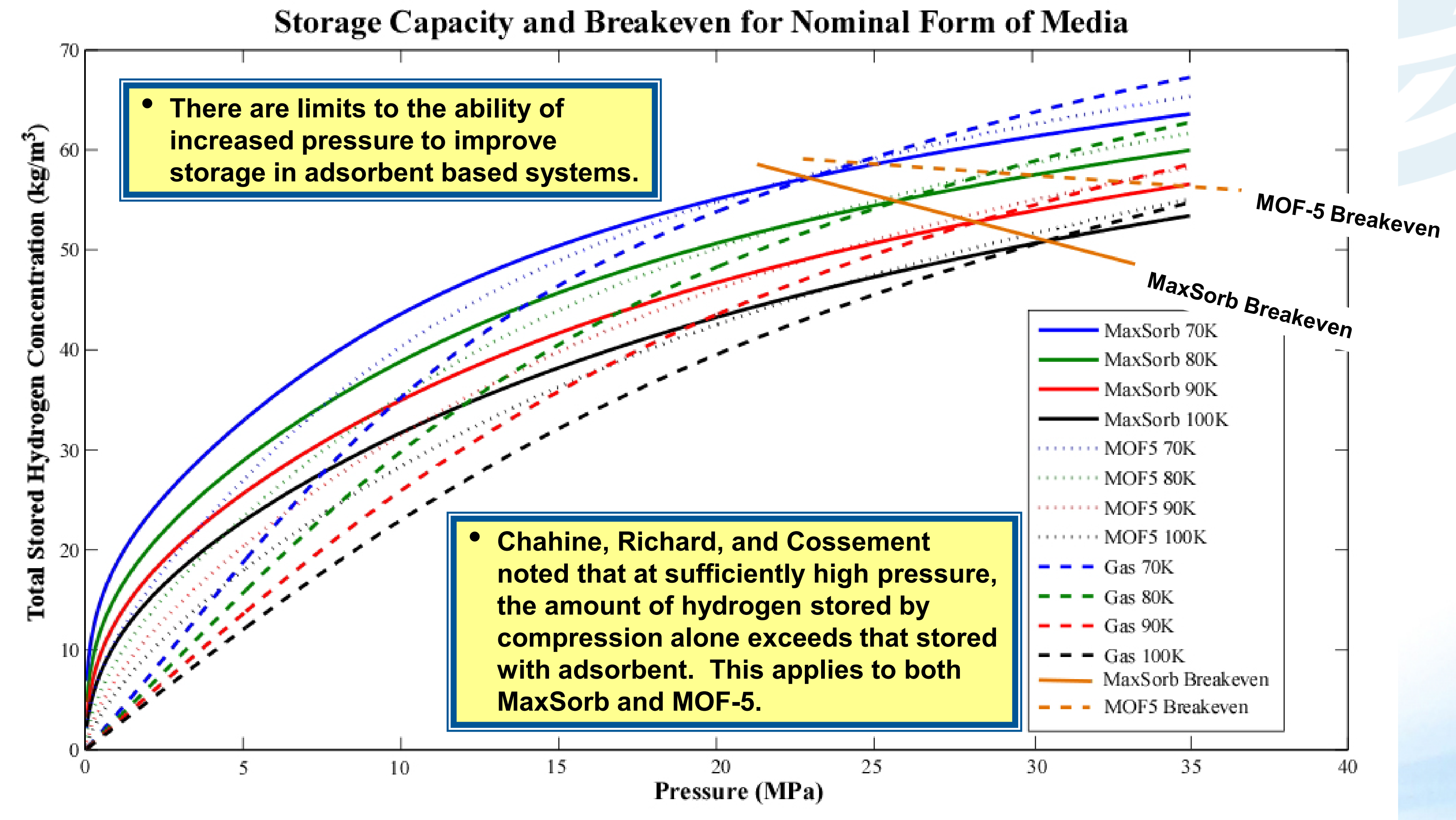
SRNL will:

- Examine the performance of the Modular Adsorption Tank Insert using the system models
- Validate, tune and refine the detailed models to make them applicable for scale-up and alternative applications of hydrogen storage technology
- Continue the flow-through cooling experiments, investigating MOF-5 in powder and compacted forms, as applicable
- Optimize the adsorbent system with respect to pressure work, enthalpy of hydrogen discharge flow, dormancy conditions and thermal interaction with the container wall
- Select an adsorbent, and form thereof, for use in the prototype
- Design the prototype and develop an experimental test matrix

Technical Back-up Slides

Accomplishments and Progress – Thermodynamic Considerations: Limits to Adsorbent Pressurization

- There are limits to the ability of increased pressure to improve storage in adsorbent based systems.



- Chahine, Richard, and Cossement noted that at sufficiently high pressure, the amount of hydrogen stored by compression alone exceeds that stored with adsorbent. This applies to both MaxSorb and MOF-5.

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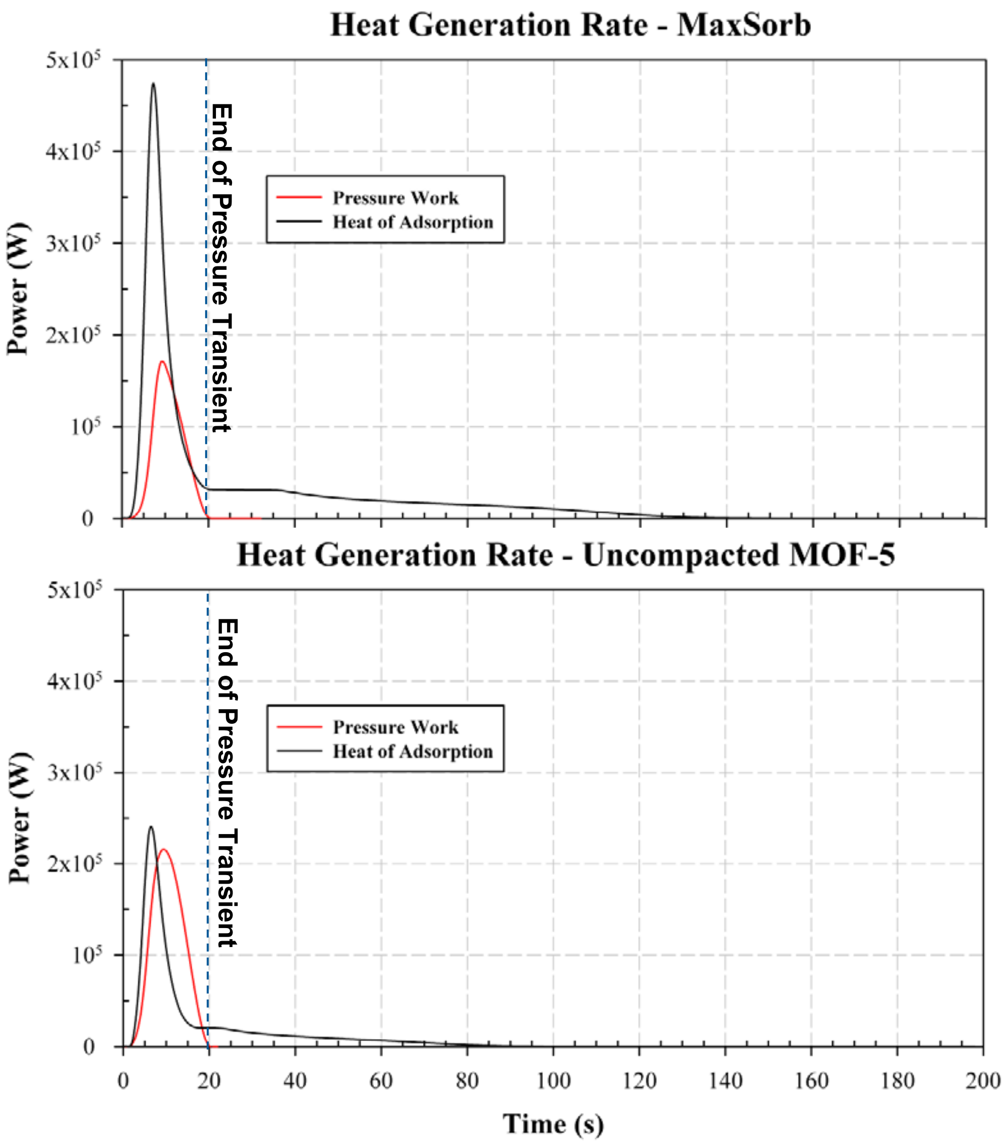
Accomplishments and Progress – Heat Dissipation During Charging



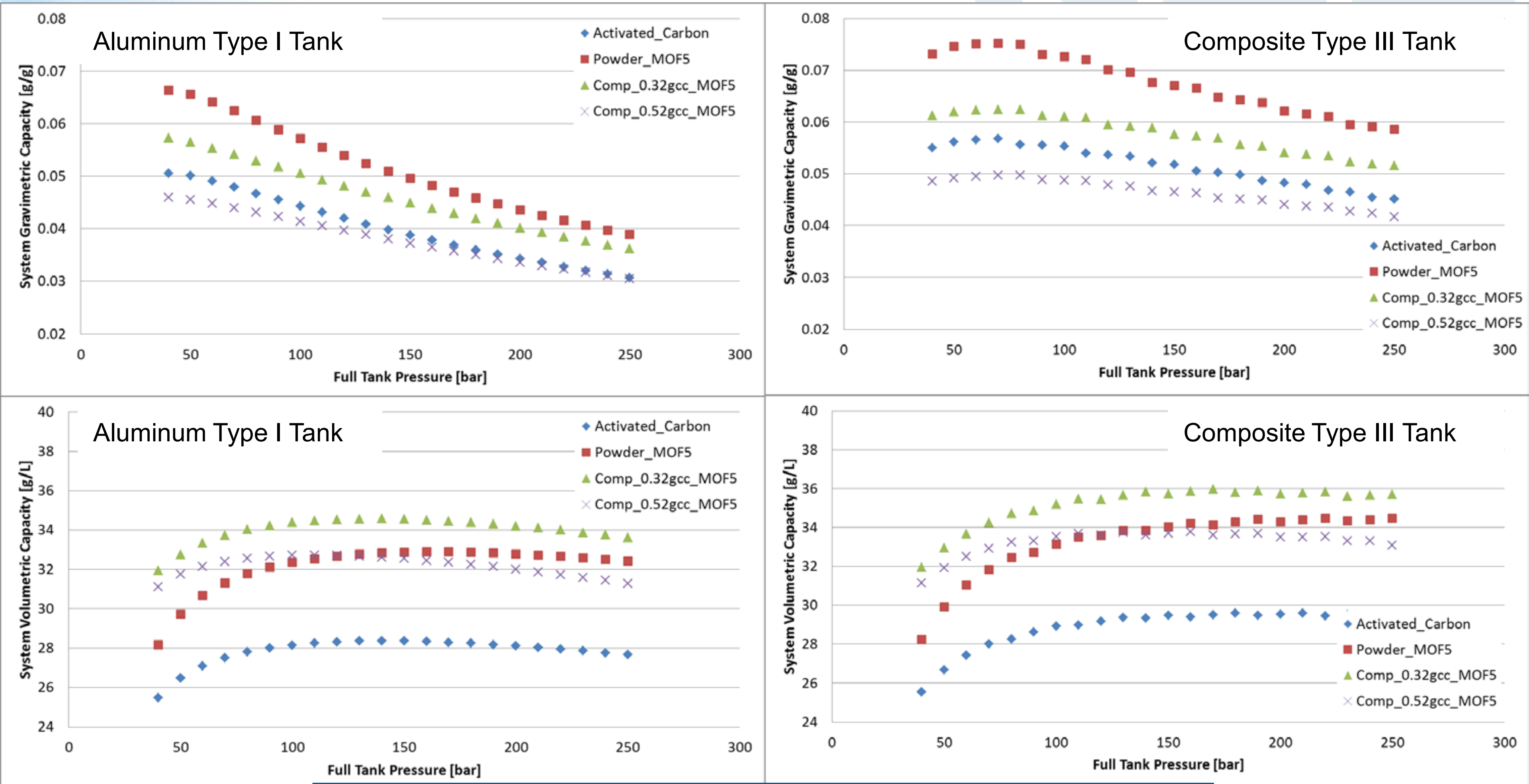
$$\text{Generation by Pressure Work} = -\varepsilon \frac{T}{c} \frac{\partial c}{\partial T} \frac{\partial P}{\partial t}$$

$$\text{Generation by Heat of Adsorption} = -\rho_{Ads}\left[\frac{\partial}{\partial t}\left(\Delta U_a + n_a u_0\right) - h\frac{\partial n_a}{\partial t}\right]$$

	Total Pressure Work (MJ)	Total Heat of Adsorption (MJ)
MaxSorb	1.39	4.81
MOF-5	2.03	2.14

- **Difference in pressure work is due to different porosities**
- **Pressure work is more important for MOF-5 because it is approximately equal to the heat of sorption**

Accomplishments and Progress – Tank Design Comparisons for Several Material Forms at T_{full} = 40 K, T_{empty} ≈ 120 K



- **Type I and Type III tanks have comparable volumetric capacities.**
- **Type III tanks have better gravimetric capacities.**

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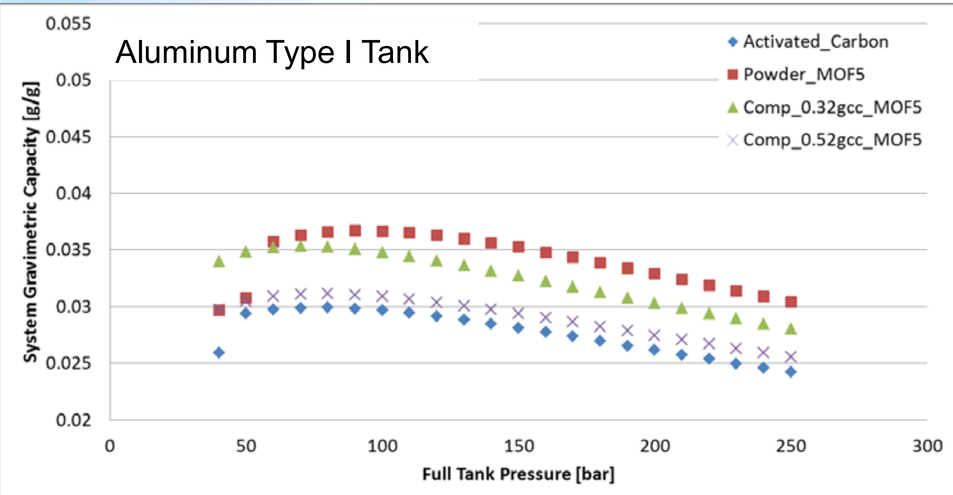
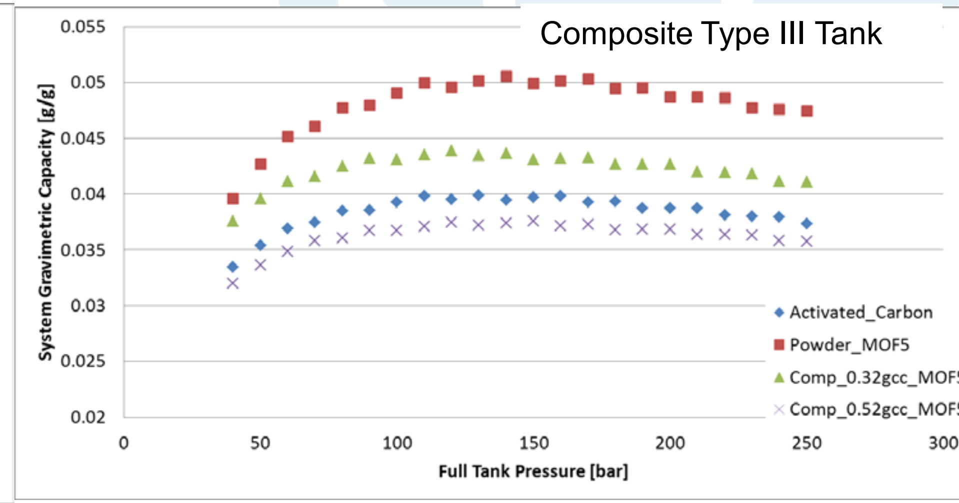
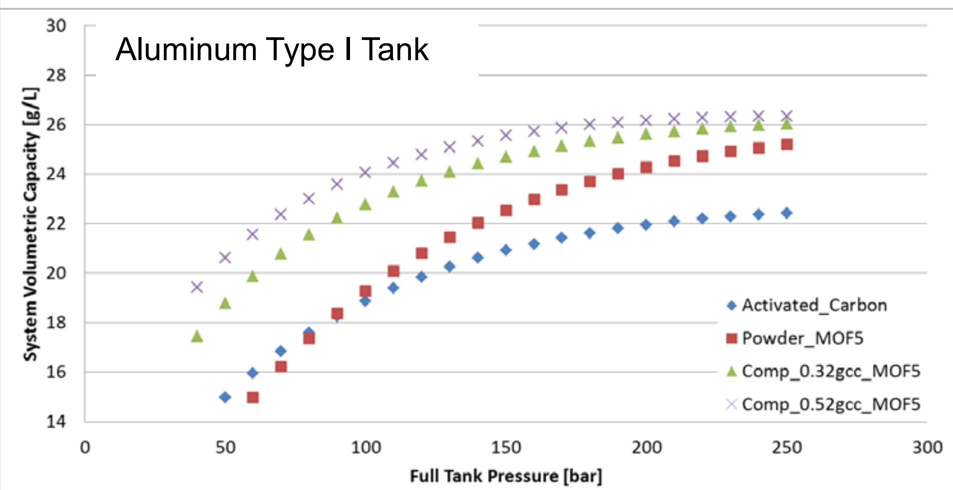
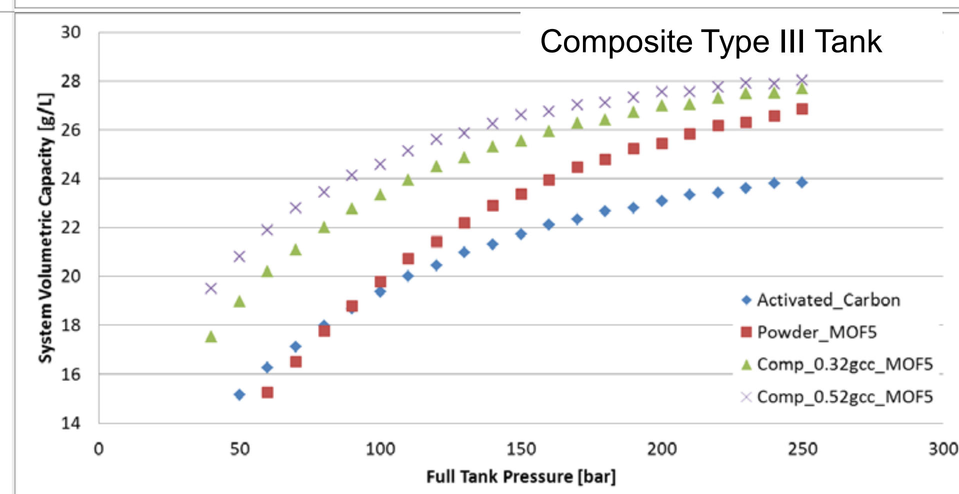
Accomplishments and Progress – Tank Design Comparisons for Several Material Forms at T_{full} = 80 K, T_{empty} ≈ 160 K









- **Type I and Type III tanks have comparable volumetric capacities.**
- **Type III tanks have better gravimetric capacities.**

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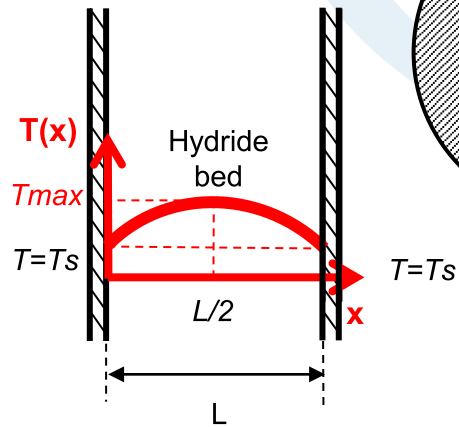
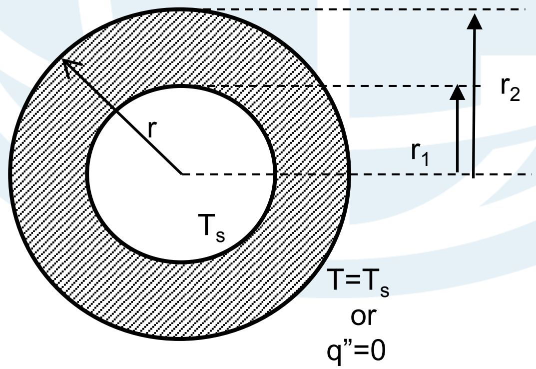
Accomplishments and Progress – MH Acceptability Envelope (Now Also Available on the Web)

- **Acceptability Envelope = "BlackBox Analysis"**
  - Based on energy balance
  - Relates characteristics of media and system to storage system performance targets
  - Combined with DOE Technical Targets, it serves as media screening tool
    - Guide for material development
    - Defines acceptable media & storage vessel parameter ranges
  - Assumptions:
    - 1D heat transfer process
      - *Rectangular (RC) and Cylindrical coordinates (CC)*
    - Steady state process during charging time
    - Constant thermal conductivity inside bed
    - Negligible convective heat transfer
    - Negligible compression or expansion work





$$\Delta T = \frac{L^2 \cdot \rho_{Bed} \cdot \frac{\Delta H_{overall}}{MW_{H_2}} \cdot \frac{\Delta M_{H_2}}{\Delta t}}{m \cdot k_{eff} \cdot M_{Hydride}}$$

$$\Delta T = T_{\max} - T_{\min}$$

Cylindrical

$$L^2 = r_1^2 - r_2^2$$

$$m = 8$$

Rectangular

L= (fin spacing)

$$m = 4$$

L	**Distance between heat transfer surfaces (m)**
ΔT	**Temperature range required for acceptable chemical kinetics (to give specified charge/discharge rate) (K)**
$\Delta H_{overall}$	**Overall heat of reaction (kJ/mol H_2)**
ρ_{Bed}	**Hydride bed density (kg/m^3)**
k_{eff}	**Effective bed thermal conductivity (W/m K)**
$M_{Hydride}$	**Mass of hydride required to load target amount of hydrogen (kg)**
MW_{H_2}	**Molecular Weight of Hydrogen (kg H_2/mol H_2)**
$\frac{\Delta M_{H_2}}{\Delta t}$	**Rate of charging/discharging (kg H_2/s)**

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