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

Design and Testing of Adsorbent Storage

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Savannah River National Laboratory

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Hydrogen Storage Engineering
CENTER OF EXCELLENCE

Project ID#ST044

Overview

Timeline

- Start: February 1, 2009
- End: September 30, 2015
- 90% Complete (as of 3/1/14)

Budget*

- FY13 Funding: $1,030,000
- FY14 Funding: $1,400,000
- Total DOE Project Value $10,180,000

* Includes $240,000 for the Université du Québec à Trois-Rivières (UQTR) as a subrecipient for FY13/FY14 and funding for SRNL's activities for HSECoE management.

Barriers

- A - System Weight and Volume
- C - Energy Efficiency
- E – Charging/Discharging Rates

Partners

SRNL, United Technologies Research Center, OSU Oregon State University, Los Alamos National Laboratory, GM, Hexagon Lincoln, Michigan, Pacific Northwest National Laboratory, Ford, HRI UQTR, NREL National Renewable Energy Laboratory, BASF The Chemical Company, JPL, California Institute of Technology

Relevance: Project Objectives

Phase 3: 2013-2015

- Design, fabricate, test, and decommission the **subscale prototype systems** for adsorbent storage materials. **In Progress**
- Validate the detailed and system model predictions against the subscale prototype system to **improve model accuracy** and **predictive capabilities**. **In Progress**

Approach: FY2013 / FY2014 Milestones

SMART Milestones for SRNL/UQTR:

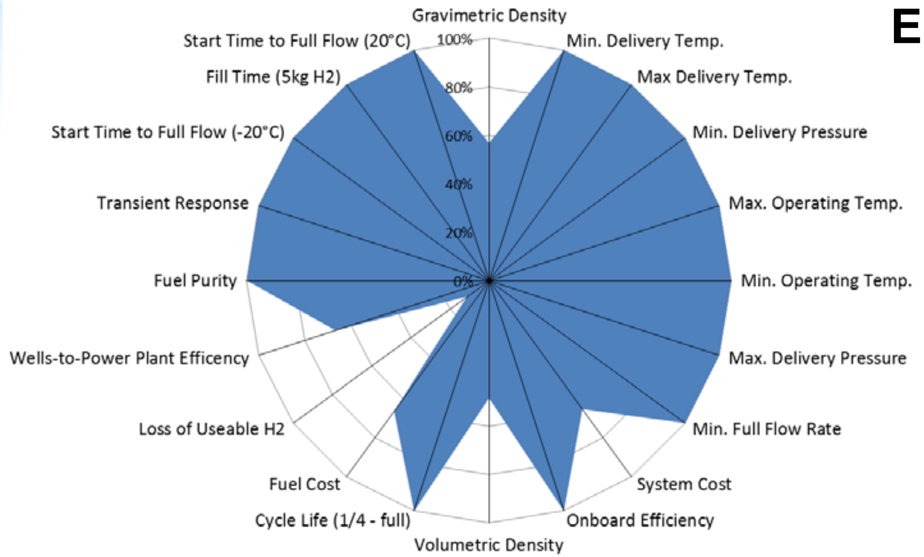
- Design and construct a hydrogen cryo-adsorbent test station capable of evaluating the performance of a two liter cryo-adsorbent prototype operating between 80-160K, which would meet all of the performance metrics for the DoE Technical Targets for On-Board Hydrogen Storage Systems. In Progress
- Design a 2L adsorbent subscale prototype utilizing a hex-cell heat exchanger storing 46g of available hydrogen, internal capacities of 0.13g/g gravimetric, and 23.4g/L volumetric. Complete, Assembly in Progress
- Update the cryo-adsorbent system model with Phase 3 performance data, integrate into the framework; document and release models to the public. Joint effort with NREL, PNNL, UTRC and Ford. In Progress, Some Models Released

Transport Phenomena Technology Milestones for SRNL/UQTR:

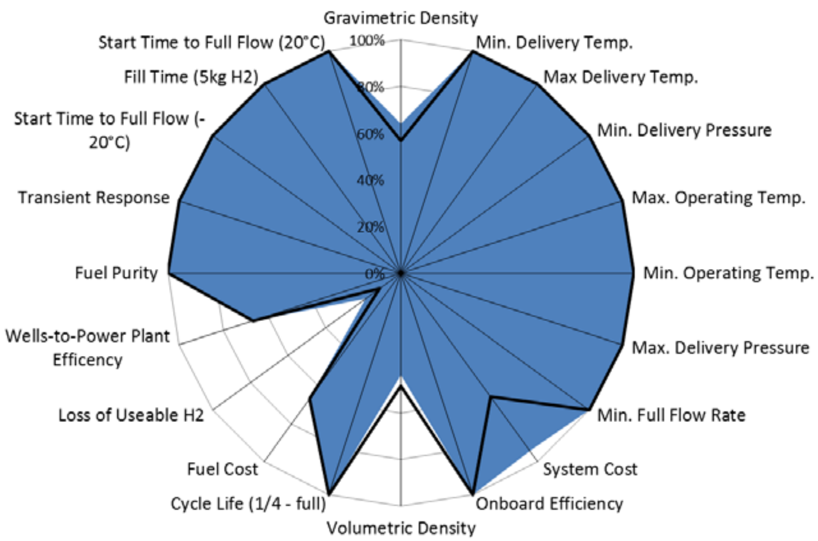
1. Refine the detailed models for scaled-up and alternative H_2 storage applications. Complete
2. Continue the FT cooling experiments, investigating MOF-5 powder, pellet, and compacted forms. Employ various HX concepts as applicable. Complete
3. Optimize the adsorbent system with respect to pressure work, enthalpy of H_2 discharge flow, dormancy conditions, and thermal interaction with the container well. Complete
4. Select an adsorbent, and form thereof, for use in the Phase 3 prototype. Complete - Selected MOF-5
5. Final design of a 2L hex-cell sub-scale adsorbent system. Complete
6. Complete test matrix for evaluation of the 2L hex-cell sub-scale adsorbent system. In Progress
7. Model validation for 2L hex-cell model against experiments. In Progress
8. Design, assemble and perform preliminary tests with the MATI heat exchanger. Design in Progress

Accomplishments: Performance With Respect to DOE Targets

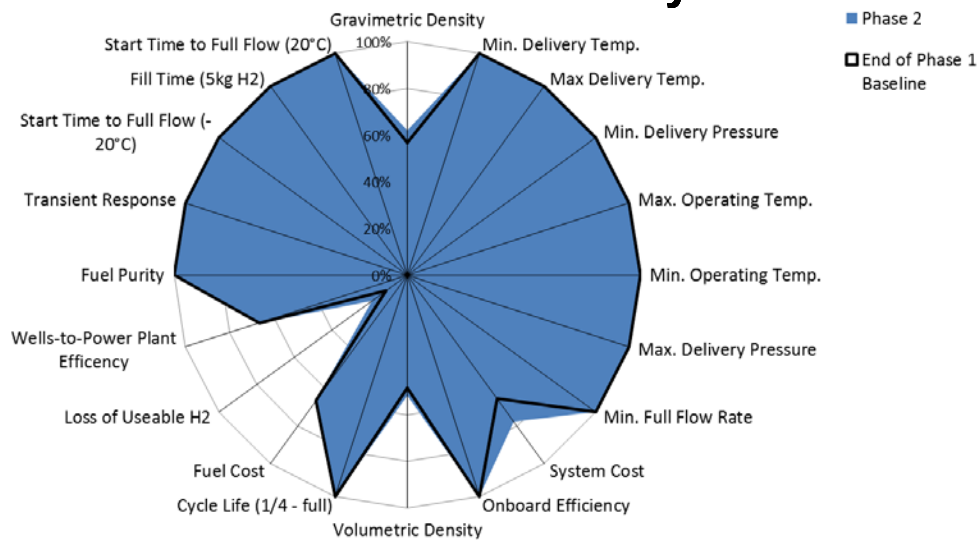
End of Phase 1



End of Phase 2 Hex-Cell System



End of Phase 2 MATI System



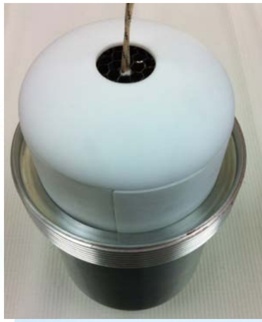
Accomplishments: UQTR/SRNL Charging and Discharging Experiments

- **Component level experiments for MOF-5 charging and discharging were conducted at UQTR**
  - 0.5L vessel with hex-cell heat exchanger
  - Flow through cooling was used for the charging process
  - Heating via a resistive rod was used for the discharge process
- **Phase III experimental components are being assembled at UQTR**
  - 2L vessel with hex-cell heat exchanger
  - Test plan is in preliminary form
- **Models developed/applied by SRNL replicate the experimental conditions**
  - Purpose is validation of models against data to ensure predictive capability
    - Verify that physical processes are properly included/represented

Accomplishments: Chronology of UQTR Experiments

- **Small scale (0.5L vessel) experiments and models**
  - Purpose was to investigate component performance and validate models
  - MOF-5 flow-through cooling (charging) experiments
    - Discussed at previous AMR
  - Heating (discharge) experiments
    - Rig assembly – leak tests, heater behavior/characterization, hex-cell assembly
    - Tests with empty hex-cells
    - Tests with alumina filled hex-cells
    - Tests with MOF-5 powder
  - Model validation

- **Prototype (2L vessel) experiments and models**
  - Design and assemble:
    - Vessel and internal components
    - System components and test stand
  - Develop test Matrix
  - Conduct preliminary experiments and tests
  - Model validation



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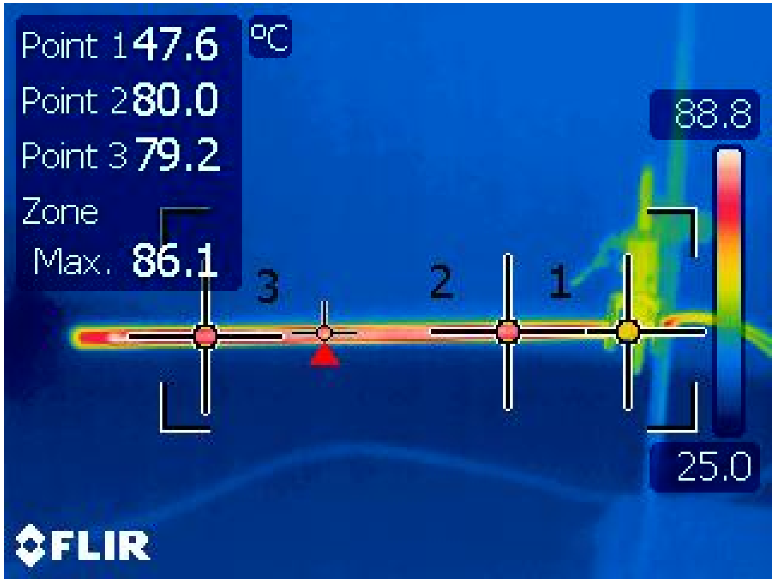
Accomplishments: Example of Component Issue

Power Distribution in Heating Cartridge and Redistribution by Hex-Cells

Heating Rod

Manufacturer	**Watlow®**
Max Power	**100 W**
Diameter	**0.6 cm**
Total Length	**25.4 cm**
(26.5 cm including connectors)	
Heated Length	**25.4 cm**



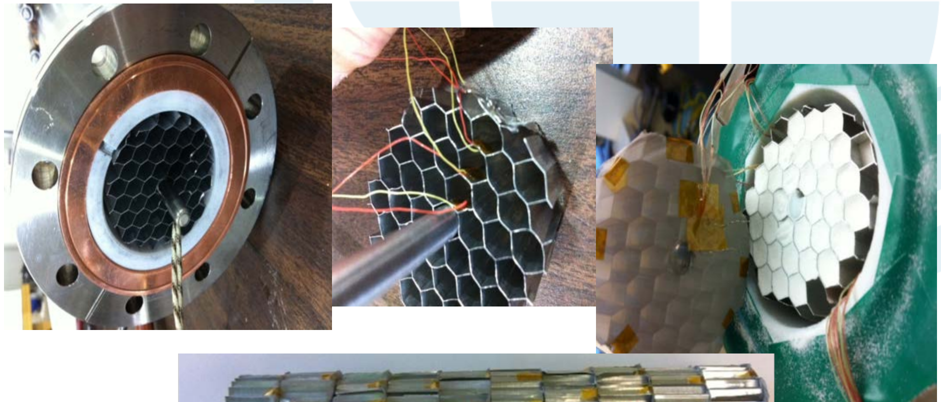
Hex-Cells

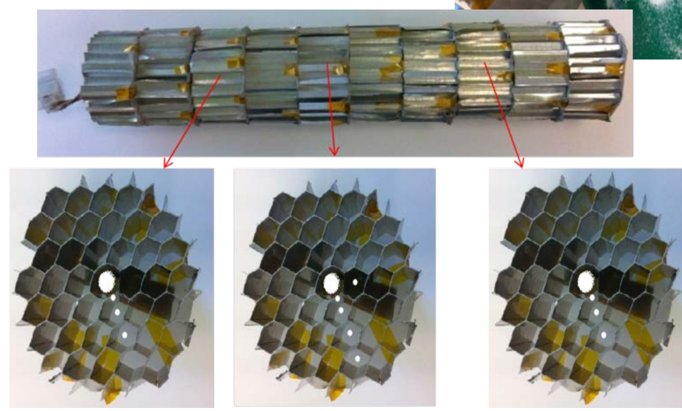
Manufacturer	**Plascore ®**
Flat-Flat distance	**0.6 cm**
Wall thickness	**0.01 cm**
<u>0.5 L Vessel</u>	
Section length	**2.54 cm**
Total length	**25.4 cm (10 sections)**
<u>2 L Vessel</u>	
Section length	**10.0 cm**
Total length	**20.0 cm (2 sections)**

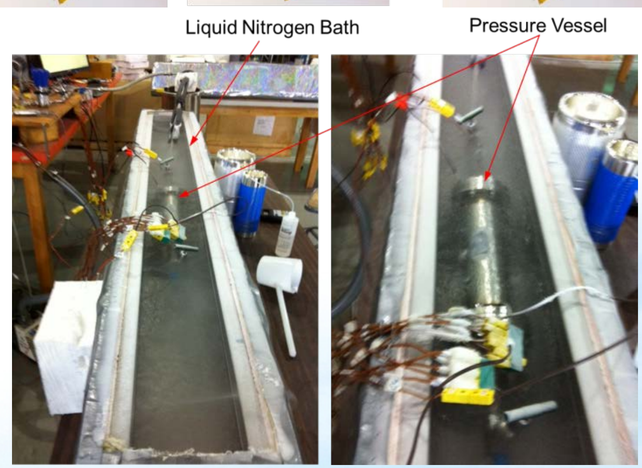
- Heating rod exhibits non-uniform power distribution
- Need to address in data evaluation & models
- Need to determine if hex-cell HX distributes thermal energy so rod can be approximated as having uniform or parabolic power

Accomplishments: 0.5L Hex-Cell Vessel Heating/Discharge Experiments

- **Empty hex-cells, no flow**
  - Vacuum
    - *Room temperature at surface*
  - 2.5 MPa hydrogen initially
    - *Room temperature and 77K at surface*
- **Filled hex-cells**
  - Alumina powder
    - *2.5 MPa hydrogen initially*
    - *No flow*
  - MOF-5
    - *3.5 MPa hydrogen initially, room temp at surface, no flow*
    - *3.5 MPa hydrogen initially, 77K at surface, no flow*
    - *5.6 MPa hydrogen initially, 77K at surface, hydrogen outflow between 0 and 100 slpm**
    - *6.5 MPa hydrogen initially, 77K at surface, hydrogen outflow 25 slpm**



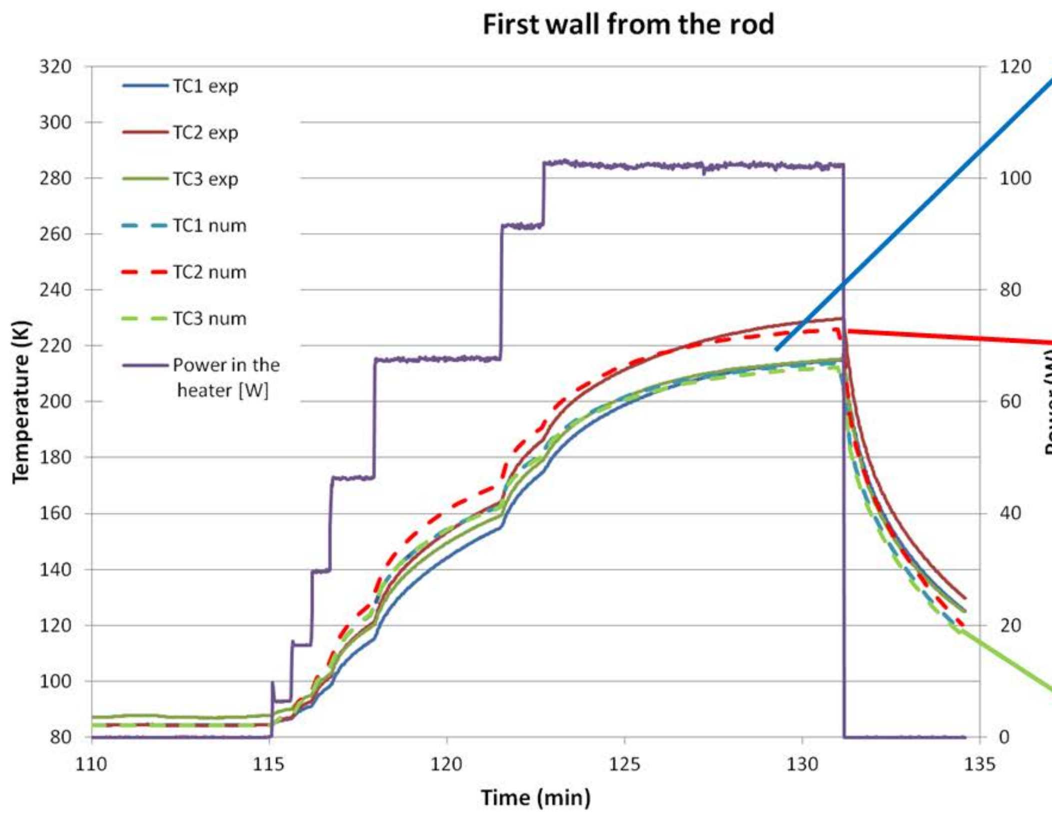


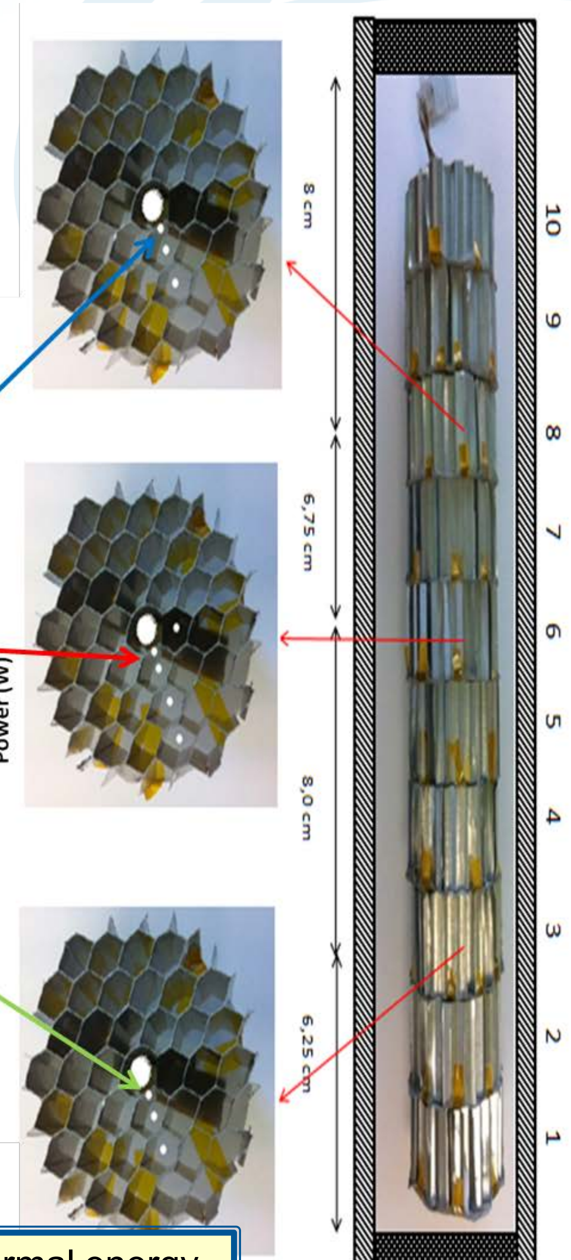


* reference T=21.1°C, P=1atm=101325 Pa

Accomplishments:
0.5 L Vessel Data and Model Comparison

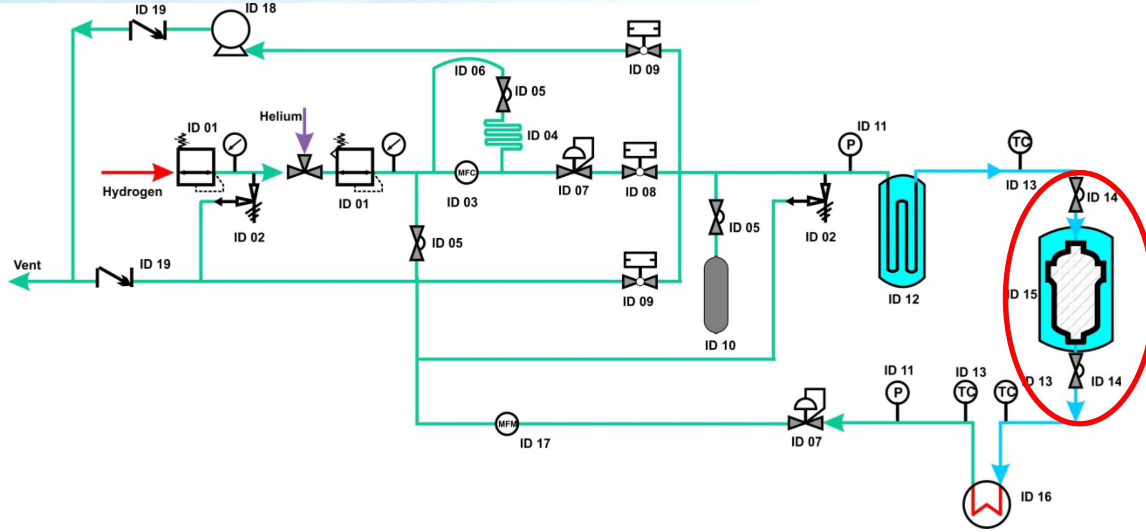
MOF-5, Initially 3.5 MPa hydrogen, 77K at vessel surface, no outflow





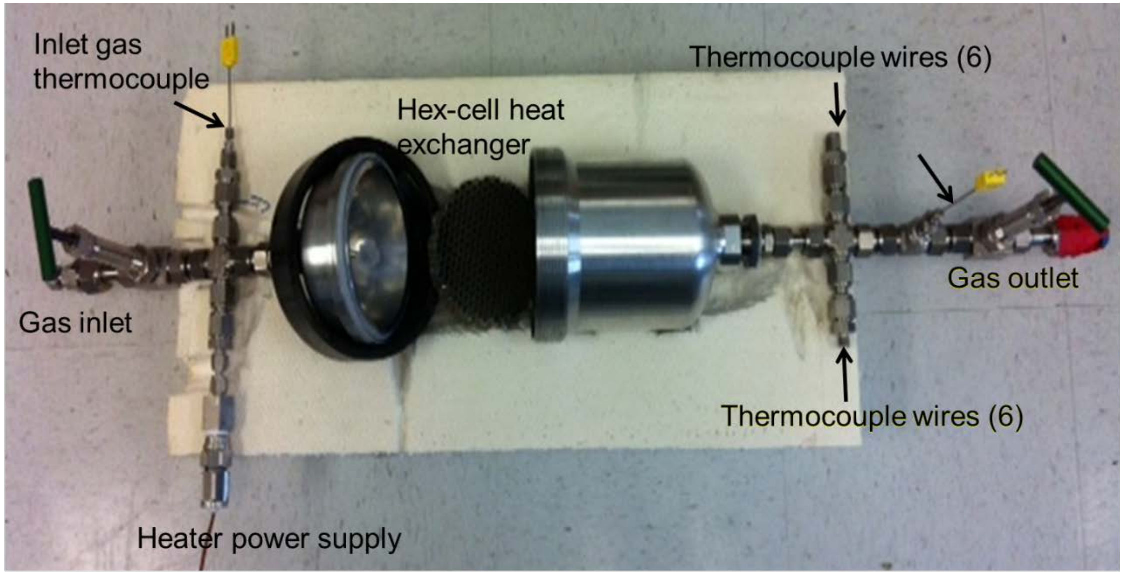
- ○ The hex-cell HX does distribute thermal energy
- ○ Results shown for uniform heater power profile
  - Also good for parabolic power profile

Accomplishments: Phase III Hex-Cell Prototype and Test Facility



Vessel, internals and test facility were designed and assembled

Can control cold hydrogen flowrate to 1000 splm for flow through cooling



Accomplishments: Installation of Heating Cartridge in Hex-Cell

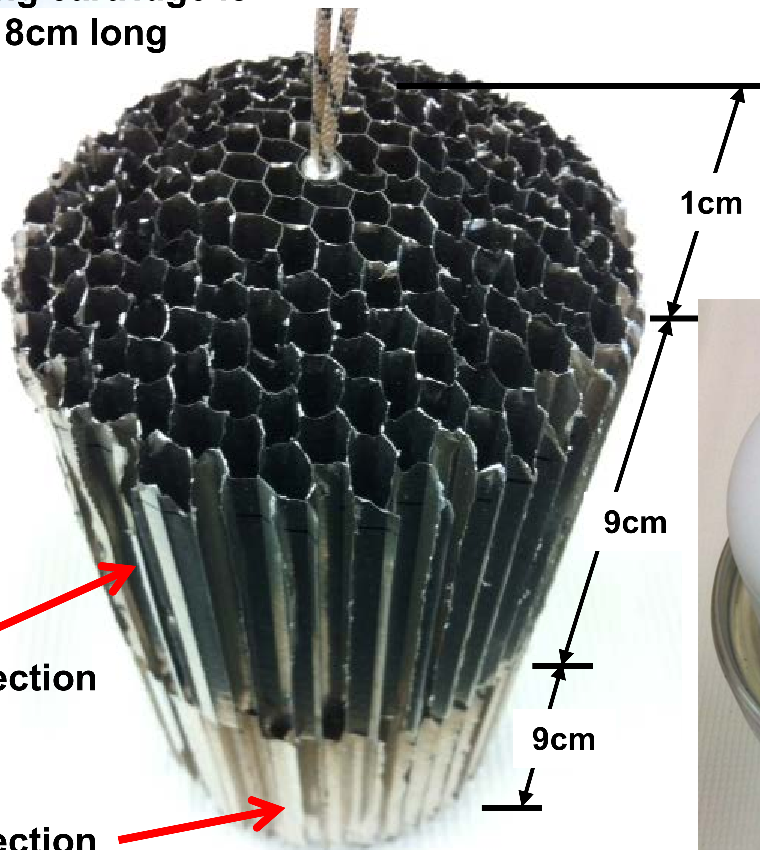
Single heater configuration was selected

- Simpler installation
- Requires fewer TC's to monitor temperature profile
- Can use symmetry in model
- However, takes longer time to reach (160-170K)

0.5 L vessel tests indicated need for thermal isolation from tank wall

A 0.125in thick Teflon® liner was used in the cylindrical section and in the domes of the tank

Heating cartridge is 18cm long



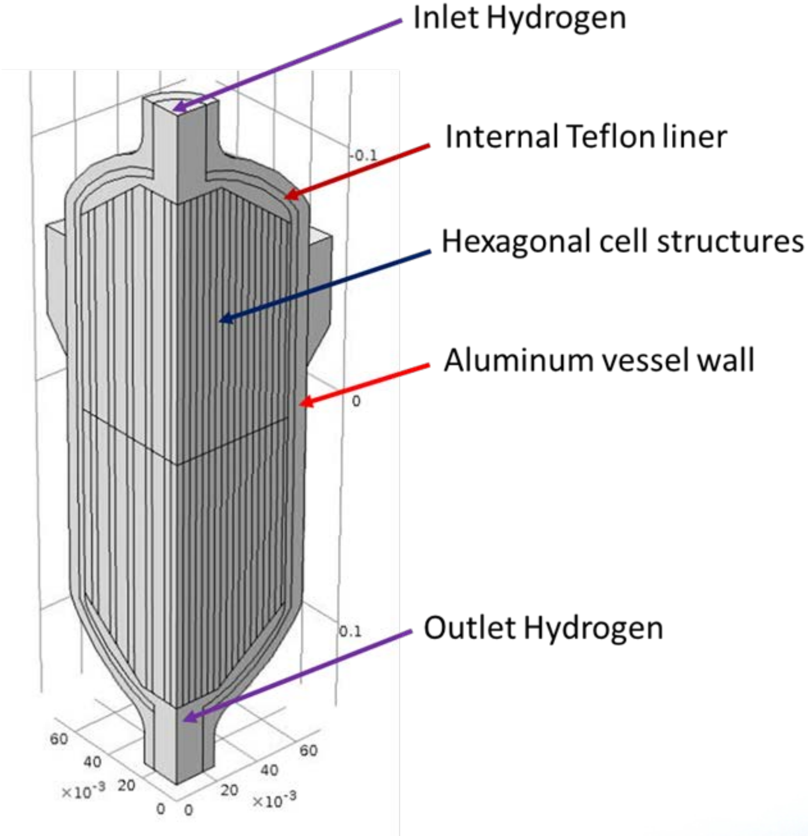
Upper section

Lower section

Heating cartridge is recessed by 0.8 inch (2cm) from the bottom hex-cell surface

Accomplishments: 3D Model Geometry for Hex-Cell Storage Vessel

- Geometry is in place
    - Replicates vessel and internals
- Model uses experimental BC's
- Coupled to equations
- Will validate against data



- 2L tank in 3D geometry with 90° symmetry
- Leveraged previous experience for the 0.5L tank tests
- Model successfully running and preliminary tests are currently being modeled

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Future Work: Preliminary Test Plan for 2L Hex-Cell Vessel

First set of tests will be conducted without the hex cell structure inside the tank to check the actual characteristics of the tank (volume, etc.)

Preliminary experimental tests to evaluate the actual performance of the heating rod (temperature profiles)

- **Tests will be repeated with empty cells and cells filled with alumina**
  - **Will use vacuum and pressurized H_2**

Flow through cooling/charging tests with MOF-5

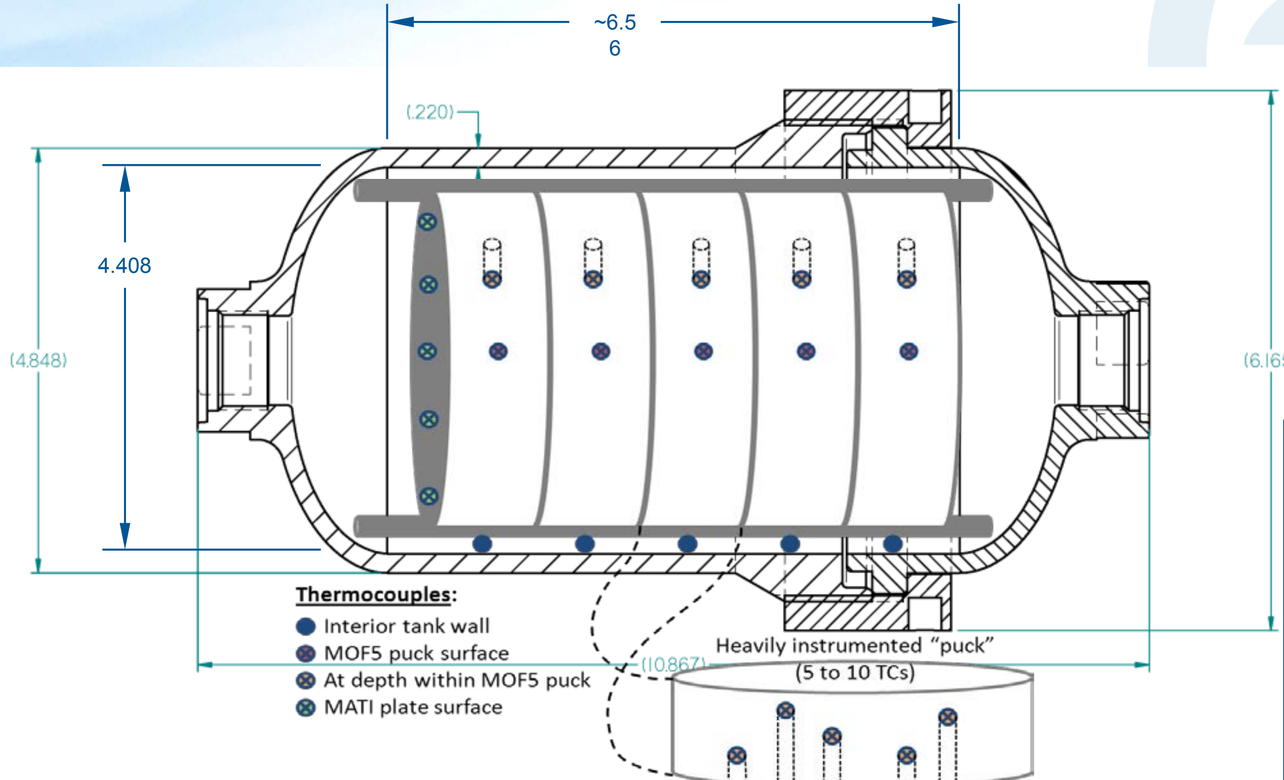
- **Hydrogen flow rates up to 1000 SLPM**
- **Inlet H_2 at 80 K, inlet gas pressure ramp**
- **Test conditions:**
  - **Adsorption for LN2 external temperature and max pressure**
  - **Adsorption with cooling and pressurization inside the tank (T=300-80K, P~0.3 - 70bar)**
  - **Additional sensitivity tests to be decided, based on initial results**

Heating/desorption tests with MOF-5

- **Room temperature at external surface, pressurized H_2, utilizing a suitable power ramp, with no hydrogen outflow**
- **External surface at LN2 temperature, utilizing a suitable power ramp, with *no* H_2 outflow**
- **External surface at LN2 temperature, utilizing a suitable power ramp, *with* H_2 outflow**

Cycling tests charge-discharge-charge, etc.

Accomplishments: Phase III Planned MATI Prototype Design



- 2-Liter Type 1 6061-T6 Aluminum tank.
- Collared opening for full diameter access.
- 100 bar max working pressure

- Planned MATI design:
  - 10 cm diameter SS plates
  - 8 to 10 ½-bed MATI sections
  - 3.1 cm from cooling plate to cooling plate
  - Mesh screen wrapping

- Planned data acquisition (TCs):
  - Profile along internal vessel wall
  - Profile along 1 cooling plate
  - Profile along external MOF surface
  - 1 embedded TC per bed
  - 1 heavily instrumented bed

- Planned Internal access to tank :
  - TC wires
  - 2x N_2 lines
  - 1x H_2 line

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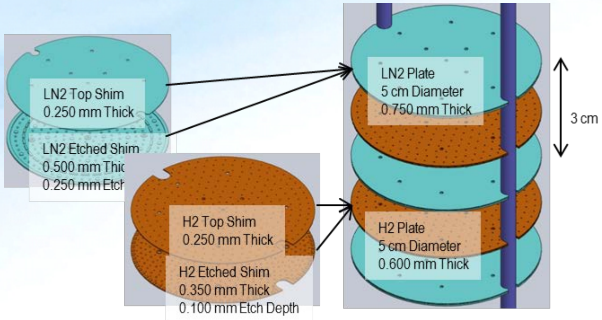
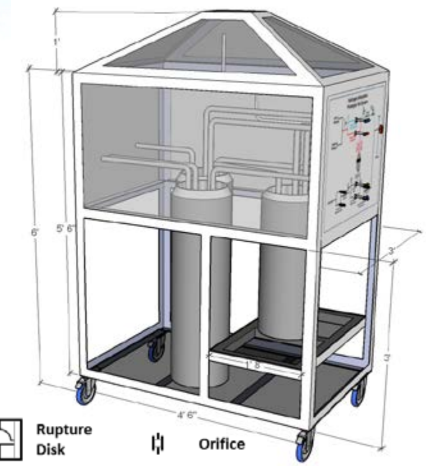
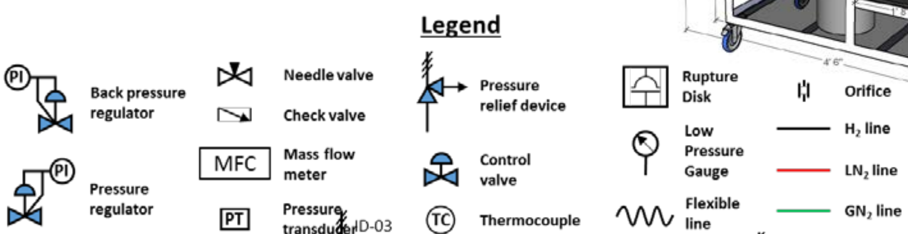
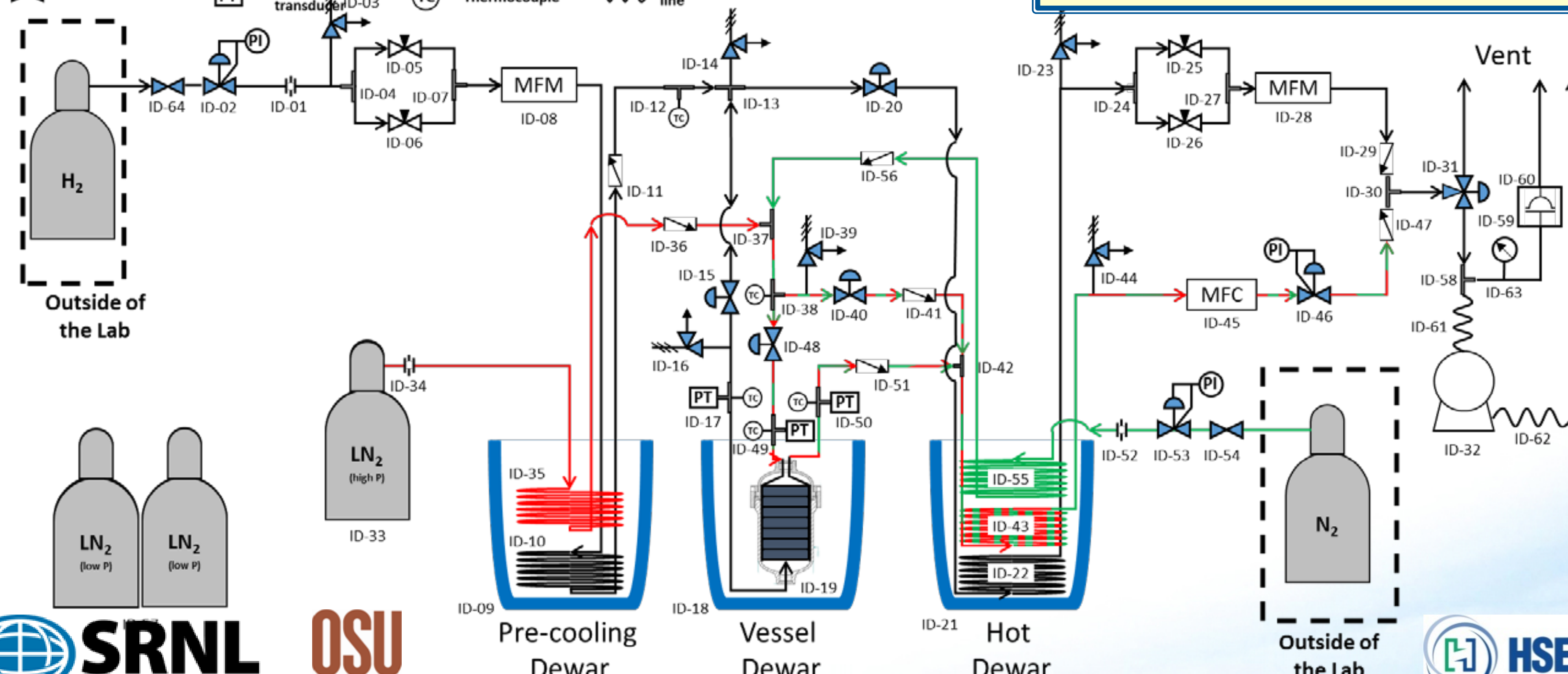
Accomplishments: P&ID for the SRNL MATI Prototype Test Facility





- Gas supply:
  - H_2 at 80 K and >100 slpm
  - LN_2 at ~7 bar and 80 K
  - N_2 at > 373 K and >100 slpm
- System Data acquisition:
  - P and T at all tank inlets/outlets
  - Mass flow control and measurements of all gas flows





Future Work: MATI Preliminary Test Plan

Initial Conditions

- System submerged within the LN_2 Dewar
- System is equalized to ~77 K – 80 K at the ***target pressure***
  - Target pressure of 60 bar (other pressures will be tested to verify system integrity)

Desorption

- Release H_2 from the pressure vessel at a fixed flow rate
- Simultaneously, run warm/hot gaseous N_2 through the MATI to induce desorption
  - Later testing may mimic driving conditions more closely by using a control scheme
- Continue desorption until the system reaches ~5 bar, ~160 K – 180 K

Adsorption

- Begin adsorption immediately after desorption phase
  - Dependent on the as-built capabilities of the Prototype Test Facility
- Pressurize the vessel with H_2 at a fixed flow rate
- Simultaneously, run LN_2 through the MATI to induce adsorption
  - Later testing may mimic driving conditions more closely by using a control scheme
- Continue charging to ~77 K – 80 K at the *target pressure*

Cycling… if possible

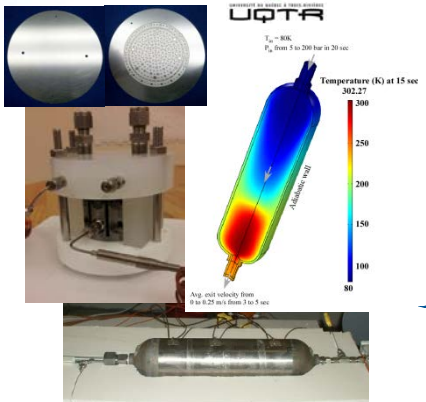
- If the system returns to near initial conditions, proceed directly to the next desorption cycle and perform at least 3 consecutive full cycles

Summary and Conclusions

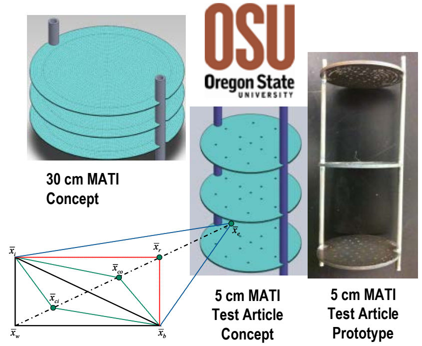
- **Hex-Cell Heat Exchanger**
  - **Small scale (0.5L) tests**
    - **Have experimentally validated hex-cell and resistance heater concept as means to discharge hydrogen**
    - **Models compare well with data**
    - **Non-uniform heater power represented well with parabolic or uniform profile**
  - **Phase III (2L) prototype**
    - **Small scale tests and models were segue to Phase III**
    - **Phase III component set-up and configuration is underway at UQTR**
      - ***Some tests performed with alumina in hex-cells***
    - **Numerical model framework for Phase III tests is in place**
      - ***Equations and geometry are implemented***
- **MATI Heat Exchanger**
  - **Test facility**
    - **Phase III prototype design/construction is underway at OSU**
    - **The test facility is currently under construction at SRNL**
      - ***Projected completion date of 01-July-2014***
  - **Models**
    - **Validation experiments to be conducted at SRNL**
    - **Numerical modeling will be performed by OSU**
      - ***Model framework & guidance will be provided by SRNL***

Internal Collaborations

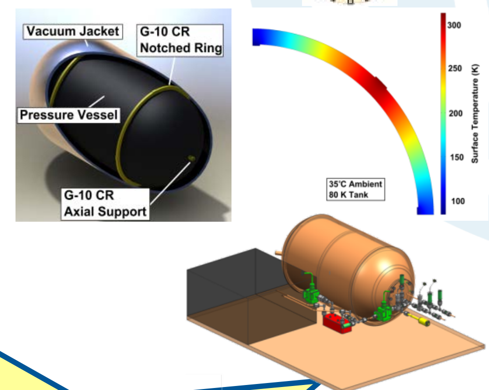
Adsorbent Prototypes: Design, Testing and Model Validation



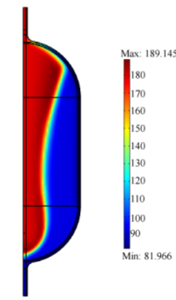
Modular Tank Insert: Optimization



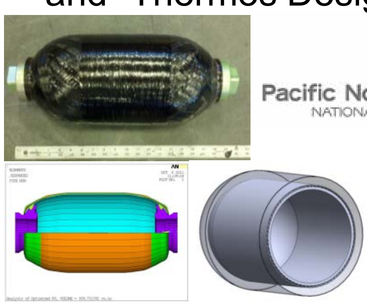
H_2 Flow and Heat Exchanger: Modeling and Analysis



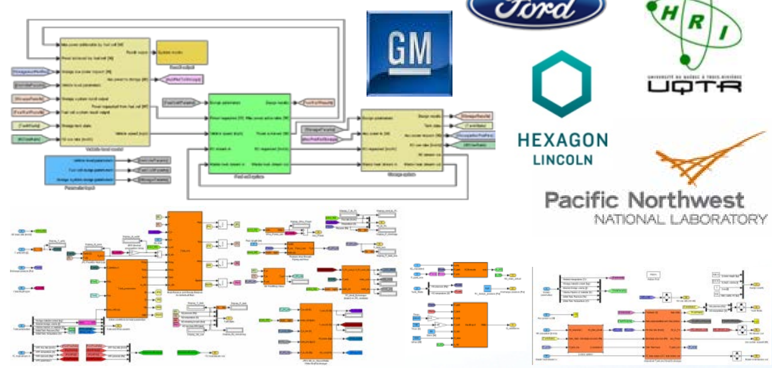
Flow-Through Heat Transfer Modeling



Pressure Vessels: Properties, Thicknesses, and "Thermos Design"



Adsorbent System Models



Compacted Media: Properties and Behavior

External Collaborations

AIST
NATIONAL INSTITUTE OF
ADVANCED INDUSTRIAL SCIENCE AND TECHNOLOGY (AIST)

Berkeley
UNIVERSITY OF CALIFORNIA

Curtin University

Griffith UNIVERSITY

MAX-PLANCK-GESELLSCHAFT

iea International Energy Agency

Remaining Challenges and Barriers

- **Hex-Cell Experiments**
  - **Models**
    - **Appropriate representation of physical processes**
  - **Thermocouples**
    - **Maintaining placement & location in adsorbent**
    - **Failure during tests**
  - **Internal Components**
    - **Adsorbent contact with heat exchanger wall**
    - **Adsorbent displacement**
      - ***May result in channeling or reduced contact with heat exchanger***
- **MATI Experiments**
  - **Set up of test facility at SRNL**
    - **Shipment and installation of MATI**
    - **Proper functioning of components**
    - **Appropriate measurements for models**

Responses to Previous Year Reviewers' Comments

Comment:
Paraphrasing similar comments by different reviewers; There is no consideration of the forecourt.

Response:
DOE mandated that while the HSECoE must identify and report on the interface between the storage system and the forecourt in terms of mass and energy transfer (including pressures, temperatures, flowrates, etc.) the primary focus of the HSECoE is the storage system. Although recognized as an important issue, detailed forecourt analysis was specifically omitted from the tasks performed by the HSECoE.

Comment:
It is unclear how the use of a Type-1 tank can lead to a go decision for Phase III. It is also unclear if this thermal mass can be cooled from 180 to 80 K in 3 minutes and what the penalty is in system efficiency due to this amount of cryogenic cooling.

Response:
A Type-1 tank was selected for the prototype tests because : it was suitable for the 60-100 bar pressure range of the tests and was approximately half the cost of a Type-3 tank; it did not require a permeation liner as did the Type-3 tank. Calculations, discussed in prior meetings, indicated that the vessel could be charged via the flow-through cooling process, using 58 kg of LN2 to cool the vessel wall and re-cool the discharged hydrogen, in less than 3 minutes.

Comment:
No interactions were mentioned with people and organizations outside of the Center.

Response:
SRNL is using its experience with the HSECoE media based storage systems in the DOE SunShot and ARPA-E MOVE programs. Metal hydride models developed by the HSECoE are being used in collaborative efforts with Curtin and Griffith Universities in Australia as part of solar energy and solar generated hydrogen storage programs, respectively. Further, there is collaboration with AIST (Japan) and the IEA.

Comment:
Because of the complex interactions and relationships with other teams it is difficult to judge the contributions of the SRNL/UQTR team.

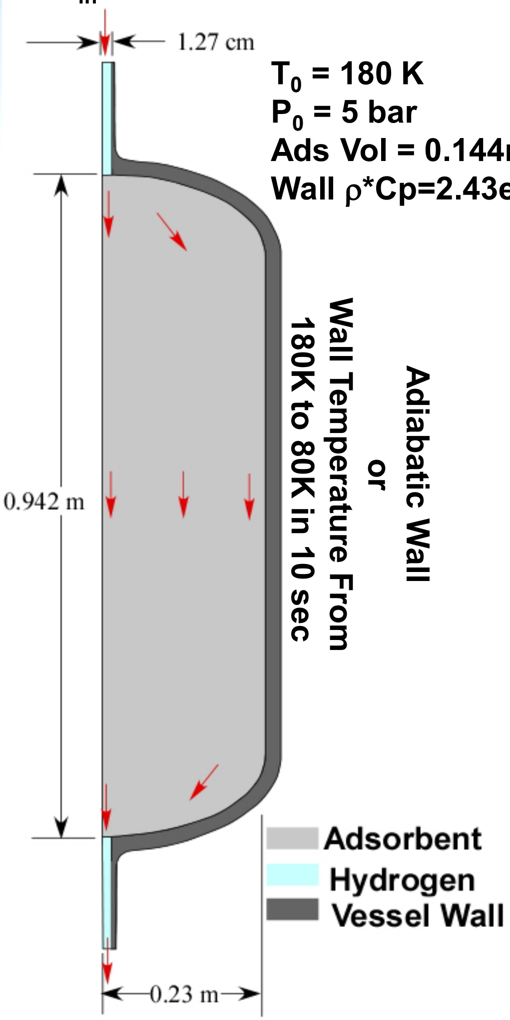
Response:
An effort has been made to clarify the SRNL/UQTR contributions in this presentation.

Technical Backup Slides

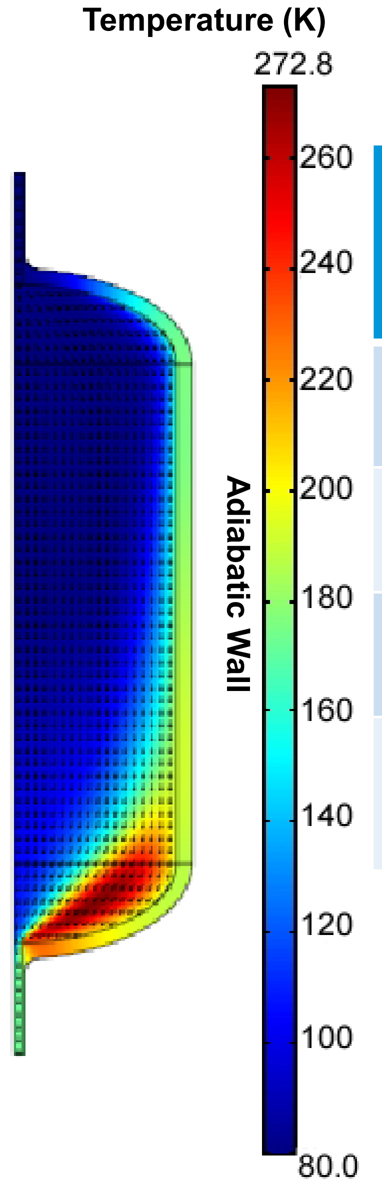
Flow-Through Cooling Adiabatic Wall & LN2 Assisted Cooling

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

T_0 = 180 K
P_0 = 5 bar
Ads Vol = 0.144m^3
Wall ρ*Cp=2.43e6 (J/m^3-K)



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



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	$>1.836 \times 10^7$

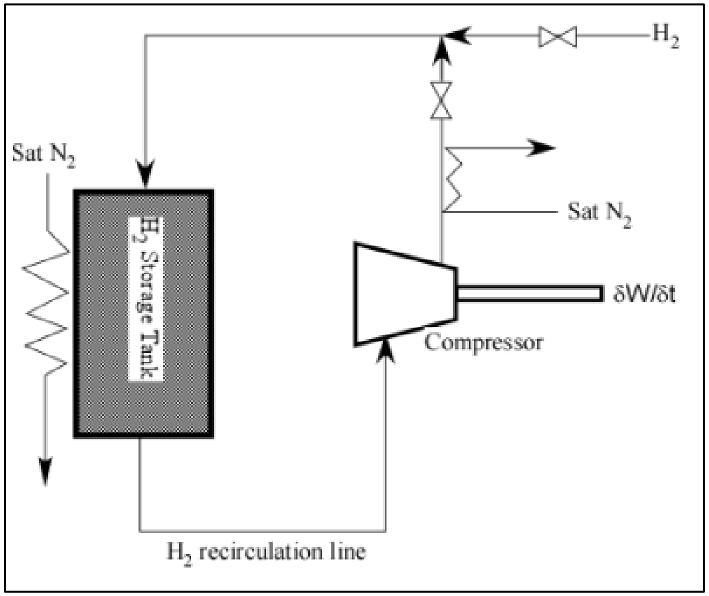
A preliminary JPL test indicated that the time required to cool the outer wall is longer than assumed in the model (~1.5 minutes from 180 K to 80K).

PNNL is currently conducting more detailed experiments.

Cost Analysis for Flow-Through Cooling

<u>Model Assumes</u>

- Saturated liquid nitrogen is boiled during cooling process
- Boiled nitrogen is vented (not reclaimed)
- Isentropic (adiabatic, reversible) H_2 compression to inlet pressure followed by isobaric cooling to 80K



<u>Time –Dependent Input from Finite Element Models</u>

- Mass of available hydrogen
- Areal average exhaust pressure
- Enthalpy of exhaust hydrogen
- Rate of heat transfer from tank wall

<u>Model Calculates</u>

- Mass of nitrogen boiled to cool tank wall
- Mass of nitrogen boiled to cool compressed hydrogen
- Total cost of nitrogen boiled off

Filling a non-optimized 60 bar tank requires ~ 58kg of saturated LN2
For a non-optimized 200 bar tank ~ 63kg of saturated LN2 is required

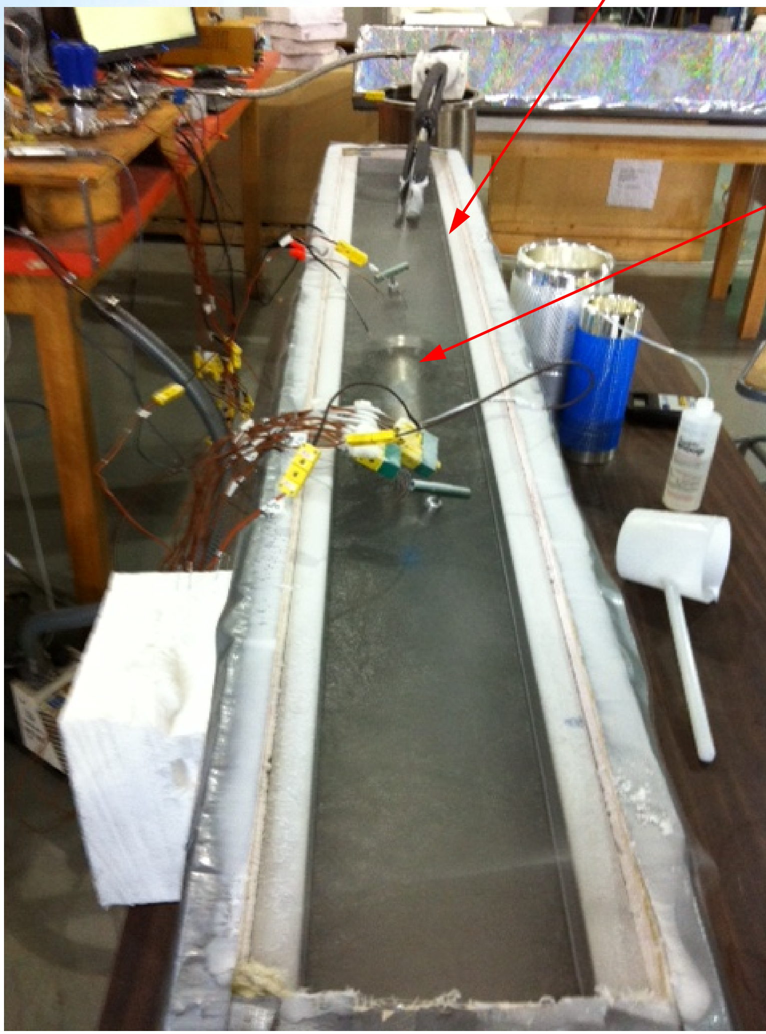
Hydrogen is Reclaimed – <u>Not Wasted</u>

Flow Through Cooling is Reasonable Based on Mass of LN2 Required

Experimental Apparatus for LN2 Boundary Conditions

Liquid Nitrogen Bath

Pressure Vessel



Detailed Storage System Models

- **Description**
  - **Models couple:**
    - Conservation equations for mass, momentum and energy
    - Equation of state for the gas
    - Chemical kinetics and thermodynamic equations
    - Other ancillary equations
  - **Any system, of any size, can be represented by the models by assigning appropriate geometry, components and boundary conditions**
- **Application**
  - **Within the HSECoE, the detailed models have:**
    - Led the direction of the HSECoE program for metal hydrides and adsorbents
    - Governed all important decisions regarding experiments, designs and storage system capability
    - Predicted, in a general sense, results of experimental tests before they were conducted
      - *This is why the models are used to select experimental designs having a high likelihood of meeting the technical targets*
      - *Experiments provide validation of model prediction and identify physical processes that improve resolution*
  - **Use by other organizations**
    - Griffith University, Australia is using a form of the HSECoE metal hydride model to design storage facilities for 100 kg of solar-generated hydrogen
    - The DOE SunShot program "Low-Cost Metal Hydride Energy Storage for Concentrating Solar Power," in collaboration Curtin University, Australia, is using a form of the HSECoE metal hydride model to design thermal energy storage systems for concentrated solar power

MATI: Experiment / Model Validation Considerations

1. **Uniform initial conditions**
   – Let the system temperature and pressure equalize at known values prior to beginning the experiment.
2. **Boundary conditions**
   – The pressure vessel will be submerged within the LN_2 Dewar to *provide an approximately* uniform, constant temperature *boundary temperature* throughout the experiment.
   – The H_2 supply and pressurized LN_2 supply lines will be submerged within the LN_2 Dewar to *supply feed gas at a* temperature as close to 77K as possible.
3. **Accurate measurement locations**
   – Document the geometric location of all thermocouple locations for proper model validation.

The goal of the Phase 3 prototype testing is to validate the detailed models for predictive capabilities.

MATI: Addressing DOE's Technical Targets

Target	2017 Value	Units	Measurement	Additional_Measurements
Gravimetric Capacity	0.055	g_{H2} / g_{sys}	Total Mass of Gas Stored	Total Mass of System (all equipment, tubing, tank, etc.)
Volumetric Capacity	40	g_{H2} / L_{sys}	Total Mass of Gas Stored	Total Volume of System (all equipment, tubing, tank, etc.)
System Cost	12	$/kWh	Total Mass of Gas Stored	Total cost of the full experimental set-up
Fuel Cost	2-6	$/gge	Not Measured at SRNL/OSU	
Ambient Temperature	-40 - 60 (sun)	°C	Room Temperature	
Min/Max Delivery Temperature	-40 - 85	°C	H_2 Outlet Temperature	
Operational cycle life (1/4 tank to full)	1500	cycles	Not Measured at SRNL/OSU	
Min/Max Delivery Pressure	5 / 12 bar	bar	H_2 Outlet Pressure	
On-board efficiency	90	%	Energy used to release the hydrogen (converted into H_2)	
Wells-to-Power Plant Efficiency	60	%	Energy used to refuel / reload the hydrogen (converted into H_2)	
System Fill Rate	1.5	kg_{H2} / min	Time to completely fill the tank (function of operating conditions)	Scaling this to our 2-Liter tank, it would only be a 4 second fill for the ~100 grams of H2
Min Full Flow Rate	0.02	(g/s)/kW	Not Measured at SRNL/OSU	
Start time to full flow rate (20 °C)	5	s	H_2 Flow Rate?	Time to achieve full flow rate at start-up (no "hold time" listed)
Start time to full flow rate (-20 °C)	15	s	Not Measured at SRNL/OSU	
Transient Response (10%-90% & 90%-0%)	0.75	s	H_2 Flow Rate?	Time to achieve desired response in flow rate ("driving" response to rapidly accelerate and stop)
Fuel Purity (SAE J2719 & ISO/PDTS 14687-2)	99.97	%H_2	Gas composition (via mass spec or RGA)	
Permeation & Leakage		Scch/h	Not Measured at SRNL/OSU	
Toxicity			Not Measured at SRNL/OSU	Dust cloud ignition at BASF and/or UTRC
Safety			Not Measured	Design for applicable safety standards
Loss of usable H_2	0.05	(g/h)/$kg_{H2,stored}$	Not Measured at SRNL/OSU	Simplified thermos bottle + MLVI system TBD