

# SRNL Technical Work Scope for the Hydrogen Storage Engineering Center of Excellence: Design and Testing of Adsorbent Storage

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**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: September 30, 2015
- 95% Complete (as of 4/10/15)

## Budget\*

- FY14 Funding: \$ 1,400,000
- FY15 Funding: \$ 670,000
- Total DOE Project Value \$10,180,000

\* Includes \$240,000 for the Université du Québec à Trois-Rivières (UQTR) as a subrecipient for FY13-FY15 and funding for SRNL's activities for HSECoE management.

## Barriers

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

## Partners



# 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**
- Develop and demonstrate acceptability envelope for adsorbents. **Completed**

# Relevance:

## FY2013 / FY2014 Milestones

### SMART Milestones for SRNL/UQTR:

- Design and construct a hydrogen cryo-adsorbent test station capable of evaluating the performance of a 2L cryo-adsorbent prototype, operated from 80-160K, which meets all of the performance metrics for the DoE Technical Targets for On-Board Hydrogen Storage Systems. **Completed**
- Demonstrate a 2L hydrogen adsorption system containing a MATI internal heat exchanger provided by Oregon State University, characterizing its performance against each of sixteen performance DoE Technical Targets for On-Board Hydrogen Storage Systems. **In Progress**
- Demonstrate performance of subscale system evaluations and model validation of a 2L adsorbent system utilizing a hex-cell heat exchanger having 46g available hydrogen, internal densities of 0.13g/g gravimetric, and 23.4g/L volumetric. **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**

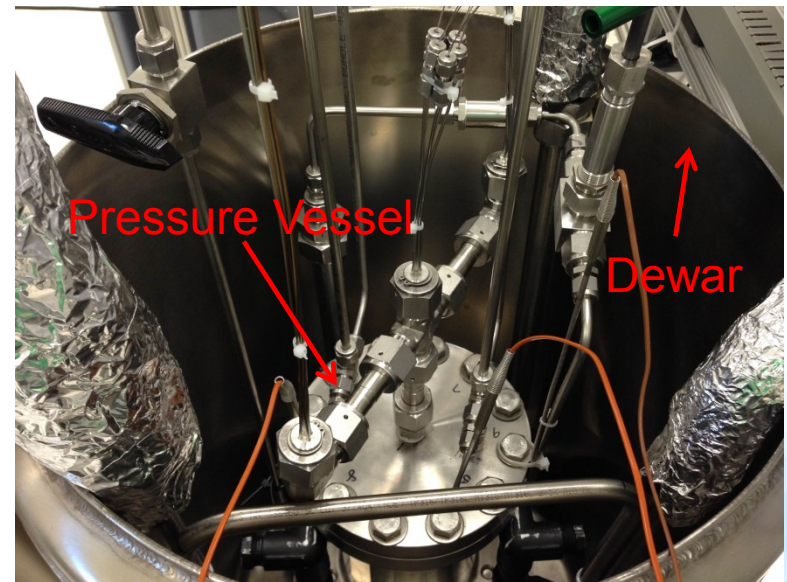
### Transport Phenomena Technology Milestones for SRNL/UQTR:

1. Final design of a 2L hex-cell sub-scale adsorbent system. **Complete**
2. Complete test matrix for evaluation of the 2L hex-cell sub-scale adsorbent system. **Complete**
3. Model validation for 2L hex-cell model against experiments. **In Progress**
4. Design, assemble and perform preliminary tests with the MATI heat exchanger. **Design and Assembly Complete, Tests are in Progress**

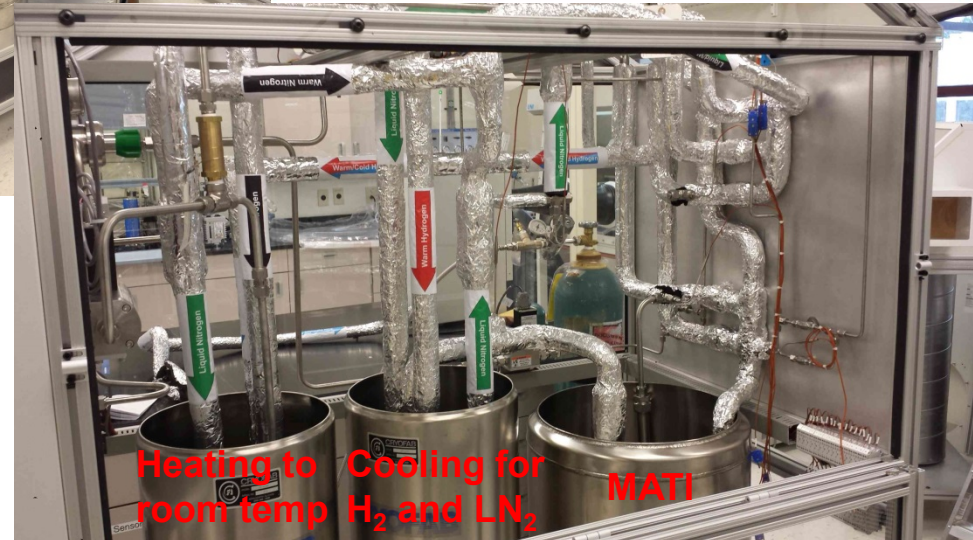
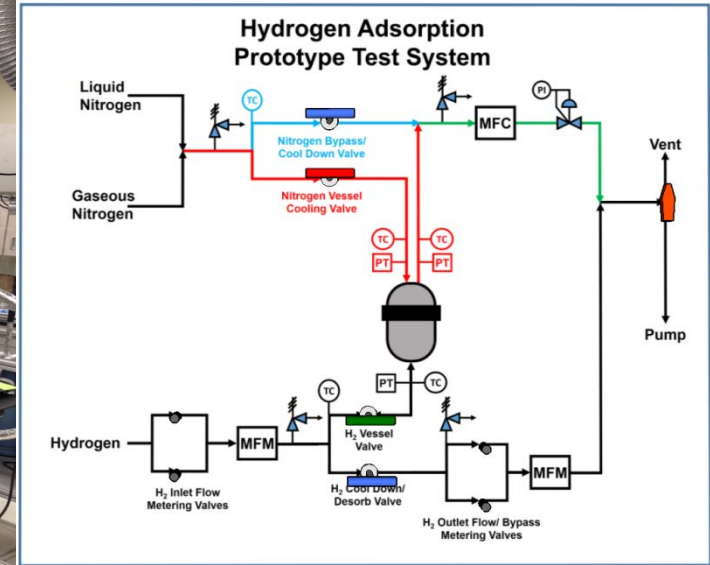
# Accomplishments:

## Overview of Test Plan for MATI Prototype

- **Verification of System Capacity**– measure the H<sub>2</sub> adsorption at 80 K, 100 bar.
- **Desorption** – measure the H<sub>2</sub> released at a fixed flow rate as the system is heated from 80 K, 100 bar to 160 – 180 K, 5 bar.
- **Adsorption** – measure the H<sub>2</sub> stored at a fixed flow rate as the system is pressurized to 100 bar.
- **Cycling** – measure the change in H<sub>2</sub> storage as the system is cycled between adsorption and desorption.



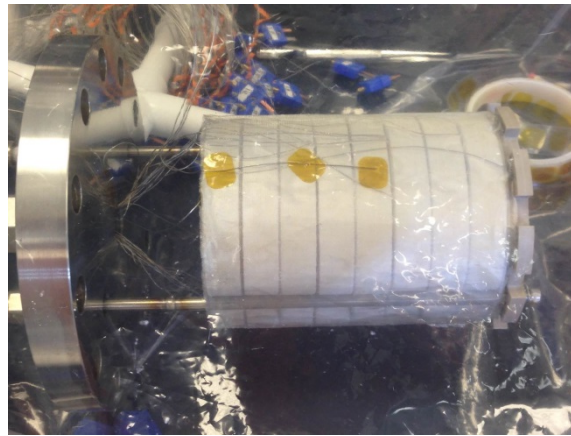
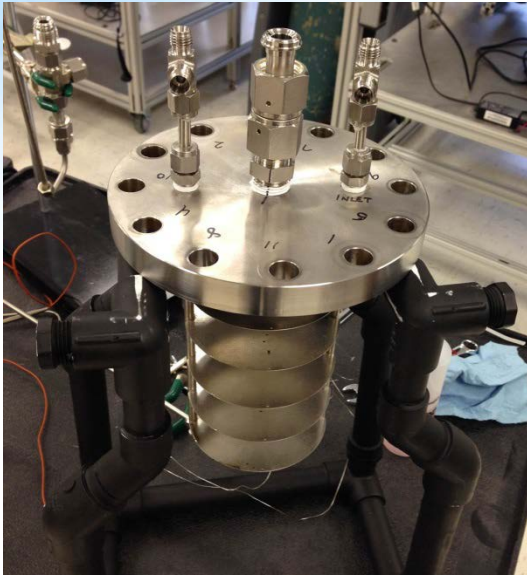
# Accomplishments: SRNL MATI Prototype Test Facility



- Prototype Test Facility is completed:
  - All lines have been leak-checked
  - All cryogenic lines have been insulated
  - The data acquisition system has been completed

# Accomplishments:

## MATI Prototype Assembly – Re-assembly at SRNL



- Re-assembled the MATI Prototype at SRNL:
  - Joint effort between SRNL and OSU personnel.
  - Fully assembled prototype with 30 internal TCs.

# Accomplishments:

## Tests With 2L Hex-Cell Vessel

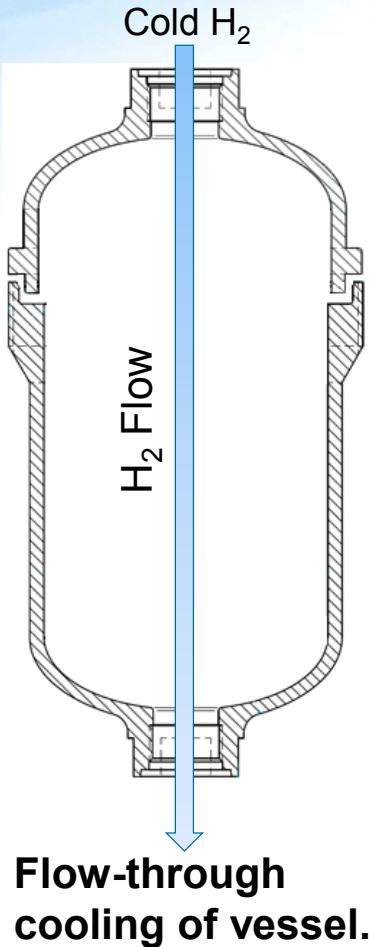
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- **Preliminary system measurements**
  - Tests were conducted without the hex cell structure to check the actual volume of tank and fittings (dead volume test)
- **Evaluation of vessel temperature profile produced by heating rod**
  - Heating rod had non-uniform power distribution
    - Tests were conducted for empty cells and cells filled with alumina for 2L vessel
    - Performed under vacuum and with pressurized H<sub>2</sub>
      - *Heat exchanger and media distributed heat*
      - *Permitted approximation as a modified parabolic power distribution*
      - *Validated power distribution in numerical model*
- **Verification of adsorbent performance**
  - Ensured that MOF-5 loaded into vessel performed as expected from its isotherms
- **Flow through cooling/charging capability**
  - Hydrogen flow rates up to 1000 SLPM
- **Heating/desorption tests with MOF-5**
  - Room temperature at external surface, pressurized H<sub>2</sub>, utilizing a suitable power ramp, with no hydrogen outflow

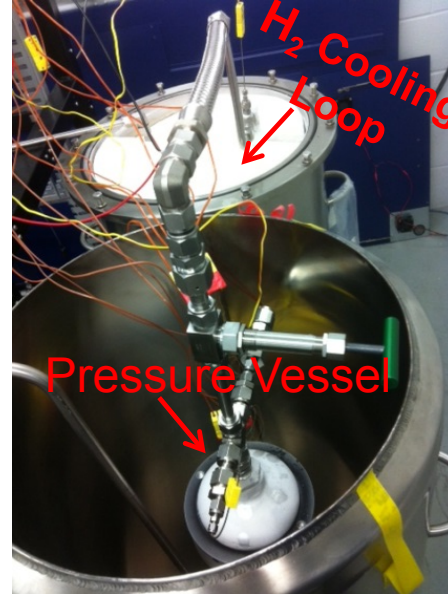


# Accomplishments:

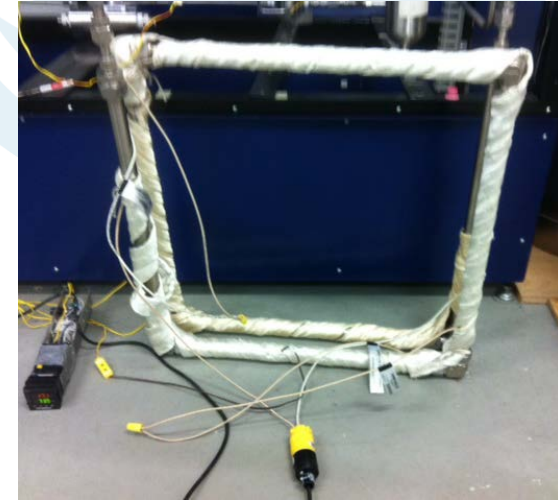
## Hex-cell 2L Flow-through Cooling System



**H<sub>2</sub> Cooling Section:**  
3 circuits of 1" tube filled with SS shot. The tubing is immersed in a Dewar filled with LN<sub>2</sub>.



Connection of cooling loop to the adsorbent tank.

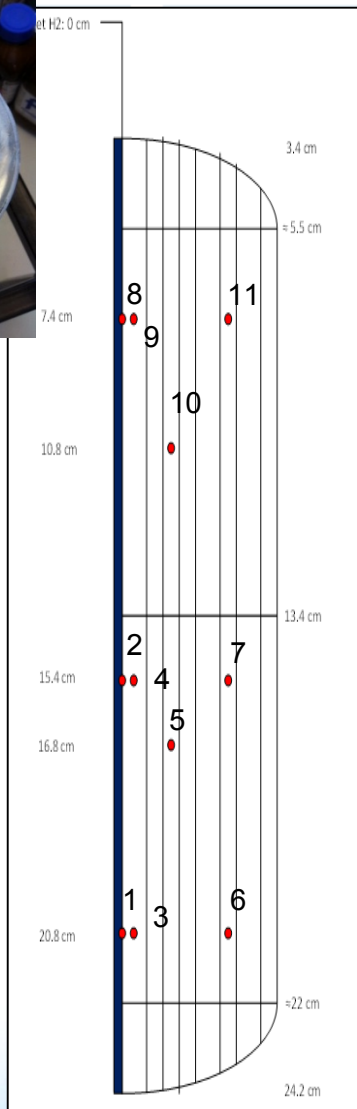
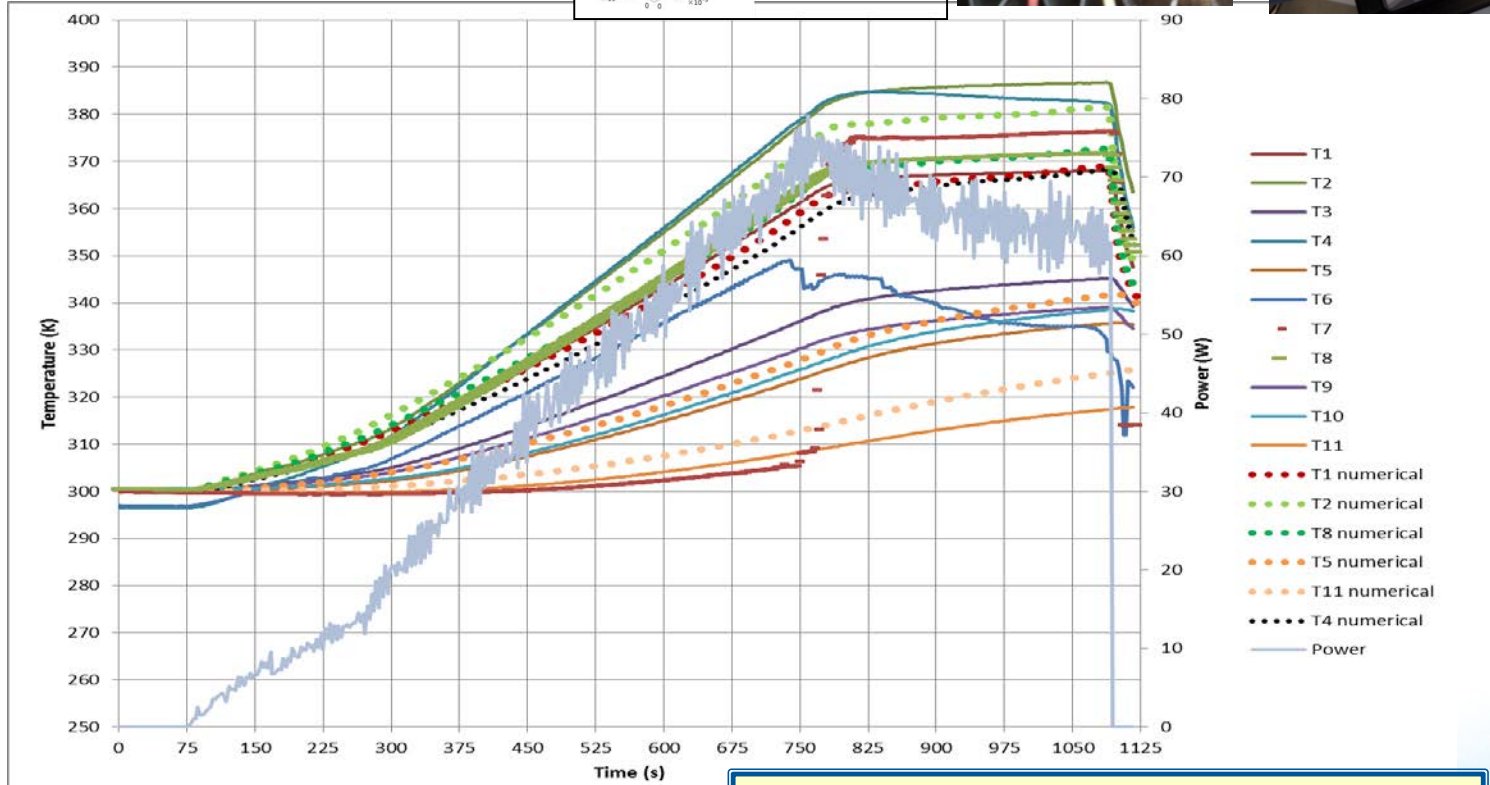
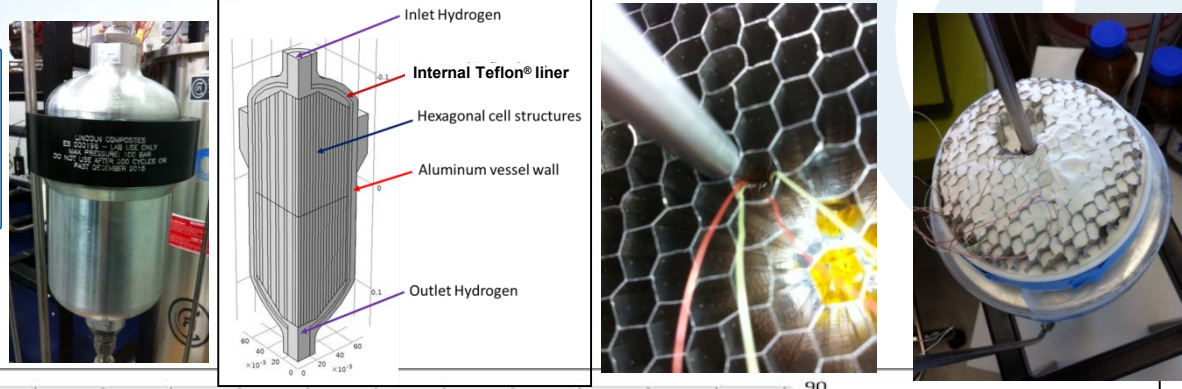


**H<sub>2</sub> Re-heating Section:**  
Heat discharged H<sub>2</sub> before reaching flowmeter  
1.5 circuits of 1" tube filled with SS shot.  
Heating element is wound over the outside of the tube.

# Accomplishments:

## Thermal Response of Alumina, Experiment vs. Model

Initial Conditions:  
 $T=300\text{ K}$   
 $P=13.5\text{ bar}$



Obtained satisfactory comparison between data and model

# Accomplishments:

## Hydrogen Desorption Test With MOF-5, Experiment vs. Model

### Initial Conditions:

T=300K

P=18.5 bar

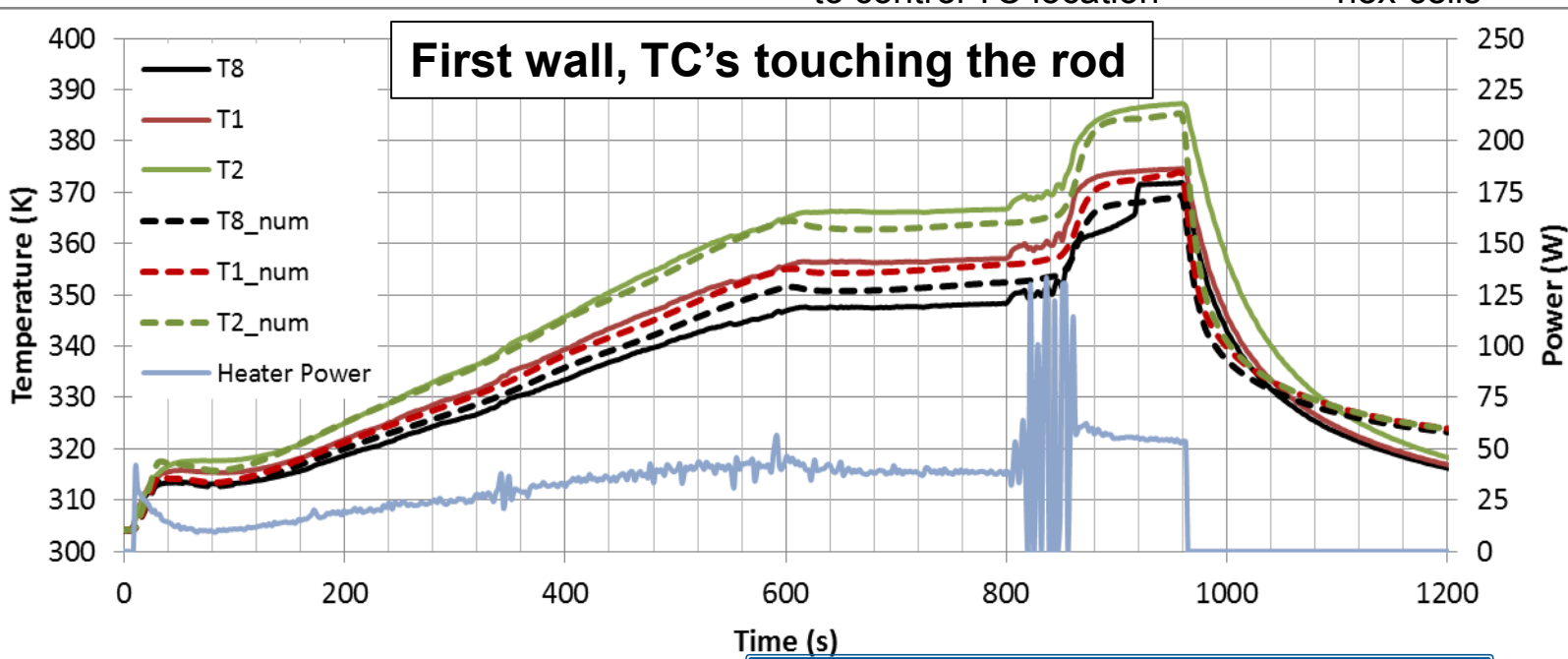
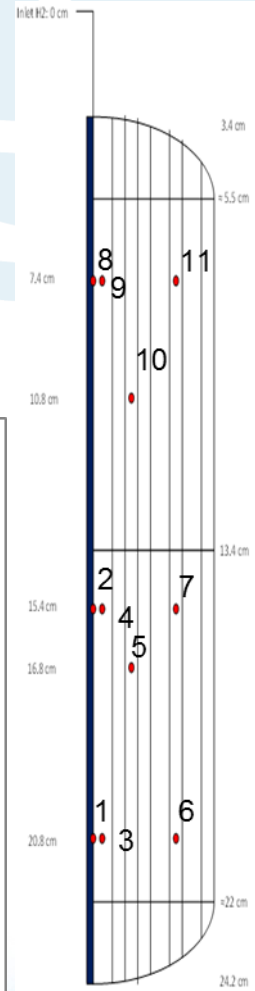
- Adiabatic boundary
- No H<sub>2</sub> outflow



Glass capillary tube used to control TC location



MOF loading in hex-cells



First wall, TC's touching the rod

Obtained satisfactory comparison between data and model

# Accomplishments:

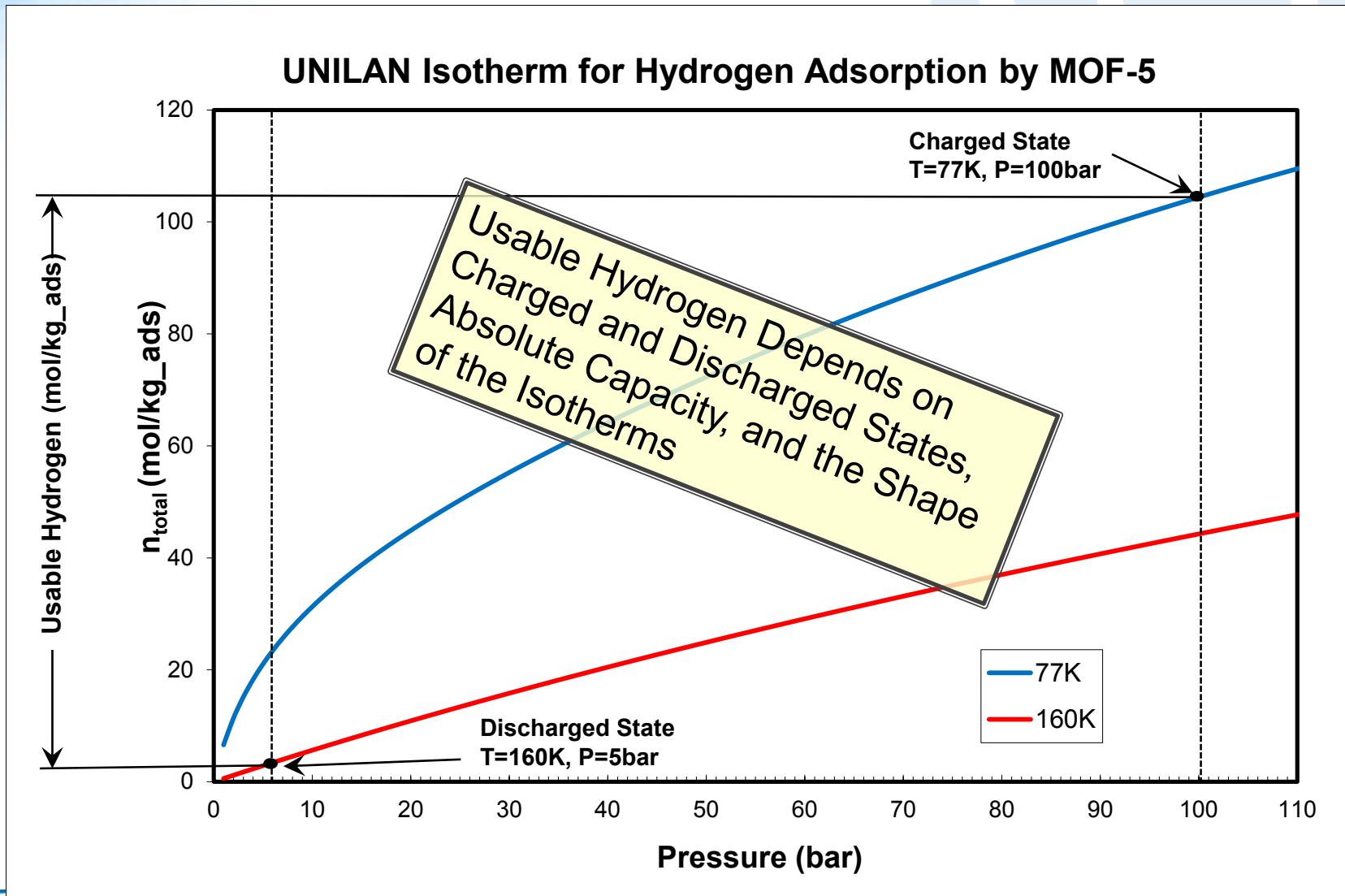
## Adsorbent Acceptability Envelope (AAE)

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- **Overall objective:**
  - Identify coupled adsorbent and storage vessel properties that make it possible to meet performance targets
- **Approach:**
  - Focus on usable (not just total) stored hydrogen
  - Identify quantifiable properties required to meet targets
  - Based on adsorbent parameters
    - Depends on charged and discharged states
    - Currently using UNILAN isotherm model
      - *Determine coupled range of isotherm parameters that meet or exceed target volumetric and gravimetric capacities*
    - Isotherms also determine excess differential enthalpy of adsorption
      - *Determines heat transfer requirements*
    - Control of bulk, crystal and skeletal densities
      - *Analysis used skeletal density, interparticle porosity and intraparticle porosity as independent variables*

# Accomplishments:

## Usable Hydrogen for Pressure and Temperature Swing



# Accomplishments:

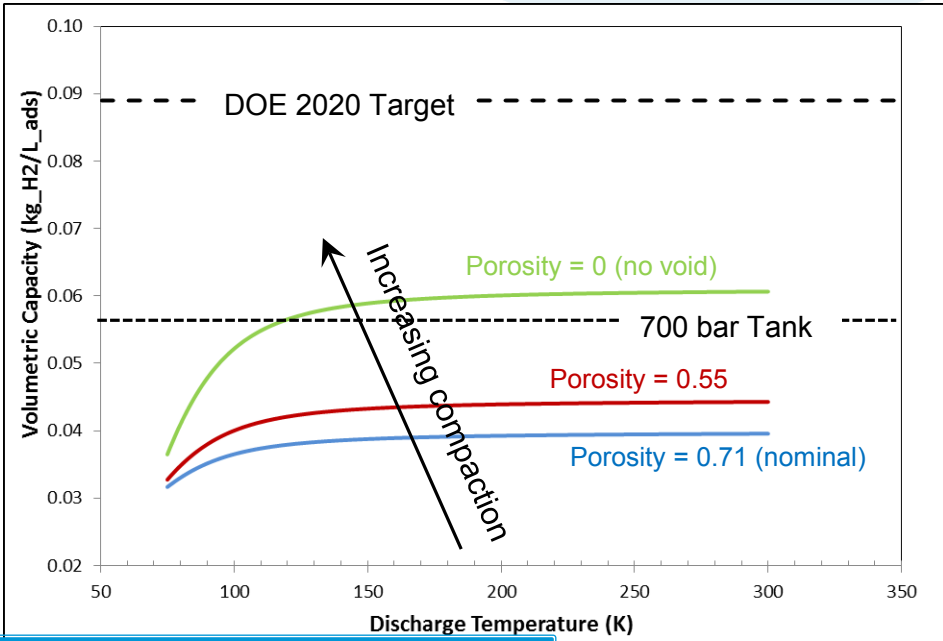
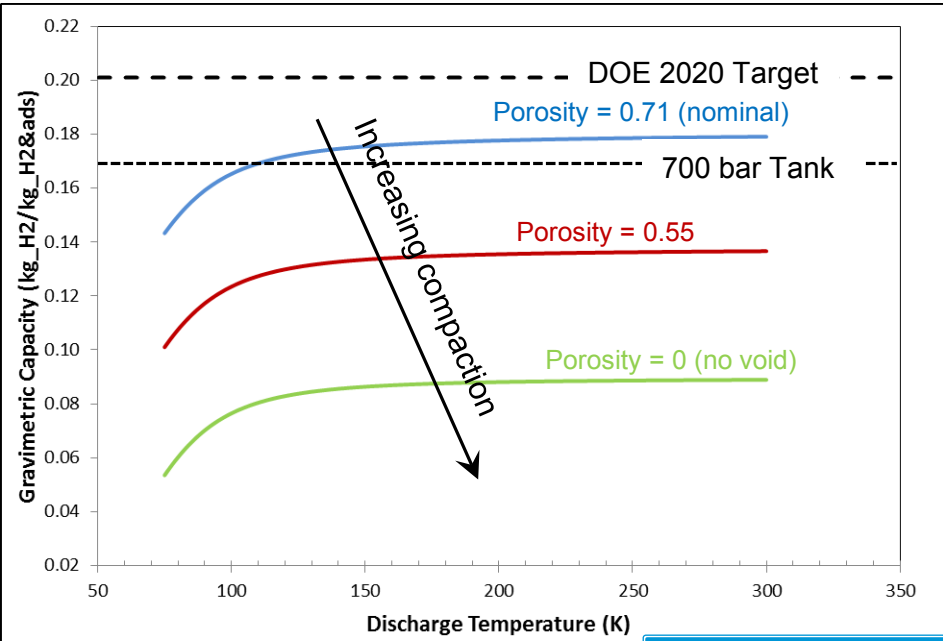
## Effect of Mechanical Compaction

Charged State T=77K, P=100bar    Discharged State T=160K, P=5bar

- Compaction was assumed to only remove the interparticle void
- The intraparticle void and the skeletal density were constant
  - Changes to these parameters are expected to change the isotherms in ways that cannot be quantified without experimental data

$$G_{cap} = \frac{\text{Usable mass of } H_2}{(\text{Total Mass of } H_2 \text{ at full charge}) + (\text{Mass of clean adsorbent})}$$

$$V_{cap} = \frac{\text{Usable mass of } H_2}{\text{Volume of adsorbent (L)}}$$



While mechanical compaction increases volumetric capacity it reduces gravimetric capacity due to reduction of inter-particle void

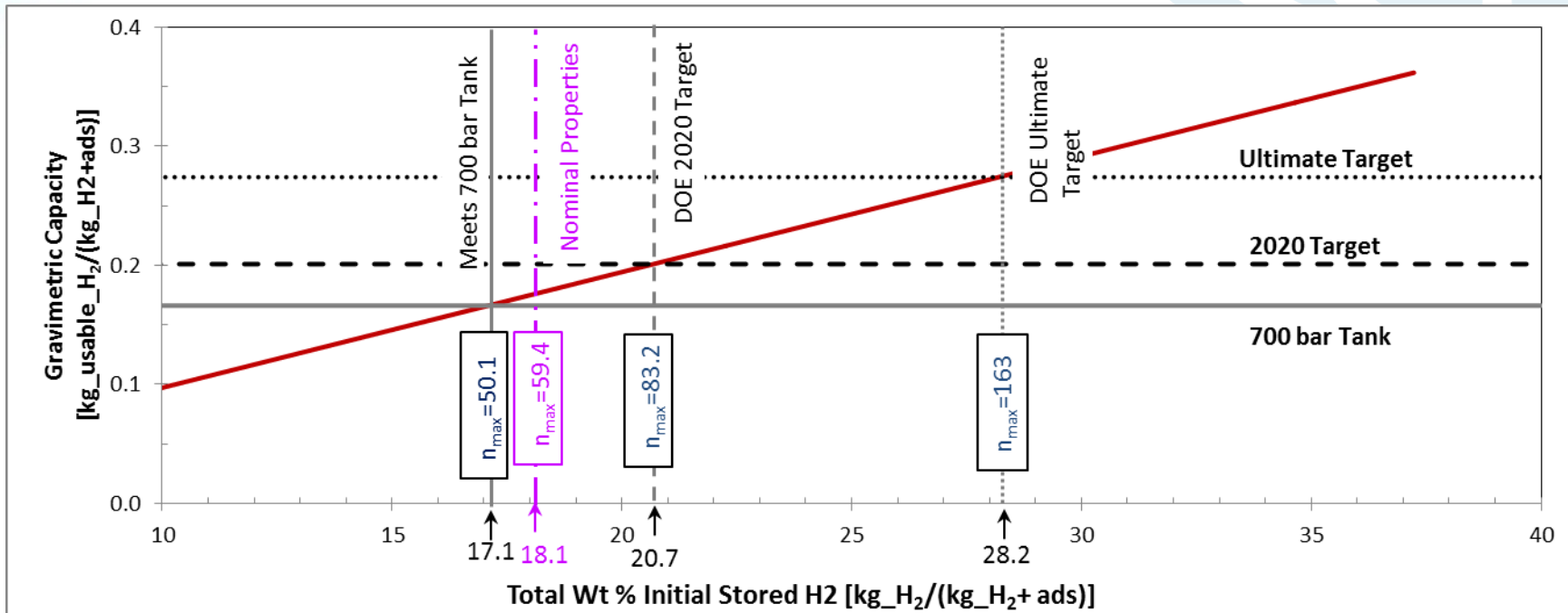
Mechanical compaction is insufficient to meet the DOE volumetric and gravimetric targets together – something more is needed



# Accomplishments: Required Specific Number of Adsorption Sites

Charged State      Discharged State  
T=77K, P=100bar    T=160K, P=5bar

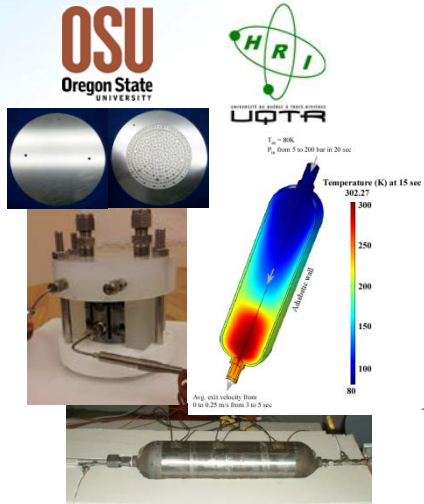
The number of adsorption sites ( $n_{\max}$ ) is varied while keeping all other adsorbent properties constant



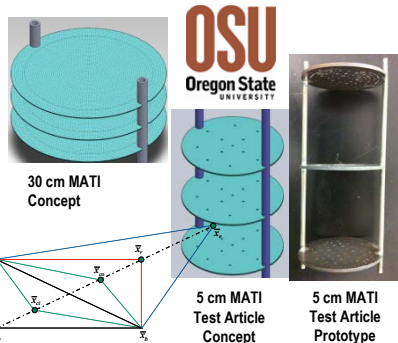
- MOF-5 exceeds the gravimetric capacity of a 700 bar tank
- Reaching the DOE 2020 target will require a 40% increase in the specific number of adsorption sites

# Internal Collaborations

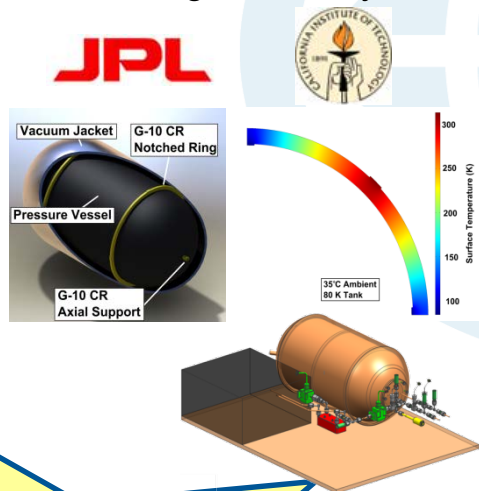
Adsorbent Prototypes:  
Design, Testing and  
Model Validation



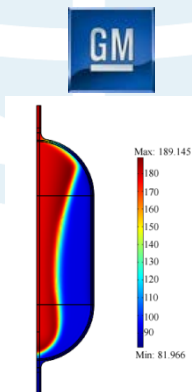
Modular Tank Insert:  
Optimization



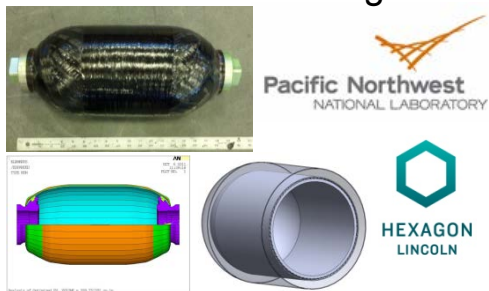
H<sub>2</sub> Flow and Heat Exchanger:  
Modeling and Analysis



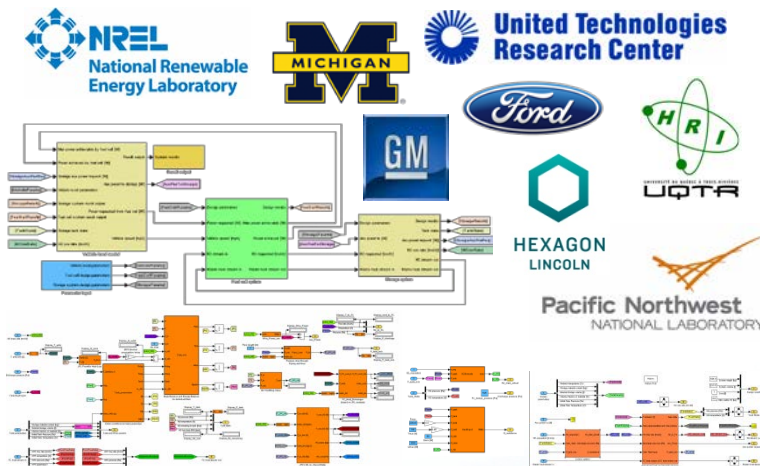
Flow-Through Heat  
Transfer Modeling



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



Adsorbent System Models



Compacted Media:  
Properties and Behavior





# External Collaborations



MAX-PLANCK-GESELLSCHAFT



# Future Work:

## 2 Liter Hex-Cell Vessel

- **Flow through cooling/charging tests with MOF-5**
  - Hydrogen flow rates up to 1000 SLPM
  - Inlet H<sub>2</sub> 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=300-80 K, P~0.3 – 100 bar)
    - Additional sensitivity tests to be decided, based on initial results and available time
- **Heating/desorption tests with MOF-5**
  - Room temperature at external surface, pressurized H<sub>2</sub>, utilizing a suitable power ramp, with no hydrogen outflow
  - External surface at LN2 temperature, utilizing a suitable power ramp, with no H<sub>2</sub> outflow
  - External surface at LN2 temperature, utilizing a suitable power ramp, with H<sub>2</sub> outflow
- **Perform model validation and incorporation of additional physics as indicated by experiments (at SRNL)**

# Future Work:

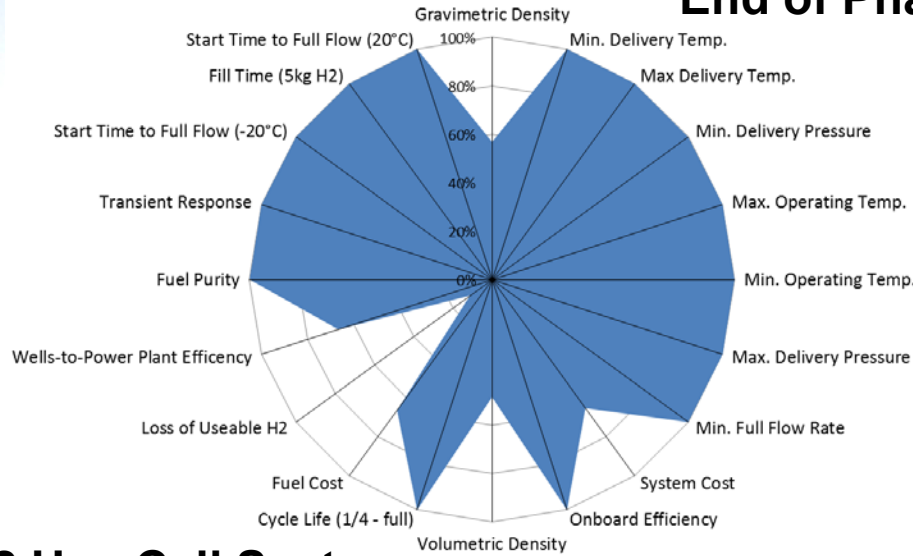
## MATI

- **Preliminary Tests**
  - System submerged within the LN<sub>2</sub> Dewar
  - Target pressure of 100 bar (lower pressures will be tested initially to verify system integrity)
- **Desorption**
  - Release H<sub>2</sub> from the pressure vessel at a fixed flow rate
  - Simultaneously run warm/hot gaseous N<sub>2</sub> through the MATI to induce desorption
    - If time allows, later testing can 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<sub>2</sub> at a fixed flow rate
  - Simultaneously, run LN<sub>2</sub> through the MATI to induce adsorption
    - If time allows, later testing can mimic refueling conditions more closely by using a control scheme
  - Continue charging to ~77 K – 80 K at 100 bar (lower pressures will be tested initially to verify system integrity)
- **Cycling... if possible & time permits**
  - If the system returns to near initial conditions, proceed directly to the next desorption cycle and perform at least 3 consecutive full cycles
- **Model validation and incorporation of additional physics (by OSU)**

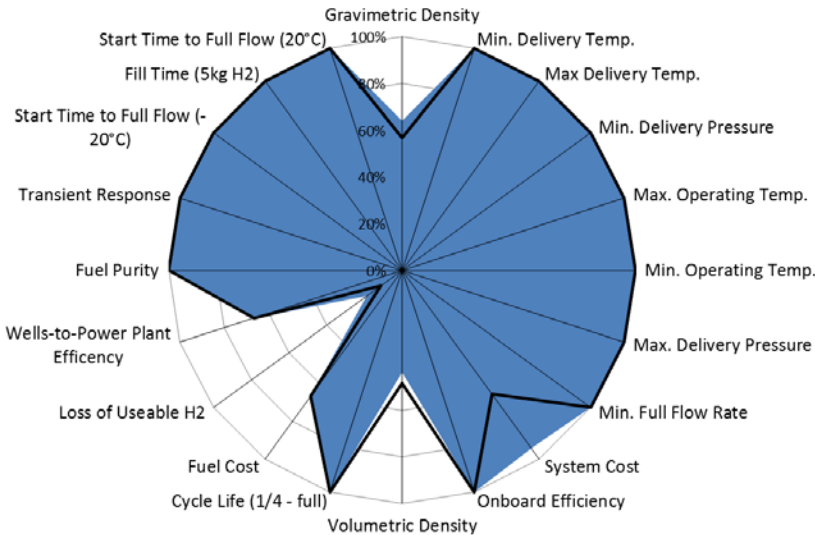
# Summary:

## Performance With Respect to DOE Targets

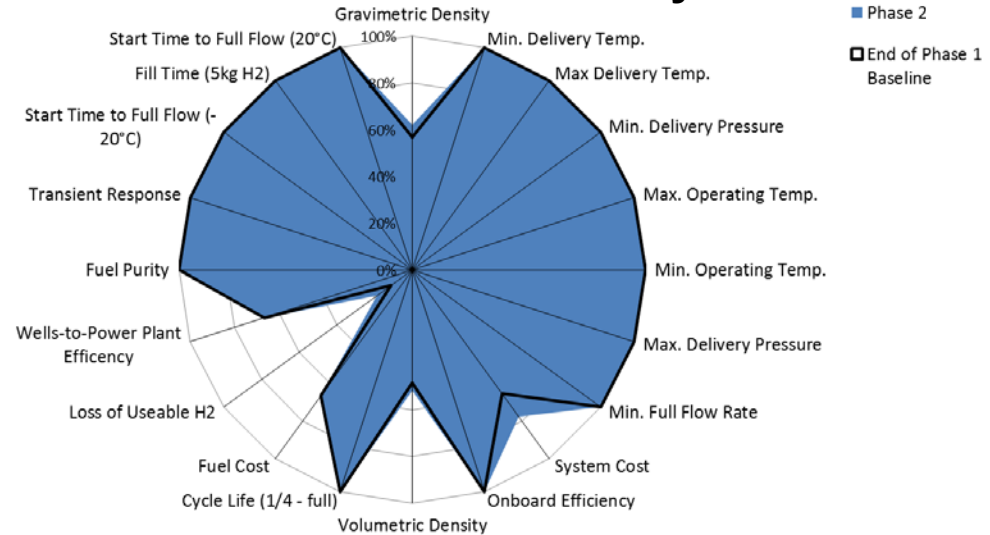
### End of Phase 1 Adsorbent System



### End of Phase 2 Hex-Cell System



### End of Phase 2 MATI System



■ Phase 2  
 □ End of Phase 1 Baseline

# Summary

- **Hex-Cell Heat Exchanger**
  - Phase III (2L) prototype
    - Test facilities have been validated
      - *Volume measurements, heating tests & characterization, adsorbent performance*
    - Tests performed with alumina (non-adsorbing material)
    - Tests with MOF-5
      - *Ambient temperature & no H<sub>2</sub> flow*
  - Numerical model framework for Phase III tests is in place
    - *Equations and geometry are implemented*
    - *Compares favorably with available data*
- **MATI Heat Exchanger**
  - Test facility
    - MATI was built at OSU and delivered to SRNL
    - The test facility at SRNL has been completed
    - Ready to begin tests
  - Models
    - Validation experiments to be conducted at SRNL
    - Numerical modeling will be performed by OSU
- **Adsorbent Acceptability Envelope**
  - Determines whether existing adsorbents can meet performance targets
  - Gives coupled range of required properties for new adsorbents
  - Demonstrates need to increase specific number of adsorption sites

# Remaining Challenges and Barriers

- **Hex-Cell Experiments**
  - Thermocouples
    - Maintaining placement & location in adsorbent
      - *Appears to be resolved with capillary tube*
    - Failure during tests
  - Internal Components
    - Contact between adsorbent and heat exchanger wall
    - Adsorbent displacement
      - *May result in channeling or reduced contact with heat exchanger*
  - Models
    - Appropriate representation of physical processes
  - Completing experiments in remaining time
    - Need to include time to implement data in models
- **MATI Experiments**
  - Ensure proper functioning of components
    - Integrity of adsorbent “pucks”
  - Collecting suitable data for models
  - Completing experiments in remaining time
    - Need to include time to implement data in models
- **Both Systems**
  - High throughput/high pressure mass flowmeters (1000SLPM/100 bar) can be problematic



# Responses to Previous Year Reviewers' Comments

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## **Comment:**

The project is listed as 90% complete but hasn't completed the most important tasks of actually testing these adsorbent storage systems which have been under study since 2009.

## **Response:**

The effort preceding the prototype experiments, including: storage media evaluation, system design, Go/No-Go decisions, model development and validation, subcomponent testing, pre-prototype tests, test station design and construction; required more than 90% of the HSECoE resources. Even though the prototype experiments are of paramount importance, they require approximately 10% of total resources.

## **Comment:**

Combining comments from 2 reviewers: It continues to be difficult to estimate how much collaboration actually occurs between Center participants. Roles not clear.

## **Response:**

As in the 2014 AMR presentation, an effort has been made to clarify the interaction between members of the HSECoE.

## **Comment:**

The PI should focus on evaluating affects of vibration on the system performance.

## **Response:**

It is acknowledged that vibration testing is very important to a number of aspects of storage system performance. However, vibration tests are not in the scope of work for the HSECoE.

## **Comment:**

There should be an outlook or recommendation for the usage of other materials (not MOF-5) with better performances to be tested in that vessel.

## **Response:**

Required/recommended properties of improved adsorbents are addressed through the adsorbent acceptability envelope.

## **Comment:**

How is "the loss of usable hydrogen" problem being addressed?

## **Response:**

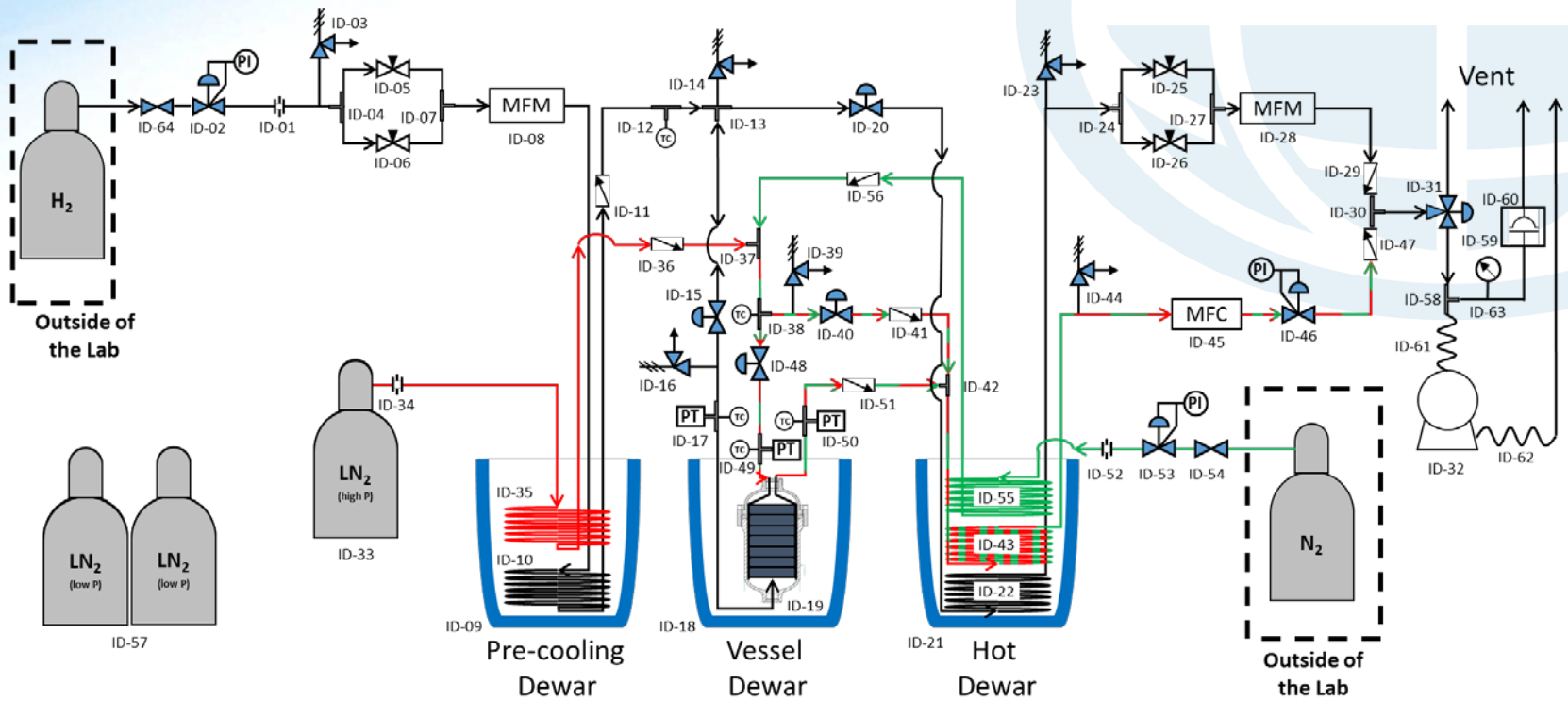
Loss of usable hydrogen is mitigated through tank insulation and the operational scheme. Specifics are determined from system and detailed models.



# Technical Backup Slides



# P&ID for the SRNL MATI Prototype Test Facility



**Legend**


- Gas supply:
  - H<sub>2</sub> at 80 K and >100 slpm
  - LN<sub>2</sub> at ~7 bar and 80 K
  - N<sub>2</sub> 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

# Specifications for Hex-Cell Test Rig

## Vessel Operating Conditions

- Hydrogen inflow temperature range: 80 K - 298 K
- Hydrogen inflow temperature control:  $< \pm 2$  K at 80 K and 298 K
- Hydrogen inlet flow rate: 0-1000 SLPM
- Maximum vessel pressure: 101 bar
- Total hydrogen capacity: 13.98 m<sup>3</sup> at STP (standard 6000 psi hydrogen cylinder)

## Measurement Specifications

- Temperature accuracy and resolution [ $\pm$  K]: Accuracy:  $\pm 2.2$  K or  $\pm 2\%$  for temperature range 77-273 K and  $\pm 1$  K or  $\pm 0.75\%$  for temperature range 273-623 K. Resolution: 0.07 K.
- Pressure accuracy and resolution ( $\pm$  bar): Accuracy:  $\pm 0.04$  bar (0.02% FS), Resolution: 0.004 bar (1/50,000 parts of the full range which is 3000 psia).
- Flow rate accuracy and resolution ( $\pm$  SLPM): Accuracy: 1% of the flow for the flow rate between 200 and 1000 SLPM. For flow rates below 200 SLPM, accuracy is 2 SLPM. Resolution : 0.02 SLPM



# Accomplishments:

## Nominal MOF-5 With Respect to DOE Targets

UNILAN Isotherm Model was used in Analysis

$$n_a = \frac{n_{max}RT}{(E_{max} - E_{min})} \ln \left( \frac{e^{-\Delta S_0 / R} + \frac{P}{P_0} e^{E_{max}/RT}}{e^{-\Delta S_0 / R} + \frac{P}{P_0} e^{E_{min}/RT}} \right)$$

$$n_{Total} = n_a + c(V_v - V_p)$$

$$n_{Usable} = n_{Total}(T_{chg}, P_{chg}) - n_{Total}(T_{disch}, P_{disch})$$

Charged State:  $T_{chg} = 77K$   
 $P_{chg} = 100 \text{ bar}$

Discharged State:  $T_{disch} = 160K$   
 $P_{disch} = 5 \text{ bar}$

### UNILAN Parameters, and bulk density, for Nominal MOF-5

	$n_{max}$ (mol/kg_ads)	$E_{max}$ (J/mol)	$E_{min}$ (J/mol)	$\Delta S_0$ (J/mol-K)	$\rho_{bulk}$ (kg/m <sup>3</sup> )
Nominal MOF-5	59.4	4640	2071	-65.8	181

Usable gas goes from nominal 0.215 to 0.230 kg\_H<sub>2</sub>/kg\_ads when  $E_{max} = E_{min} = 4491 \text{ J/mol}$   
 $\Rightarrow$  No heterogeneity for adsorption sites  
*Consistent with Bhatia and Myers, "Optimum Conditions for Adsorptive Storage," Langmuir 2006 (2)*

### Technical Targets

Target	$G_{cap}$ (kg_H <sub>2</sub> /kg_Total)	$V_{cap}$ (kg_H <sub>2</sub> /L_Total)	Basis
2020 System	0.055	0.040	System
Ultimate System	0.075	0.070	System
700 bar Tank	0.045	0.025	System
2020 Adsorbent	0.201	0.089	Adsorbent
Ultimate Adsorbent	0.274	0.156	Adsorbent
700 bar Tank Adsorbent	0.166*	0.055	Adsorbent

On an **adsorbent** basis for nominal MOF-5:

$G_{cap}$ (kg_H <sub>2</sub> /kg_H <sub>2</sub> +ads)	$V_{cap}$ (kg_H <sub>2</sub> /L)
0.176*	0.039

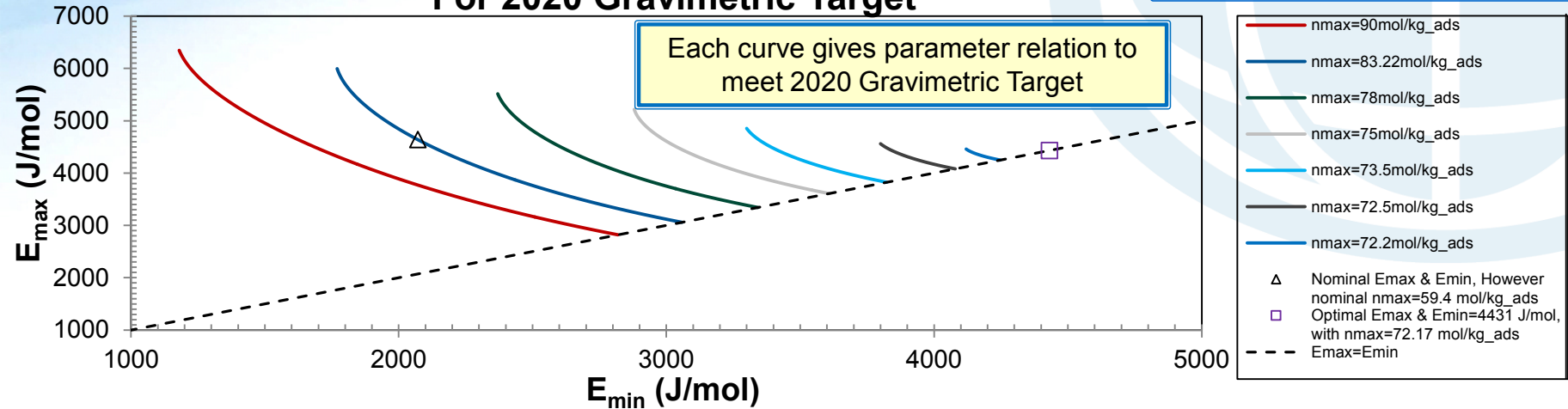
\*  $G_{cap}$  exceeds 700 bar tank value

# Accomplishments:

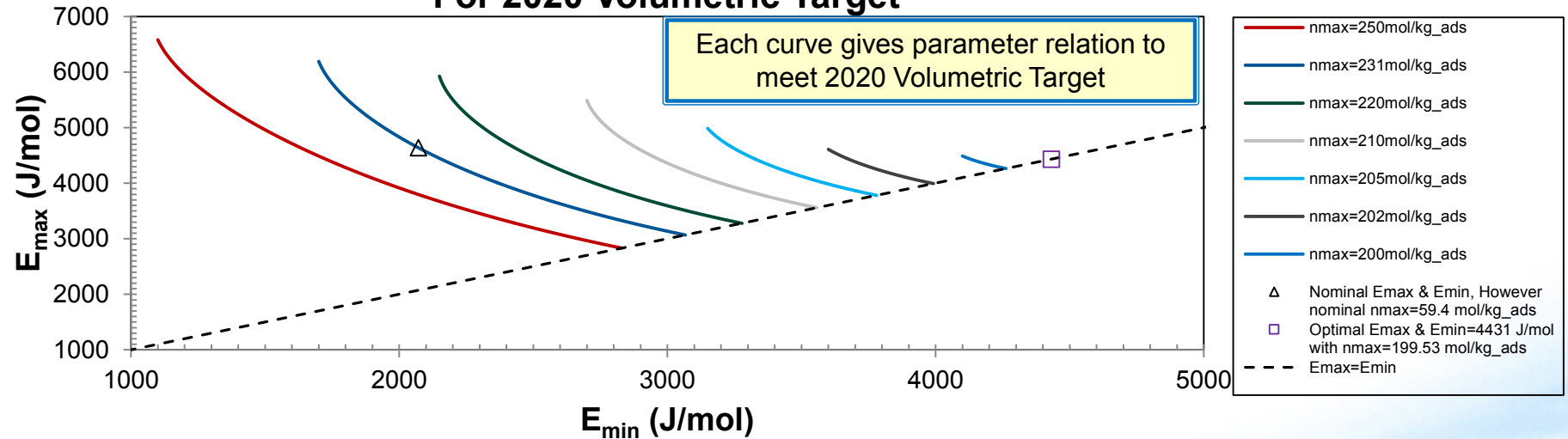
## Relation Between $n_{max}$ , $E_{max}$ & $E_{min}$

Charged State:  $T_{chg}=77K$   
 $P_{chg}=100$  bar  
 Discharged State:  $T_{disch}=160K$   
 $P_{disch}=5$  bar

### For 2020 Gravimetric Target



### For 2020 Volumetric Target



Defines the relationship between site density and site energy range for material design efforts

# Effect of Modifications to Isotherm Parameters

Charged State:  $T_{\text{chg}}=77\text{K}$ ,  $P_{\text{chg}}=100\text{ bar}$  Discharged State:  $T_{\text{disch}}=160\text{K}$ ,  $P_{\text{disch}}=5\text{ bar}$

	$n_{\text{max}}$ (mol/kg_ads)	$E_{\text{max}}$ (J/mol)	$E_{\text{min}}$ (J/mol)	$\Delta S_0$ (J/mol-K)	$\rho_{\text{bulk}}$ (kg/m <sup>3</sup> )	$G_{\text{cap}}$ (kg_H2/kg_total)	$V_{\text{cap}}$ (kg_H2/L)
Nominal MOF-5	59.4	4640	2071	-65.8	181	0.176	0.039
Optimized $E_{\text{min}}$ & $E_{\text{max}}$	59.4	4491	4490	-65.8	181	0.186	0.042
$n_{\text{max}}$ for 2020 $V_{\text{cap}}$	200	4491	4490	-65.8	181	0.325	0.089
$n_{\text{max}}$ for Ultimate $V_{\text{cap}}$	398	4491	4490	-65.8	181	0.452	0.156
$n_{\text{max}}$ for 700bar Tank $V_{\text{cap}}$ Optimized $E_{\text{max}}$ & $E_{\text{min}}$	99	4491	4490	-65.8	181	0.231	0.055
$n_{\text{max}}$ for 700bar Tank $V_{\text{cap}}$ Nominal $E_{\text{max}}$ & $E_{\text{min}}$	114.6	4640	2071	-65.8	181	0.231	0.055
$\rho_{\text{bulk}}$ for 700bar Tank $V_{\text{cap}}$ Nominal $E_{\text{max}}$ & $E_{\text{min}}$	59.4	4640	2071	-65.8	529	0.231	0.055

## Targets

	$G_{\text{cap}}$ (kg_H2/kg_total)	$V_{\text{cap}}$ (kg_H2/L)
2020 System	0.055	0.040
Ultimate System	0.075	0.070
2020 Adsorbent	0.201	0.089
Ultimate Adsorbent	0.274	0.156
700 bar Tank Adsorbent	0.166	0.055
No Flowthru 2020 Adsorbent	0.191	0.065
No Flowthru Ultimate Adsorbent	0.260	0.114
No Flowthru 700bar Tank	0.157	0.040

Charged State:  $T_{\text{chg}}=230\text{K}$ ,  $P_{\text{chg}}=100\text{ bar}$  Discharged State:  $T_{\text{disch}}=400\text{K}$ ,  $P_{\text{disch}}=5\text{ bar}$

	$n_{\text{max}}$ (mol/kg_ads)	$E_{\text{max}}$ (J/mol)	$E_{\text{min}}$ (J/mol)	$\Delta S_0$ (J/mol-K)	$\rho_{\text{bulk}}$ (kg/m <sup>3</sup> )	$G_{\text{cap}}$ (kg_H2/kg_total)	$V_{\text{cap}}$ (kg_H2/L)	
Nominal MOF-5	59.4	4640	2071	-65.8	181	0.055	0.011	
Optimized $E_{\text{min}}$ & $E_{\text{max}}$	59.4	12413	12412	-65.8	181	0.125	0.026	
$n_{\text{max}}$ for 2020 $V_{\text{cap}}$	180	12413	12412	-65.8	181	0.259	0.065	No flowthru
$n_{\text{max}}$ for Ultimate $V_{\text{cap}}$	460	12413	12412	-65.8	181	0.375	0.114	No flowthru
$n_{\text{max}}$ for 700bar Tank $V_{\text{cap}}$ Optimized $E_{\text{max}}$ & $E_{\text{min}}$	102	12413	12412	-65.8	181	0.179	0.040	No flowthru
$n_{\text{max}}$ for 700bar Tank $V_{\text{cap}}$ Nominal $E_{\text{max}}$ & $E_{\text{min}}$	514	4640	2071	-65.8	181	0.180	0.040	No flowthru
$\rho_{\text{bulk}}$ for 700bar Tank $V_{\text{cap}}$ Nominal $E_{\text{max}}$ & $E_{\text{min}}$	59.4	4640	2071	-65.8	NA	NA	NA	No flowthru