Testing, Modeling, and Evaluation of Innovative Hydrogen Storage System Designs:

Recap of 2009-2015 Highlights

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General Motors Company

June 10, 2015

Project ID: ST009

HSECoE

GM RESEARCH & DEVELOPMENT

Overview

Timeline

- Project Start Date: February 2009
- Project End Date: June 30, 2015

Relevance/Barriers Addressed

- System weight and volume (A)
- Energy efficiency (C)
- Charging/discharging rates (E)
- Thermal management (J)

Budget

- Total Project Value: $3,048,547
- Cost Share: $609,709
- DOE Share: $2,438,838
- DOE Funding Spent*: $2,351,493

*as of 3/31/15

Partners

United Technologies Research Center

JPL

Ford

SRNL
SAVANNAH RIVER NATIONAL LABORATORY

Pacific Northwest
NATIONAL LABORATORY

OSU
Oregon State
UNIVERSITY

NREL
National Renewable Energy Laboratory
Innovation for Our Energy Future

Los Alamos
NATIONAL LABORATORY

MICHIGAN

HEXAGON
LINCOLN

Plan and Approach

System Simulation Models and Detailed Transport Models for Metal Hydrides:

- System simulation models for metal hydride and cryo-adsorption (with UTRC), for testing in the integrated framework
- Build detailed 2-D models to include heat transfer, chemical rxns, guide system models
- Design & Optimization of novel heat exchangers

Pelletization of AX-21, MOF-5 (with Ford), and sodium alanate (with UTRC):

–Test binders and additives for pelletization

–Measure hydrogen uptake, thermal conductivity, and pellet strength

–Model effects of anisotropic thermal conductivity in MOF-5 pellets on temperature and refueling time

Transport Models and Experimental Model Validation for Adsorbent Systems(with SRNL):

–Construct and test detailed simulation models for adsorbent systems

–Installation and testing of a highly-instrumented cryo-adsorbent apparatus containing MOF-5 powder

–Test simulation models for system performance, performance metrics in relation to DOE targets

Other Tasks (with HSECoE partners):

–Prioritization of DOE Technical targets (OEMs)

–User testing of the integrated Framework model and the “Tankinator” tank-sizing model

–Integration of hydrogen storage models in a common framework

Progress Towards Key Tasks and Milestones

Tasks: Model MOF-5 powder system with helical coil heat exchanger; Validate desorption and adsorption models experimentally with a cryo-adsorbent test apparatus within the parameters of the milestones.

1. Discharge thermal management for adsorbent systems

- Milestones: Design and demonstrate an internal heat exchanger capable of achieving a scaled release rate of 0.02 g H_2/(sec. kW) at P = 60 – 5 bar and T = 80 – 160 K, with a mass less than 6.5 kg and a volume less than 6 liters. Validate MOF-5 powder bed having a total hydrogen density of: 18 g H_2/(100 g MOF) and 24 g H_2/(liter MOF).
- Discharge experiments with helical coil resistive heater and desorption model show the milestones of 18 g H_2/(100 g MOF) and 24 g H_2/(liter MOF) can be achieved.
- The heat exchanger for a full-scale MOF-5 powder system, based on current heater specifications, is unlikely to meet the targets of mass < 6.5 kg, volume < 6 liters.

2. MOF-5 powder system flow-through cooling tests & model validation

- Milestone: Demonstrate an internal flow through cooling system based on powder media capable of allowing less than 3 min. scaled refueling time.
- Model indicates that to refuel the 3L test vessel in less than 3 minutes within the set parameters of the milestone (5-60 bar and 150-80 K) a flow rate 1.2 g/s (800 LPM) is required, which exceeds our instrumentation’s limit of 0.7 g/s.

Accomplishment I – Design of Heat Exchangers and Framework Storage Modules for Thermal Management of On-board Storage Systems (2010-11)

- **Two heat exchanger (HEX) system designs** for the surrogate metal hydride material (sodium alanate) were explored. **The dual bed system** with a conventional shell-and-tube design HEX was considered in detail for gravimetric and volumetric densities.

- The second design, **a modular helical coil HEX,** offers low heat exchanger weight and provides better performance and lower cost than the dual bed system. **(A modified helical coil design with a central heating rod was later used by GM in 2012-14 in a cryogenic storage vessel with MOF-5 adsorbent material.)**

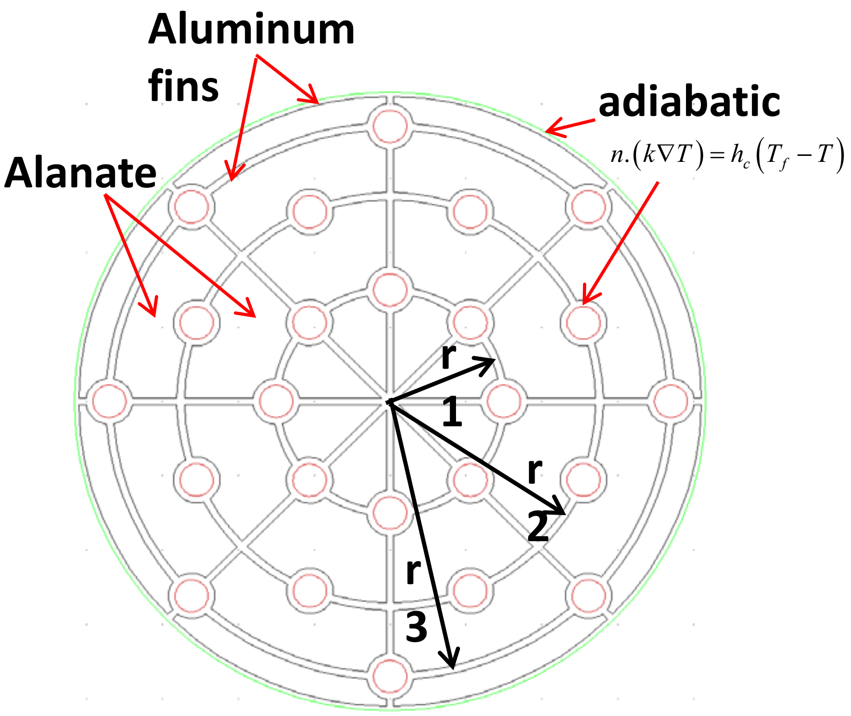
- Both systems were able to complete the four test drive cycles in the **Framework model** successfully but they **required a substantial fraction of hydrogen to be used for desorption**

- A HPMH system was also developed and was tested in the Framework. Its advantages are – good cold start capability, high efficiency (no need to burn H_2 for desorption). Characterized by lower ΔH, higher ρ, but material could be more expensive.

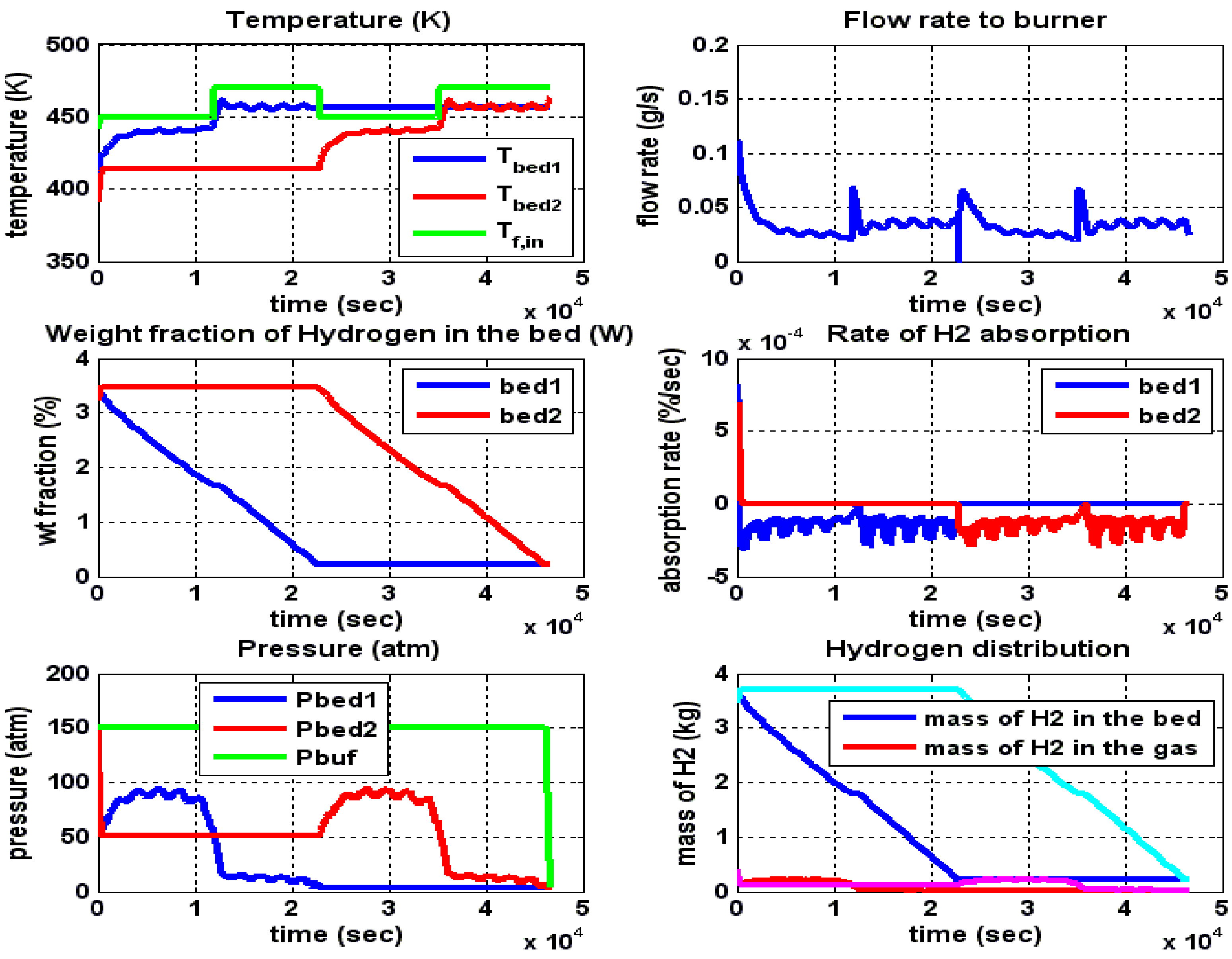
- **Design analysis and methodology developed can easily be adapted to different materials with greater potential than metal hydrides** - higher H_2 absorption capacity, lower ΔH, and higher bed density ρ**.**

Heat Exchanger Design – I
Dual Bed Design for Sodium Alanate

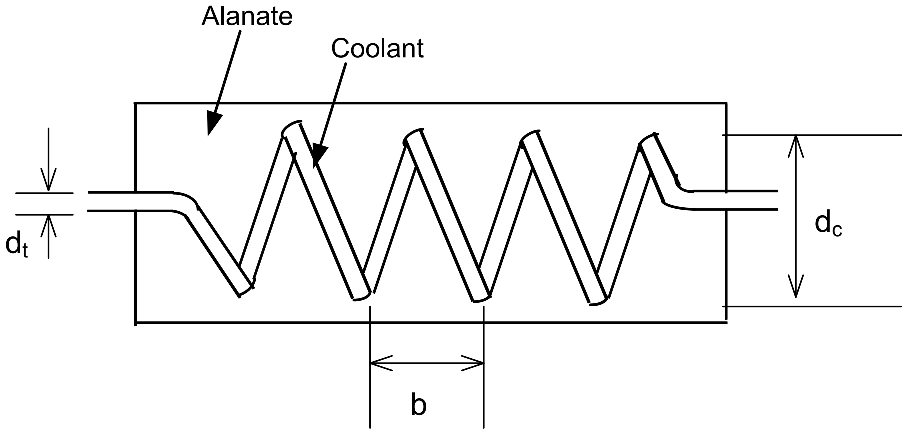
- Dual bed system - alanate in shell, cooling tubes interconnected by aluminum fins
- Heat exchanger designed to refuel the tank in 10.5 minutes (40% of DOE 2010 Target) - 3.2 wt% H_2
- Tube and fin thickness, and placement of fins, optimized for minimum heat exchanger weight
- For the optimized design, refueling simulations were performed using 2-D COMSOL® models
- Lumped parameter model formulated for system simulations in the Framework model



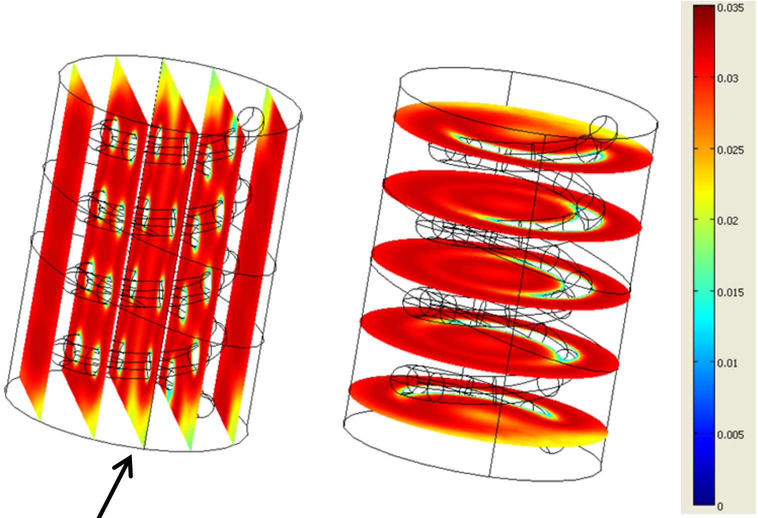
Dual Bed Results in Framework for Drive Cycle 1



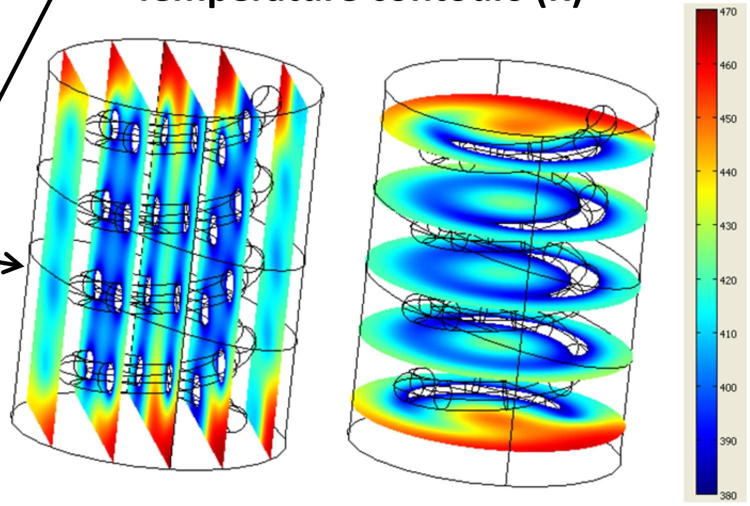
Heat Exchanger Design – II (Helical Coil Heat Exchanger with Alanate in Shell)



Weight fraction contours

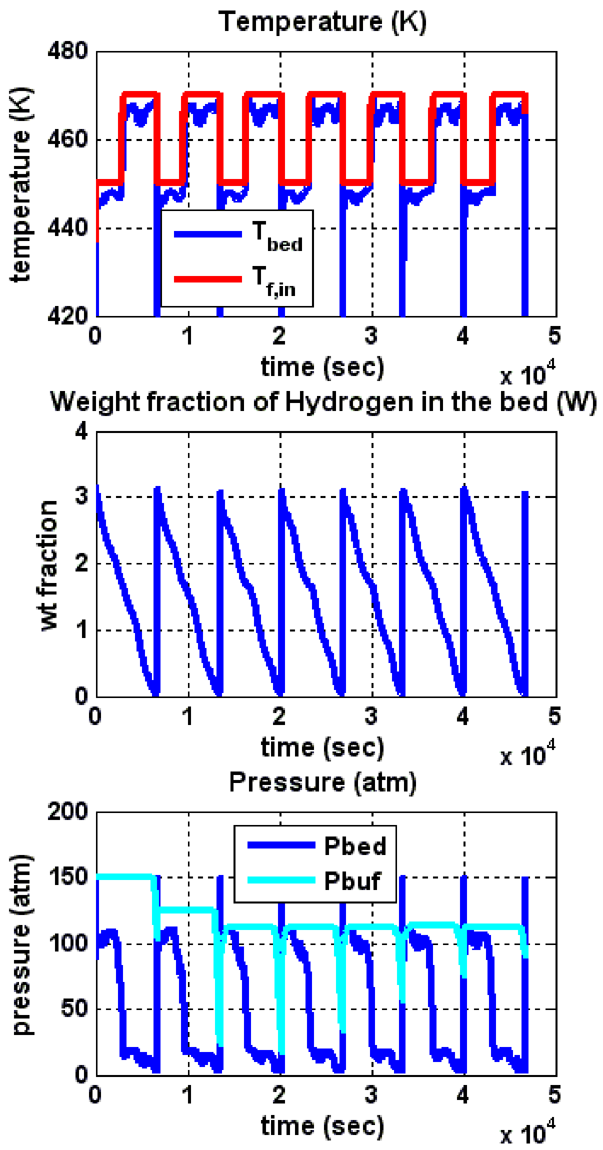


Temperature contours (K)



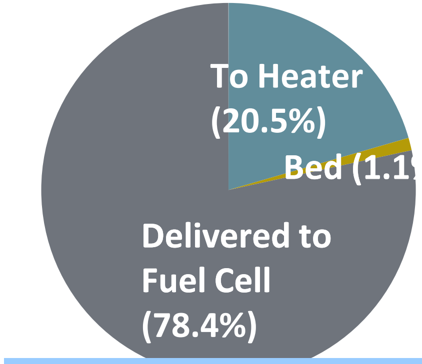
- **Helical coil heat exchanger works well with systems with internal heat generation; it has higher heat transfer coefficient than straight tubes because of higher turbulence**
- **For effective heat transfer, coil radius and pitch can be determined as a function of system properties – ΔH, k, ΔT, w, ρ_b, t_f**
- **Optimized the design using 3-D refueling simulations by changing vessel diameter, coil diameter, and pitch for sodium alanate system**
- **Heat exchanger mass is roughly 1/3 that of the conventional shell-and-tube design.**

Helical Coil Design Results in Framework for Drive Cycle 1



- Helical coil HEX weight is about 1/3 of the previous system, but for $NaAlH_4$, 7 vessels are needed

- But this design is very promising for a high capacity material with somewhat lower ΔH



H_2 distribution at the end of DC1

Accomplishment II. Hydrogen Adsorption in Cylindrical Pellets: Thermal Conductivity Effects & Optimal Pellet-Sizing (2011-13)

Pelletization offers the potential to increase volumetric storage capacity, but two issues must be addressed:

- Decrease of hydrogen adsorption capacity in adsorbent pellets
- Mass and heat transport in pellets affect the rate of adsorption and cause difficulties in meeting the refueling time targets. Increasing the pellet thermal conductivity with the additive ENG accelerates cooling within the pellets, thus decreasing refueling time.
- Therefore, it is important to understand the effect of pellet shape and size on refueling

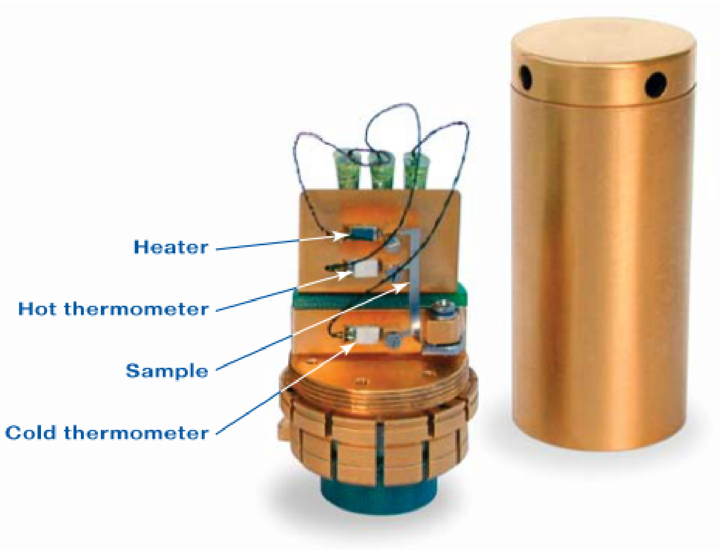
Low Temperature Thermal Conductivity Measurem

- Performed using a Quantum Design Thermal Transport System (right), for T = 3 to 350 K.
- Thermal conductivity directly calculated fron applied heat power, ΔT and sample geometry

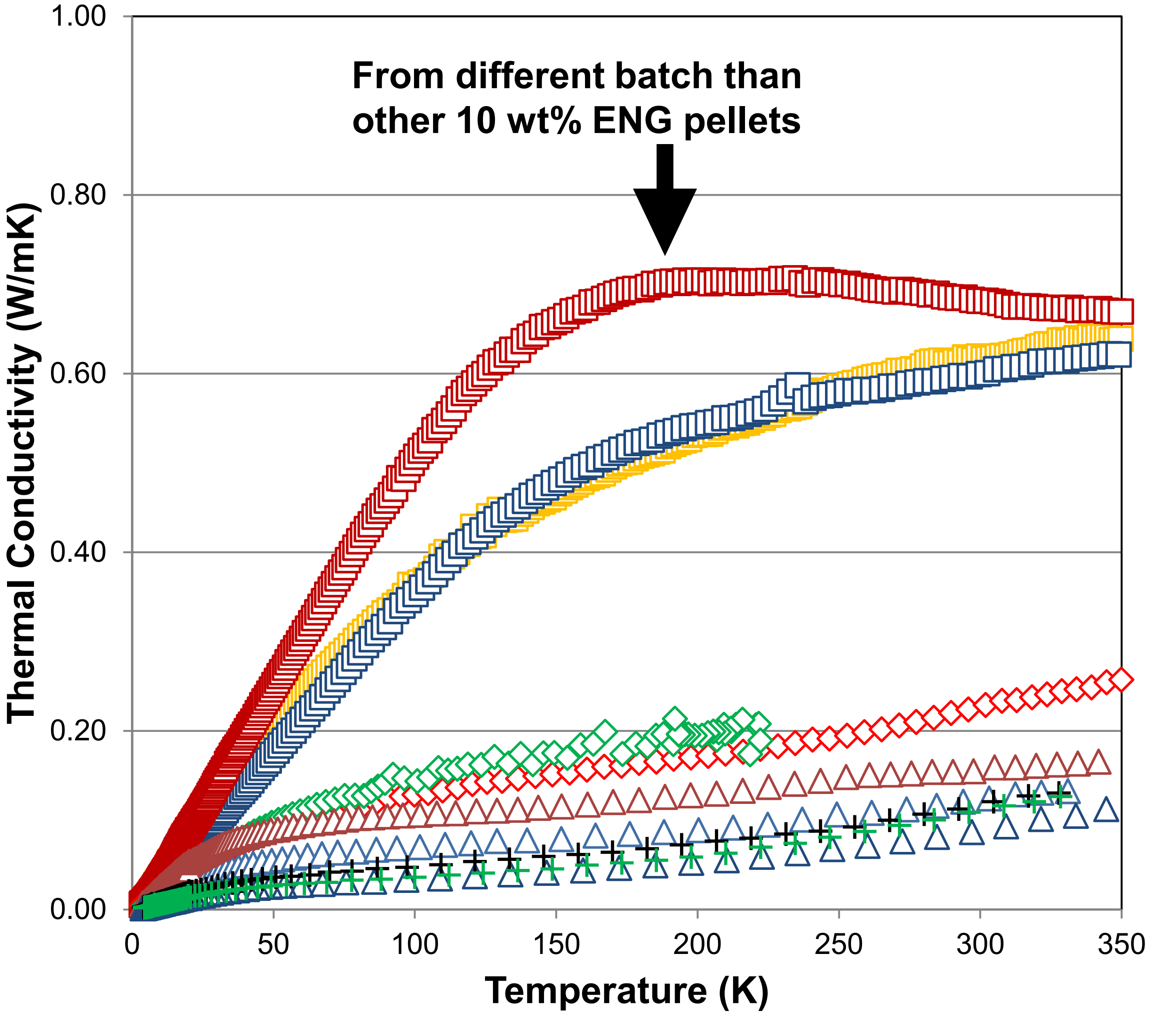
$$k = K\ (L/A),$$

where K = thermal conductance,

L = sample length, A = sample area



Low Temperature Thermal Conductivity Measurements for MOF-5 Pellets (0.5 g/cm^3)

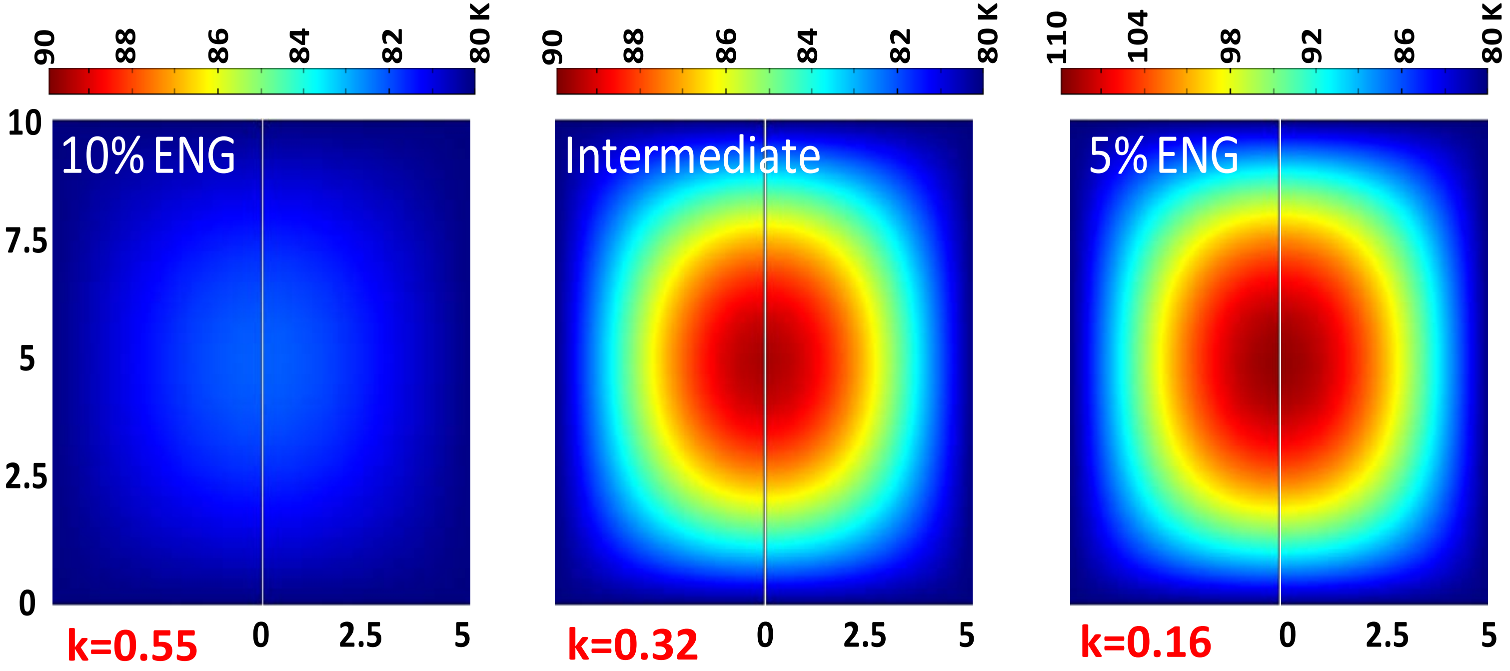


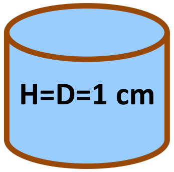
△ **0 wt% ENG (from Ford)**
+ **0 wt% ENG (GM prepared)**
◇ **5 wt% ENG (from Ford)**
□ **10 wt% ENG (from Ford)**

Wt% ENG	k @ 77K	k @ 160 K
0_#1	0.0309	0.044
0_#2	0.065	0.0829
0_#3	0.101	0.1178
0_GM#1	0.0432	0.0618
0_GM#2	0.033	0.0499
5_#1	0.114	0.1566
5_#2	0.1273	0.1841
10_#1	0.2729	0.4954
10_#2	0.2947	0.483

Hydrogen Adsorption in Cylindrical MOF-5 Pellets: Thermal Conductivity Effects & Enhanced Natural Graphite

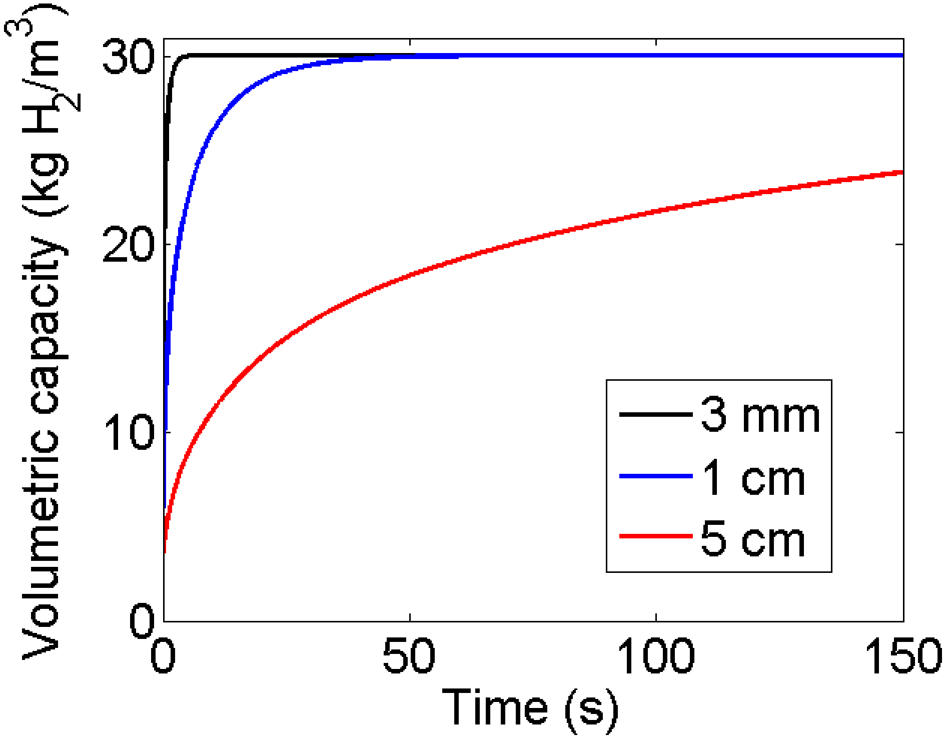
Simulation of a MOF-5 pellet at 140 K and 4 bar (empty) that is enveloped in H_2 gas at 80K and 30 bar (refueling)





Temperature contours within a 1x1 cm pellet for three different thermal conductivity (ENG) values at 25 seconds. Refueling is completed for the first case, nearing completion for the second case, but significant temperature gradients exist for MOF-5 with 5% ENG.

Effect of Pellet Size on Transient Volumetric Capacity



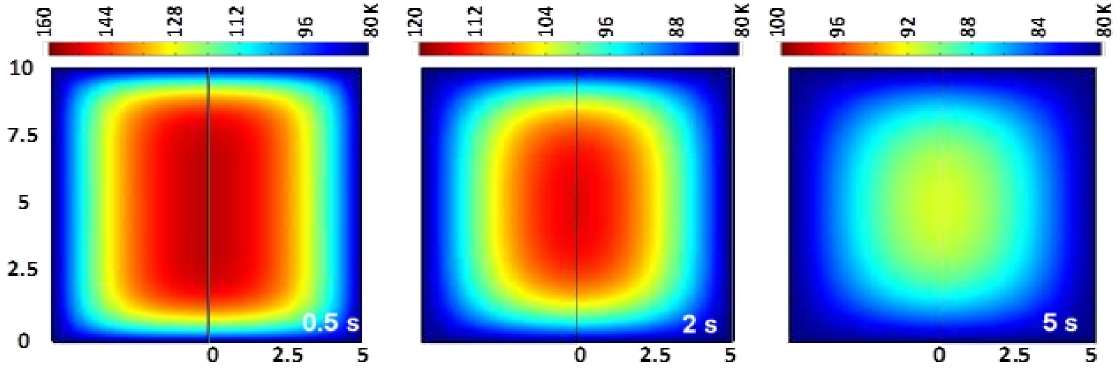
For short cylindrical geometry (H=D) pellets:

- As size increases, a pellet takes longer to equilibrate with the bulk gas, due to higher heat and mass transfer resistances
- **The transient volumetric capacity of the pellet decreases with increasing size.**
- A 1 cm pellet takes 15-20s to reach 95% capacity; a 5 cm pellet takes several minutes.

Hydrogen Adsorption in Cylindrical Pellets: Effects of Anisotropic Thermal Conductivity and Pellet Size

Experimental data indicates that the in-plane (radial) value of thermal conductivity can be 5 times greater than the axial thermal conductivity.

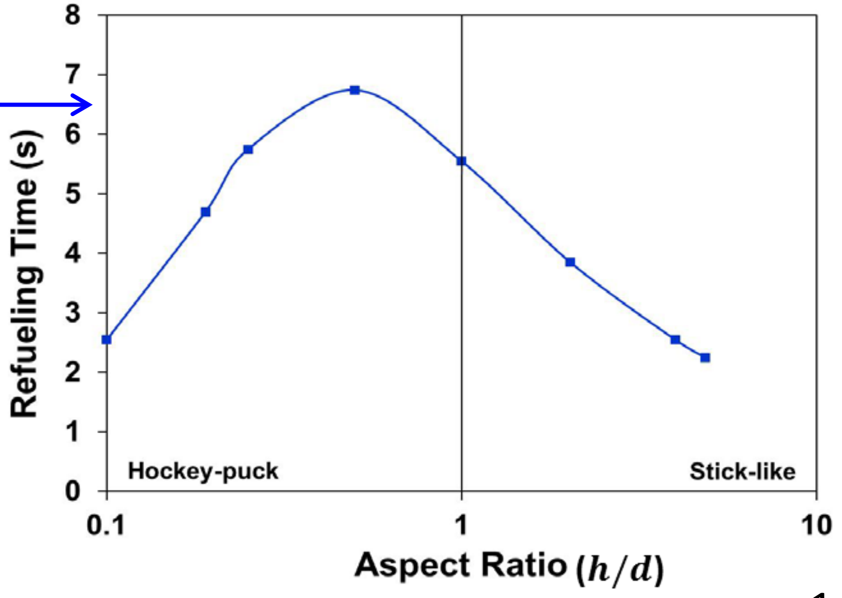
Temperature contours at times 0.5, 2, and 5 seconds for the case: $\lambda_{rad} = 4\lambda_{ax}$, 10% ENG, 1x1 cm pellet size.



Optimal Pellet-Sizing for Fast Refueling Time

Time required for a pellet with anisotropic thermal conductivity ($\lambda_{rad} = 4\lambda_{ax}$) of volume $\pi/4\ \mathrm{cm}^3$ to reach 95% of its volumetric storage capacity as a function of aspect ratio (h/d).

Both "stick-like" and "hockey-puck" pellets take less time to refuel compared to a pellet with d=2h, and may be suitable for fast refueling at relatively high storage volumes.

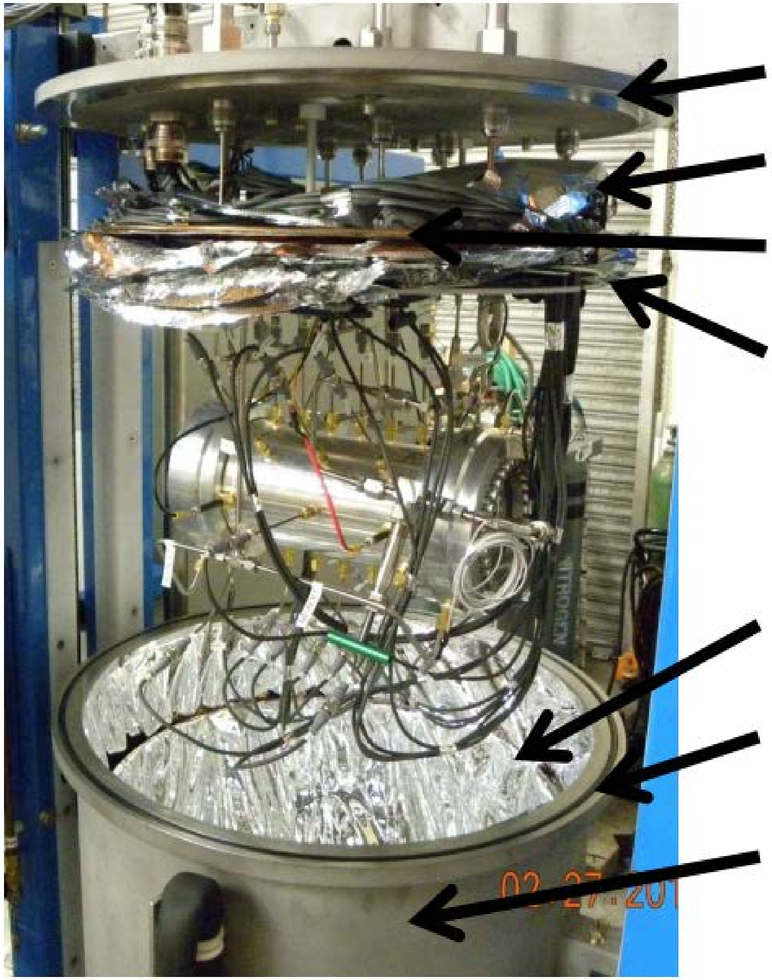


Accomplishment III. MOF-5 Hydrogen Storage System: Cryogenic Test Apparatus with Helical Coil Heat Exchanger (2012-14)

- Designed, installed and tested a highly-instrumented cryo-adsorbent apparatus containing MOF-5 powder for both adsorption and desorption experiments.
- Helical coil heat exchanger design was selected for use in the 3-liter cryogenic test apparatus to supply the heat required during discharge. The helical coil provides an efficient way of packaging a heat exchanger at low cost.
- 3-D COMSOL® model of the cryogenic test vessel with a helical coil was used to optimize the design of the heat exchanger. The helical coil design pitch and radius can easily be changed to ensure that the bed elements are within a specified distance of the heat source.
- Performed test runs with cryo-adsorbent apparatus for experimental validation of desorption model with helical coil resistive heater
- Flow-through cooling of MOF-5 powder bed during charging was examined with both experiments and model simulations.

3-Liter Cryogenic Test Apparatus with Helical Coil Heat Exchanger

- **Variable inlet and outlet flow rates up to 0.5 g/s (332 LPM)**
- **Test vessel vacuum chamber for adiabatic conditions**
- **Vessel adsorbent bed volume = 3 Liters**
- **Bed sealed on each end with porous metal disks (nominal pore size = 2 microns)**
- **Up to 22 axial positions for temperature measurements with adjustable radial position**
- **Approximately 525g of MOF-5 powder packed in vessel giving a bed density of 0.18 g/cm^3 (volume of heater removed)**



Vacuum chamber

Multi-layer Insulation

Copper cold wall

Multi-layer Insulation

Copper cold wall with multi-layer insulation on either side

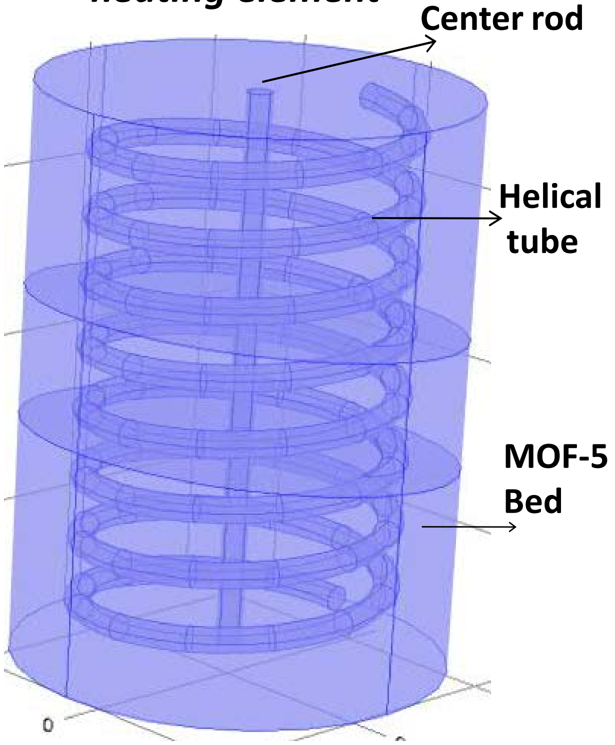
Buna-n O-ring

Vacuum chamber cylinder

Desorption model with Helical Coil Electric Heating

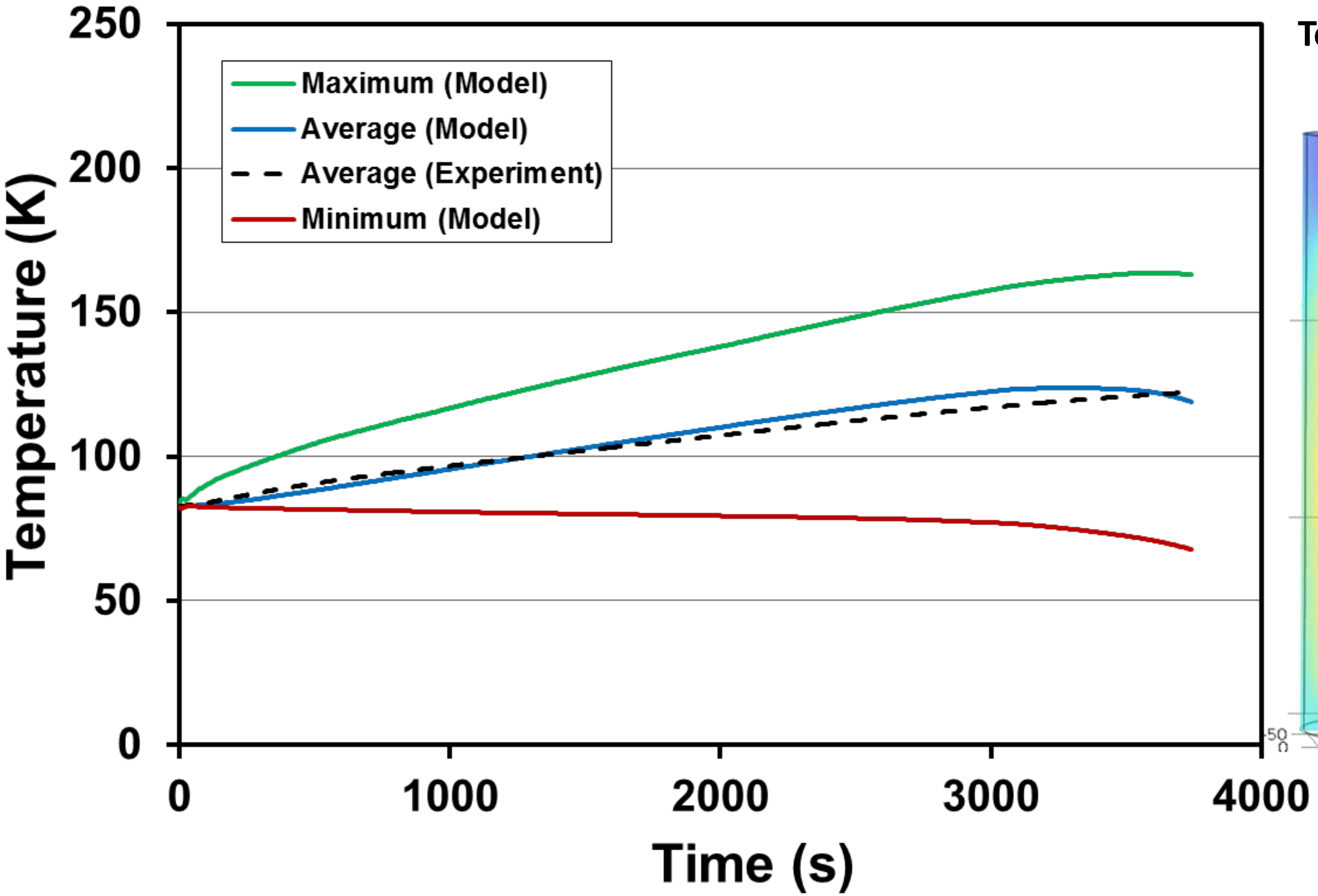
- 3-D COMSOL® model of the cryogenic test vessel includes a 3 Liter cylindrical bed, adsorbent, and a helical coil heat exchanger/center rod within the MOF-5 bed.
- Model equations include mass and energy balance, Darcy's law for pressure variation in the bed and a modified Dubinin-Astakhov (D-A) hydrogen adsorption isotherm.
- Low thermal conductivity of adsorbent materials makes internal heating device design quite challenging. In order to accommodate the low bed thermal conductivity, the design was modified to include a longitudinal heating element at the center of the bed.
- Helical coil design pitch and radius can easily be changed to ensure the bed elements are within a specified distance of the heat source.
- Hydrogen properties, D-A parameters and additional data obtained from HSECoE partner SRNL (B. Hardy).

Helical coil with central heating element

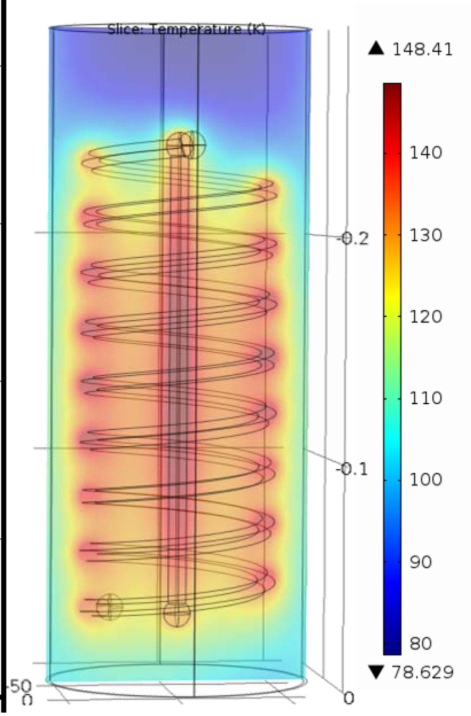


3-Liter Vessel Desorption Run: Temperature Profiles

Heat Flux = 678 W/m^2, Discharge rate = 0.02 g H_2/sec

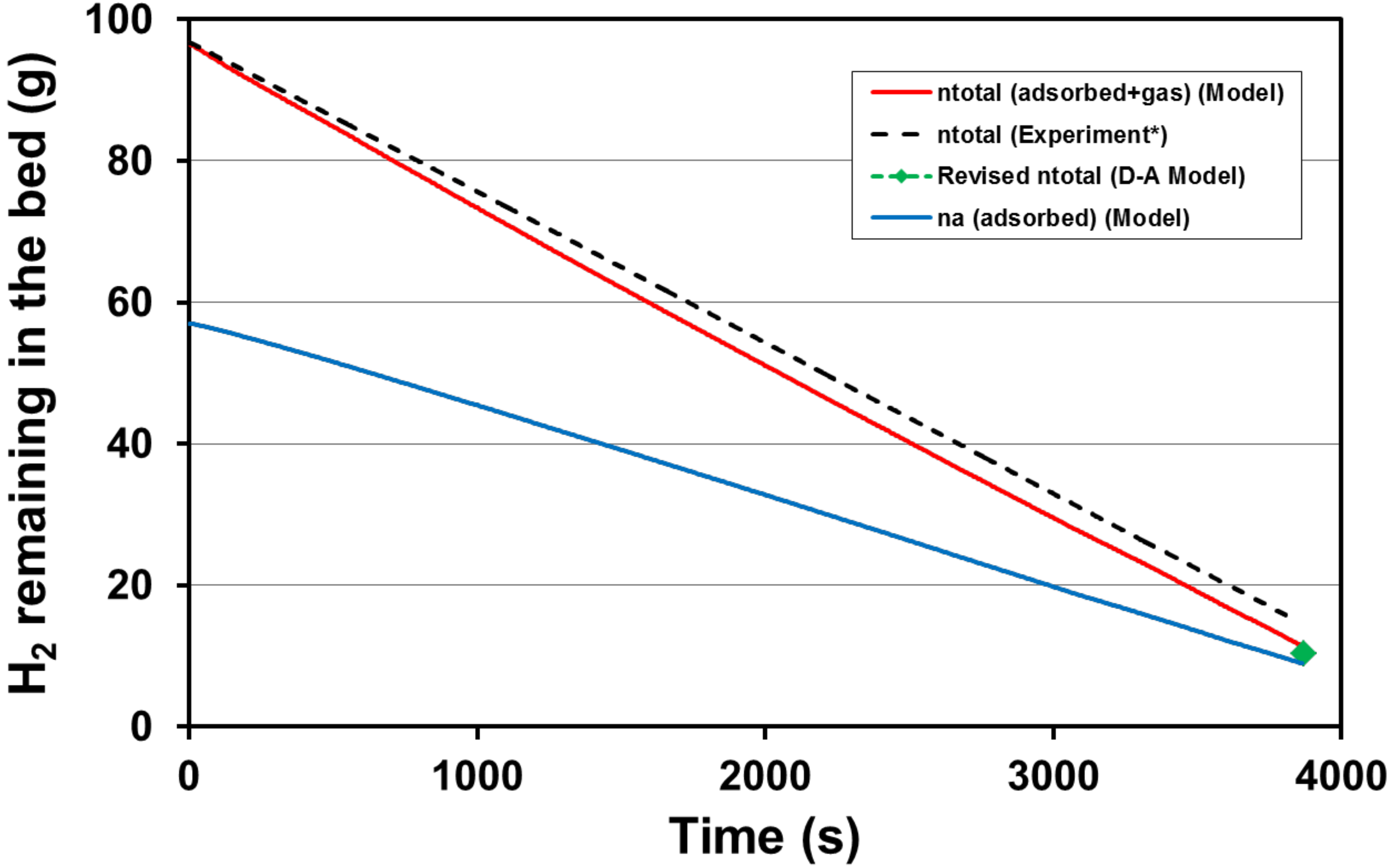


Temperature profile at 2500 s



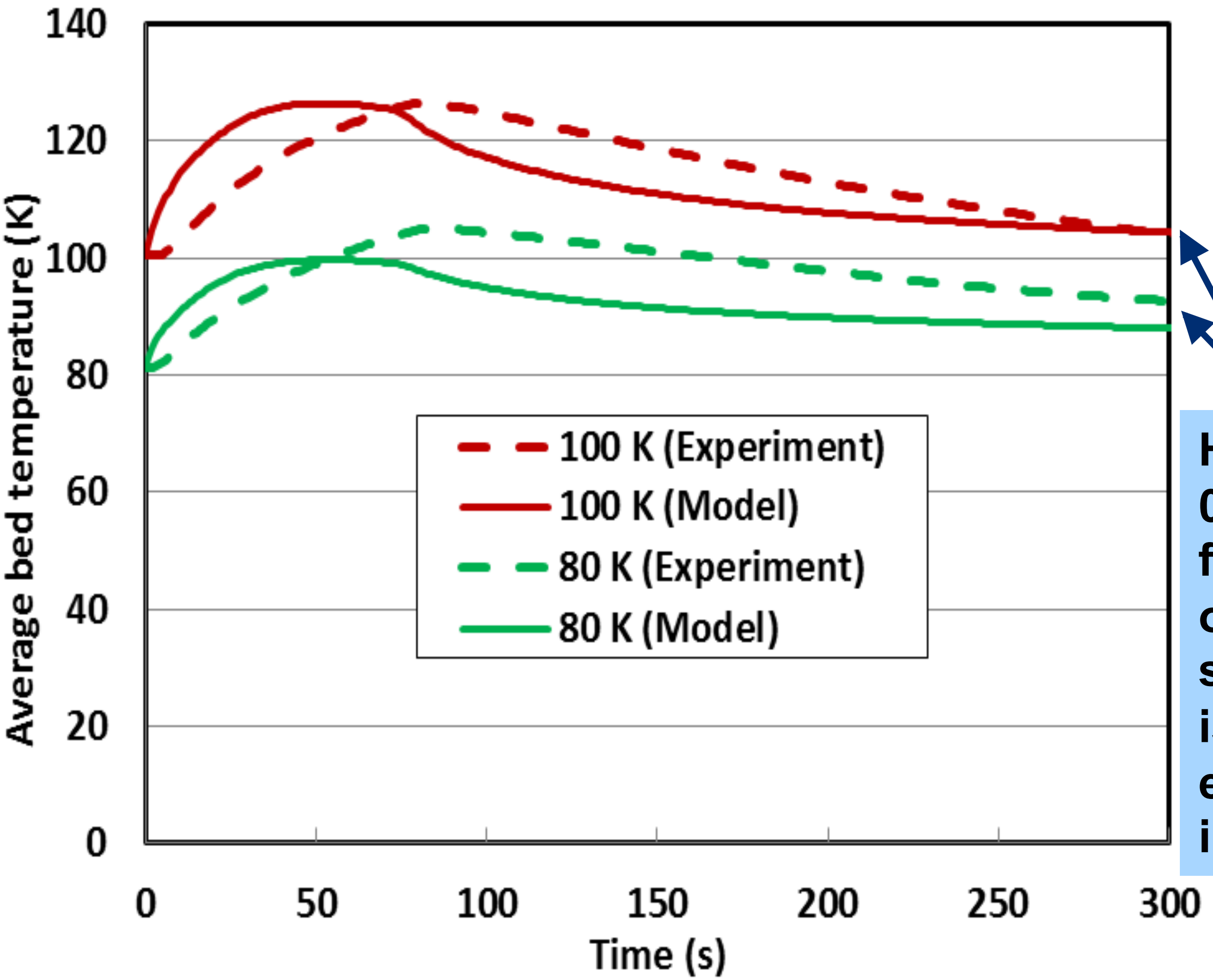
3-L Vessel Desorption Run: Total and adsorbed hydrogen in the bed

Heat Flux = 678 W/m^2, Discharge rate = 0.02 g H_2/sec



*Based on D-A Model (T_o = 83K, P_o= 60 bar) and 0.02 g H_2/sec mass flow rate.

Effect of Initial Temperature on Flow-through Cooling During Charging

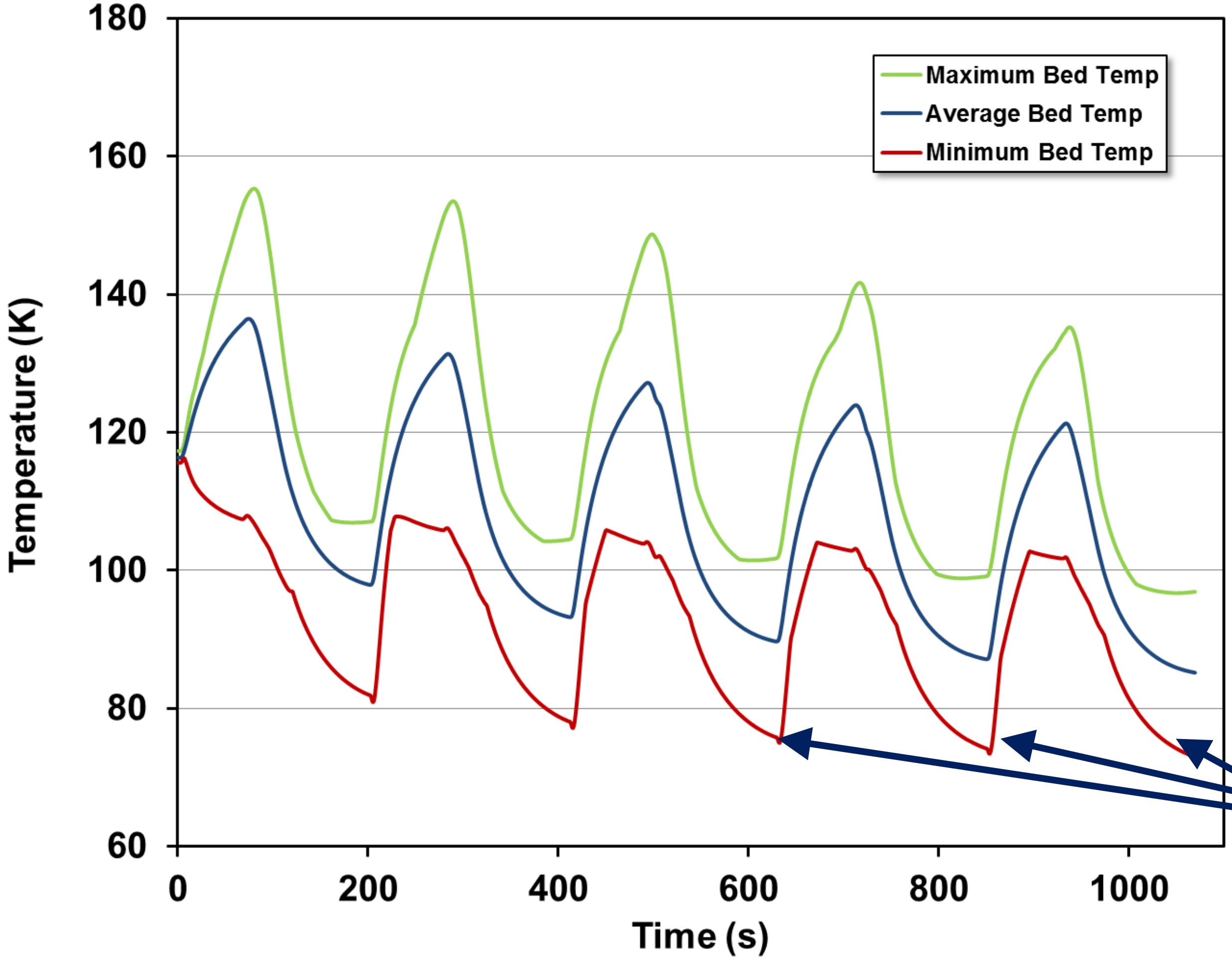


- **Initial pressure of 5 bar**
- **Outlet opened at 60 bar**
- **Continuous flow-through once 60 bar reached**

Higher flow rate than 0.5 g/s required to reach final temperature target of 80 K. Model simulation shows flow rate of 1.2 g/s is needed, which exceeds the limit of our instrumentation.

Achieving Bed Temperature of 80 K – Rapid Cooling

Starting bed temperature of 115 K



- More than half of RTDs read below 90 K
- High temperature of 96 K, low of 73 K, avg. of 85 K

Certain regions of the bed cooled to a lower temperature than the inlet H_2 (80 K)

Summary

- **Design of Heat Exchangers and Framework model testing**
  - i. A modular helical coil heat exchanger offers low weight and may provide good performance at a low cost. The design appears to be promising for a high capacity material with lower ΔH than sodium alanate.
  - ii. Both system designs (dual bed, modular helical coil) for sodium alanate complete the four test drive cycles in the **Framework model** successfully.
  - iii. Test simulations of Framework assisted in identifying improvements to model convergence; Tankinator simulations were performed to provide user feedback.
- **Hydrogen Adsorption in MOF-5 Cylindrical Pellets**
  - i. 2-D model of refueling of MOF-5 pellet with Unilan adsorption isotherm shows improved refueling times due to ENG additive and anisotropic thermal conductivity.
  - i. “Stick-like” and “hockey-puck” pellets may be suitable for fast refueling at relatively high storage volumes.
- **Cryo-adsorption Test Vessel with heat exchanger:**
  - i. Completed the design, build, and installation of the cryo-vessel with automated control instrumentation
  - ii. Installed and tested a helical coil heat exchanger in the cryo-vessel, reaching the targeted H_2 release rate
  - iii. Validated adsorption and desorption models with data from cryo-vessel experiments

Collaborations: Center Partners

Industrial Collaborators

- → **MOF-5 characterization, pure and thermally enhanced, thermal conductivity measurements, Unilan adsorption model fit parameters**
- → **Modeling Framework (integration of hydrogen storage modules), user testing of Framework model for the web**
- → **Metal Organic Framework (MOF-5) supplier (synthesis and processing)**

National Laboratory Collaborators

- → **Center management, transport model equations and H_2 properties**
- → **Optimized resistive heater for material desorption and system cost modeling**

Academic Collaborators

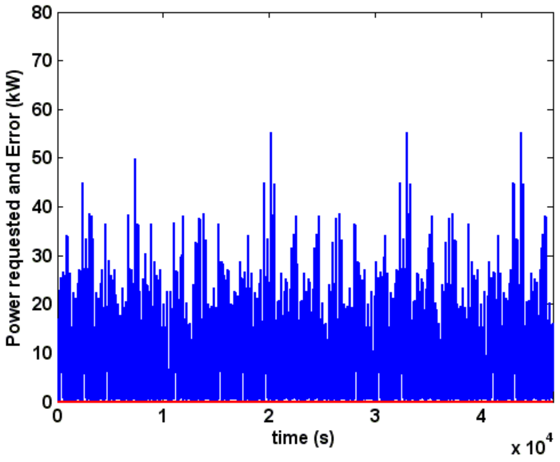
- → **Adsorbent materials member, experimental apparatus and procedure**
- → **Adsorbent materials member, experimental approach and test vessel design**

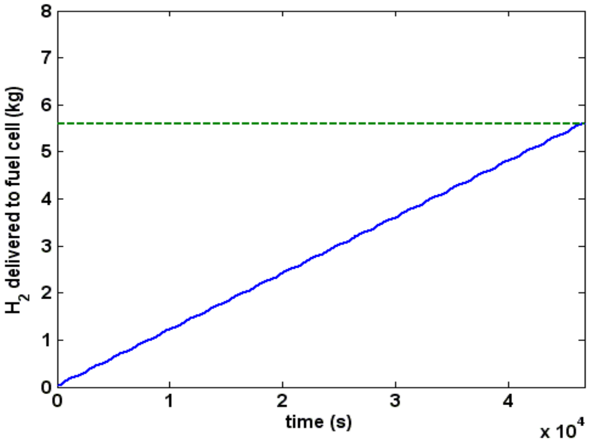
Past & Present GM Team Members

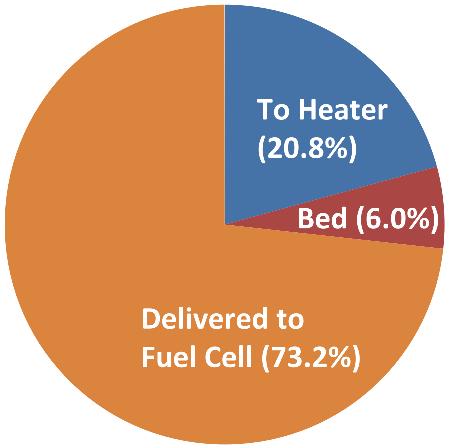
Mei Cai
Amlan Chakraborty
Greg Garabedian
Peter Hou
Niket Kaisare
Scott Jorgensen
Sudarshan Kumar
Changpeng Li
Jerome Ortmann
M. Raju
Martin Sulic
S. Kumar Vadivelu

Technical Back-up Slides

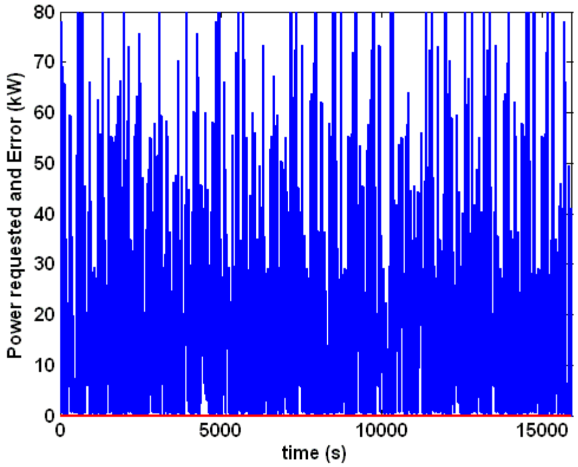
Dual Bed Results in Framework
Drive Cycles 1 (Ambient) and 2 (Aggressive)

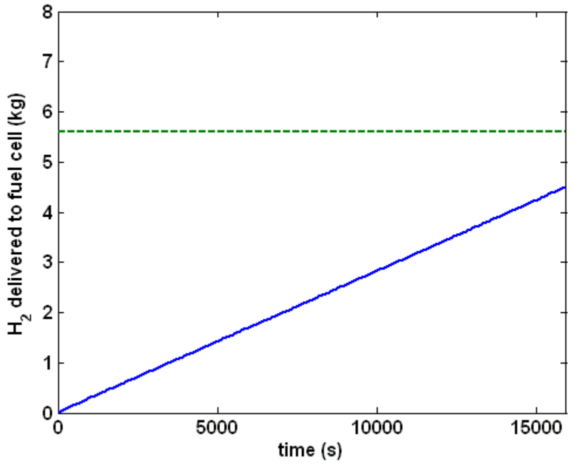


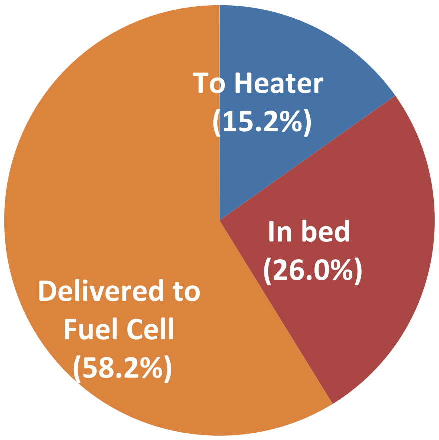




Hydrogen distribution: end of DC1

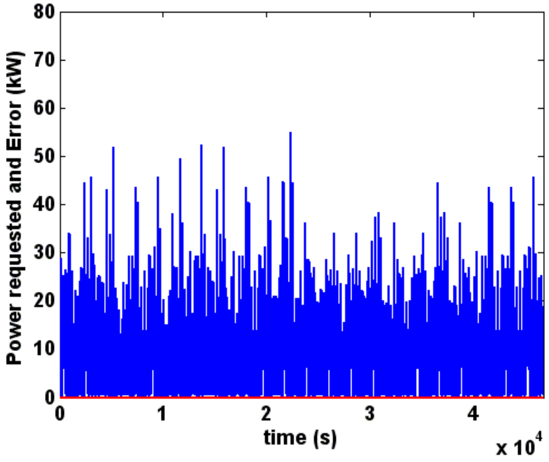


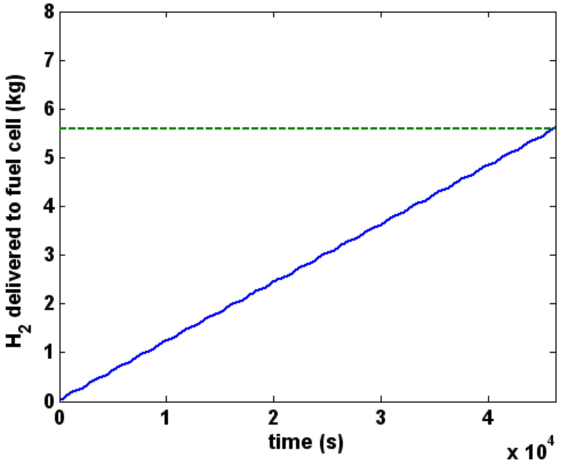


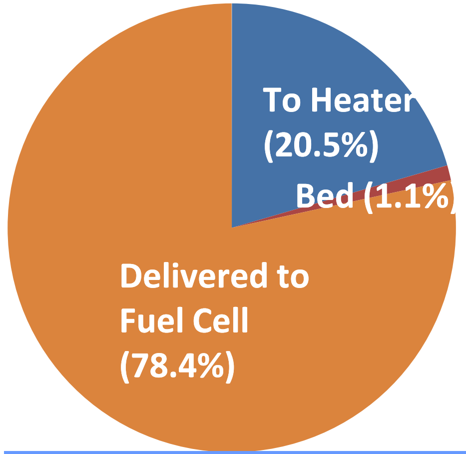


Hydrogen distribution: end of DC2

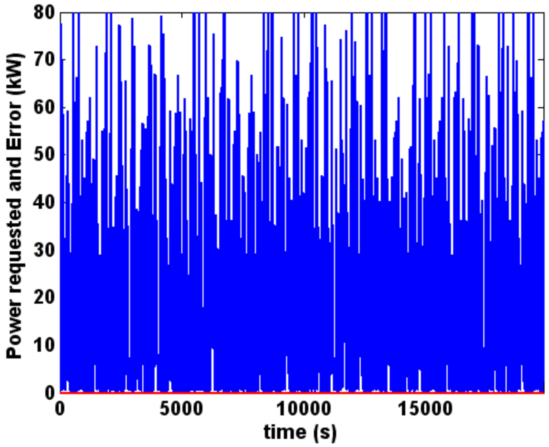
Helical Coil Design - Framework Results
Ambient and Aggressive Cycles

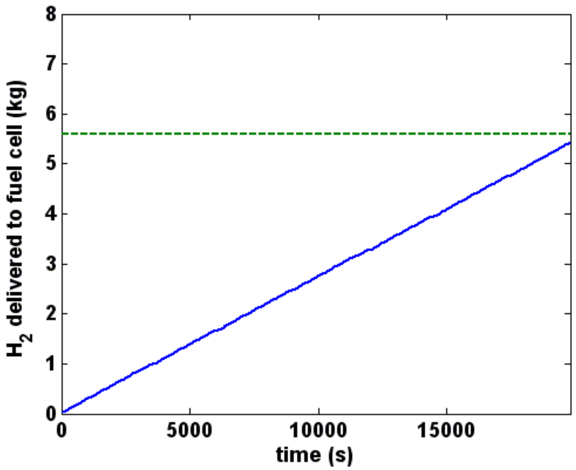


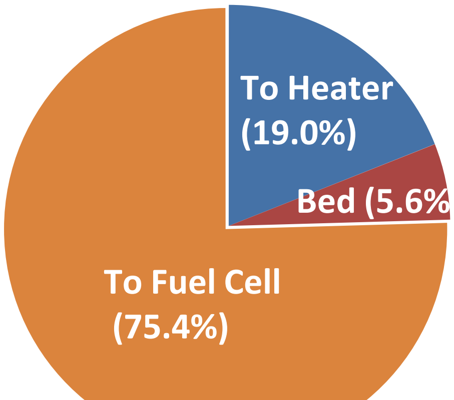




H2 distribution at the end of DC1



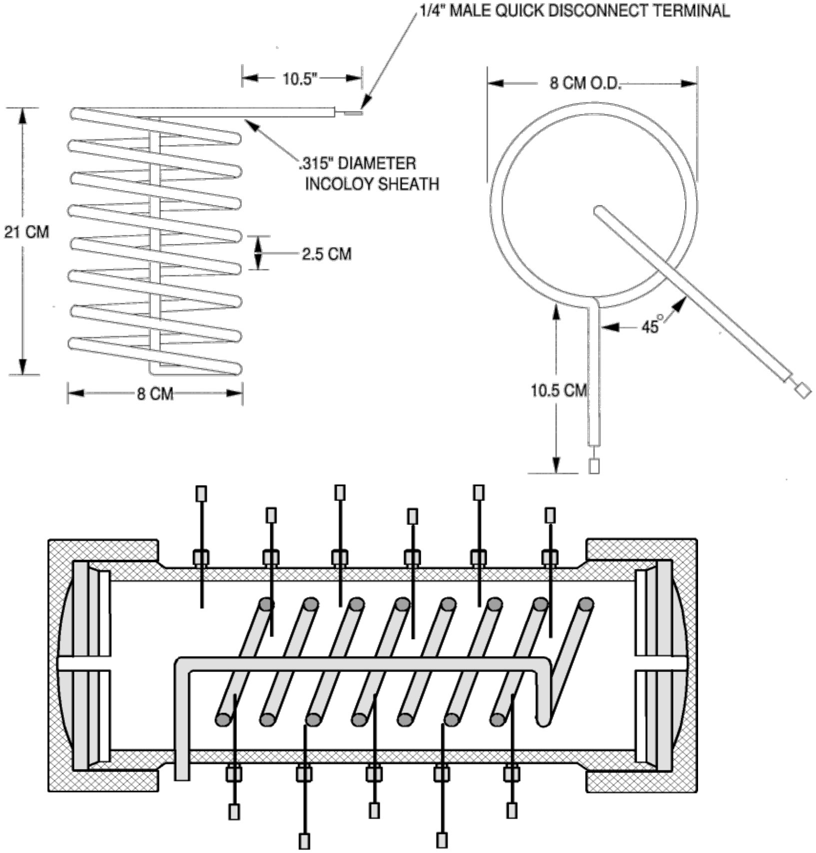




H2 distribution at the end of DC2

Instrumentation:

- **Cryo-adsorption test apparatus installed & modified for improved performance**
- **Helical coil heater with a center heating element designed and installed in vessel to supply the heat required during discharge**



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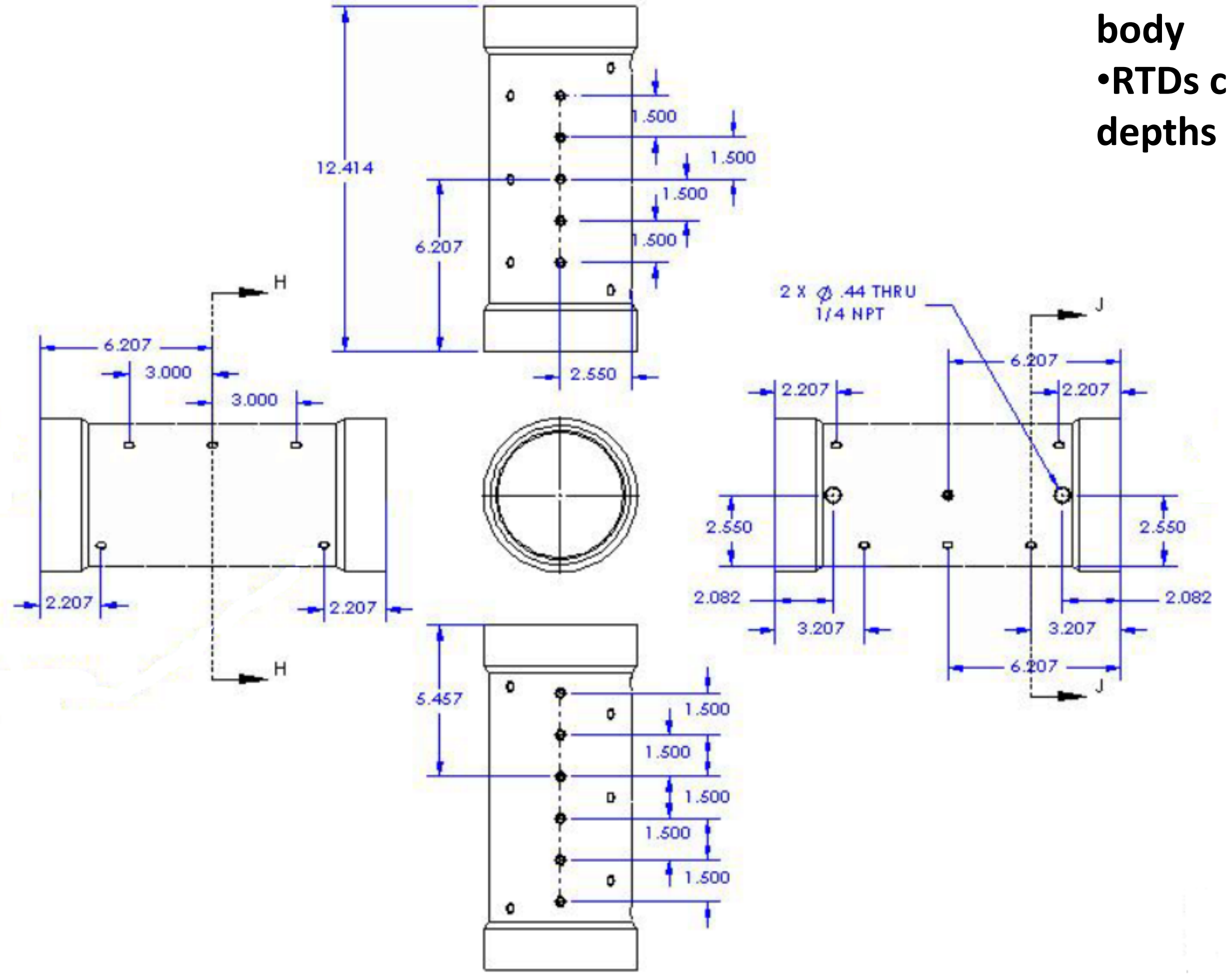
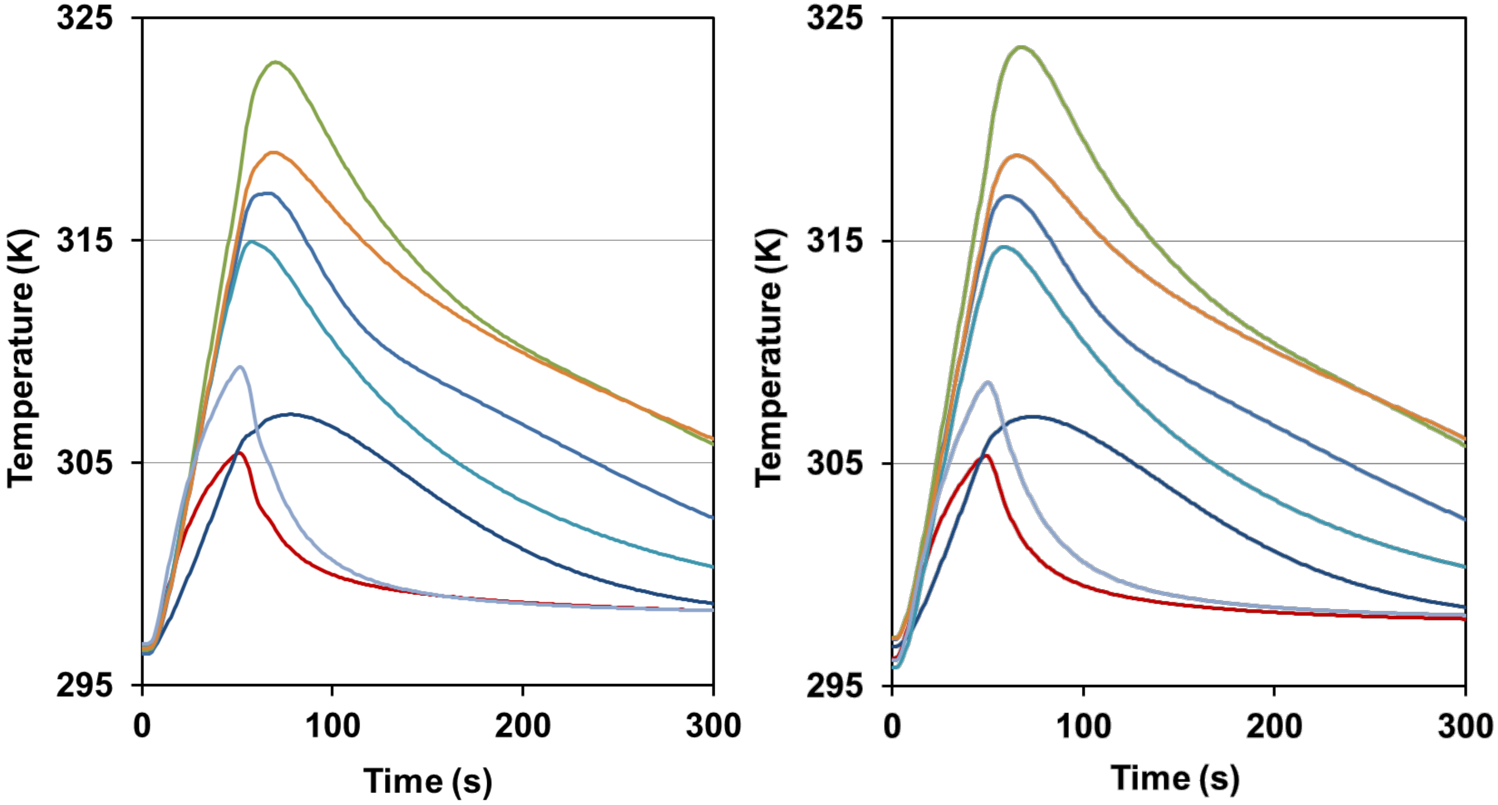
Resistance Temperature Detectors (RTDs)

- **11 down spine of vessel (5 one side, 6 other), remaining 11 along body**
- **RTDs can be positioned to various depths (from vessel wall to center)**



Horizontal vs. Vertical Vessel Positioning

Experimental temperature profiles down vessel center from inlet (red) to outlet (green) for comparable charging tests

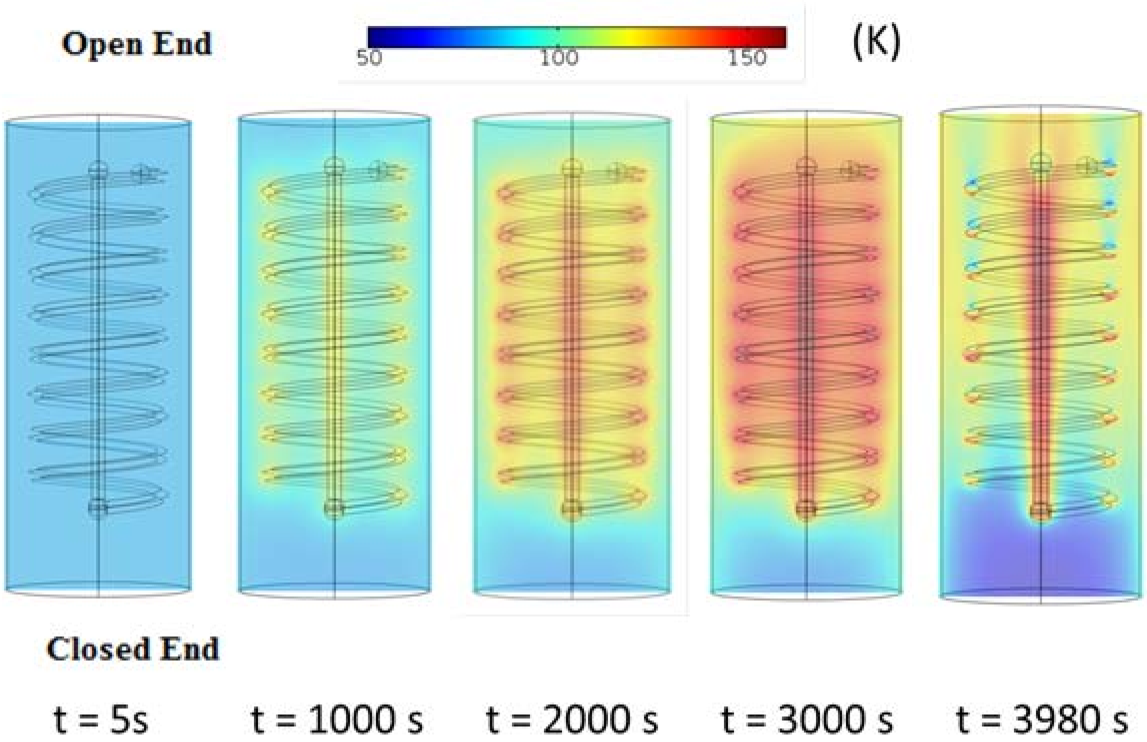


Horizontal **Vertical**

The orientation of the vessel had a negligible effect on the results.

Temperature Profiles During Discharging

T_o = 83 K, P_o = 60 bar, outlet mass flow rate = 0.02 g/s,
Supplied power = 39 W



By end of discharge average bed temp = 120 K,
minimum = 100 K and maximum = 200 K

N_{total} (adsorbed H_2 + gas) During Discharging

T_o = 83 K, P_o = 60 bar, outlet mass flow rate = 0.02 g/s,
Supplied power = 39 W