Thermal Management of On-Board Cryogenic Hydrogen Storage Systems

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General Motors Company

Project ID: ST009

HSECoE

2013 DOE Annual Merit Review
Washington DC

GM RESEARCH & DEVELOPMENT

Overview

Timeline

- Project Start: Feb 2009
- Phase II end: June 2013
- Project end: June 2014
- % complete: 85%

Relevance/Barriers Addressed

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

Budget

- DOE: $2,780,000
- GM Match: $695,000
- Funding for FY 12: $480,000
- Funding for FY 13: $425,000

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

Lincoln Composites A Member of Hexagon Composites Group

Plan and Approach

Transport Models and Experimental Model Validation for Adsorbent Systems:

- Construct and test detailed simulation models for adsorbent systems and identify operating conditions for meeting DOE S*M*A*R*T milestones *(with SRNL)*
- Detailed transport models to include adsorption and heat transfer to guide system models (with SRNL)
- Installation and testing of a highly-instrumented cryo-adsorbent apparatus containing MOF-5 powder
- Experimental validation (with cryo-adsorbent apparatus) of flow-through cooling of MOF-5 powder bed during charging
- Utilize desorption model to optimize resistance heater design of minimum weight and volume for discharge of H_2 in both a full-scale (200 liter) MOF-5 bed and the cryo-adsorbent apparatus (3 liter)
- Experimental validation of desorption model with helical coil resistive heater in cryo-adsorbent apparatus
- Determine status towards S*M*A*R*T milestones for charging and discharging both experimentally and with simulation models

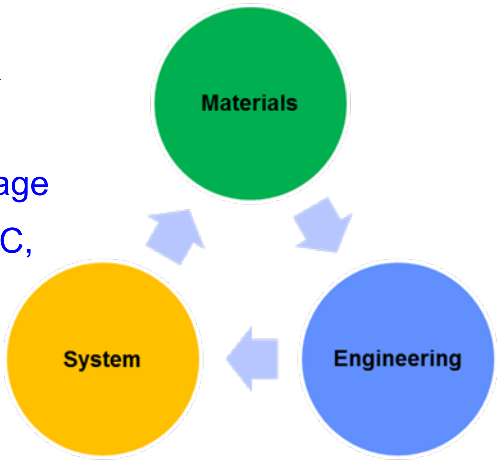
Engineering properties of materials and other *(with Ford and UTRC)*:

- Binders and additives for pelletization of MOF-5
- Modeling effects of anisotropic thermal conductivity in MOF-5 pellets on temperature and refueling time
- Determination of optimal pellet-sizing for fast refueling at relatively high storage volumes

Other Tasks (with HSECoE partners):

- Prioritization of DOE Technical targets (OEMs)
- Development of an integrated framework including the vehicle, fuel cell, and H2 storage system models (UTRC, NREL, Ford, SRNL, PNNL)

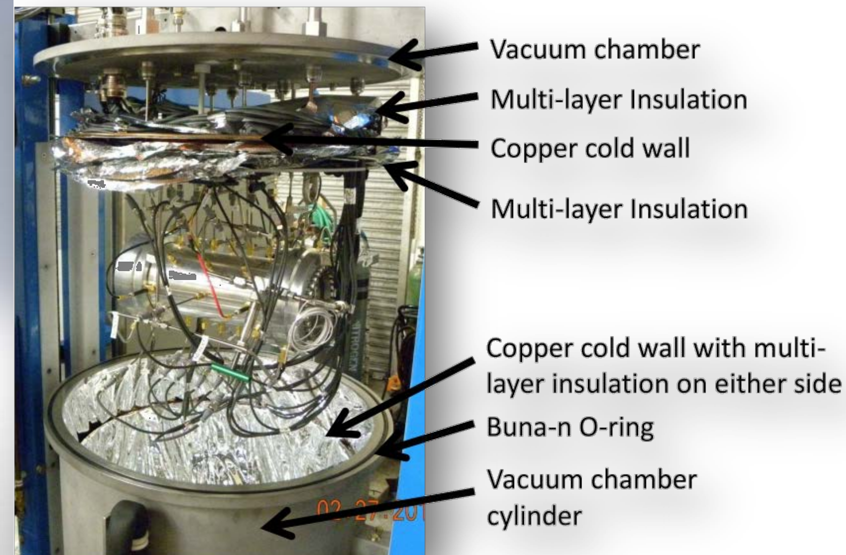
Overall Project Approach

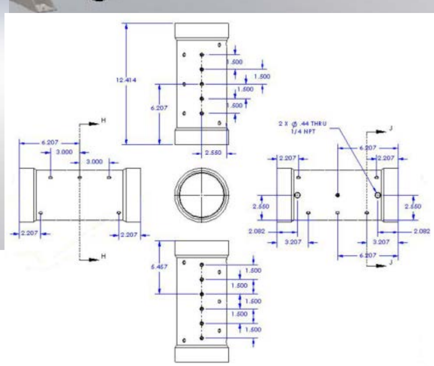


Milestones and Progress Towards:

1. **MOF-5 charging experiments and model validation**
   - Cryo-adsorption test apparatus with 3 Liter vessel installed and modified for improved performance
   - Model indicates 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
   - Model validation experiments performed for flow-through cooling and refueling processes
2. **Discharge thermal management for adsorbent systems**
   - Modeled and designed optimized resistive heater for uniform temperature distribution during discharge cycle
   - Optimized heater configuration (helical coil with center rod) installed in cryo-test vessel
   - Discharge experiments and desorption model show the milestones of 15 wt% g H_2/(g MOF-5) and 20 g H_2/(L MOF-5) can be achieved as well as scaled release rate of 0.02 g H_2/(sec. kW)
   - Full-scale heat exchanger, based on current heater specifications, unlikely to meet targets of mass < 6.5 kg, volume < 6 liters.
3. **Hydrogen adsorption in pellets (bed design)**
   - 2-D model for analysis of thermal effects on refueling, anisotropic thermal conductivity ($k_r > k_z$)
   - Collaboration with Ford to demonstrate improved thermal conductivity with additives in compacted MOF-5 (5 and 10 wt% Enhanced Natural Graphite (ENG) added to 0.3 and 0.5 g/cm^3 pellets)
   - Unilan adsorption isotherm equation included in pellet model for accurate modeling of pellets with 5 and 10 wt% ENG. (Equation fit parameters from Ford).
   - Optimal MOF-5 pellet sizes determined

Accomplishment I. Hydrogen Adsorption in MOF-5 Storage System: Cryogenic Test Apparatus

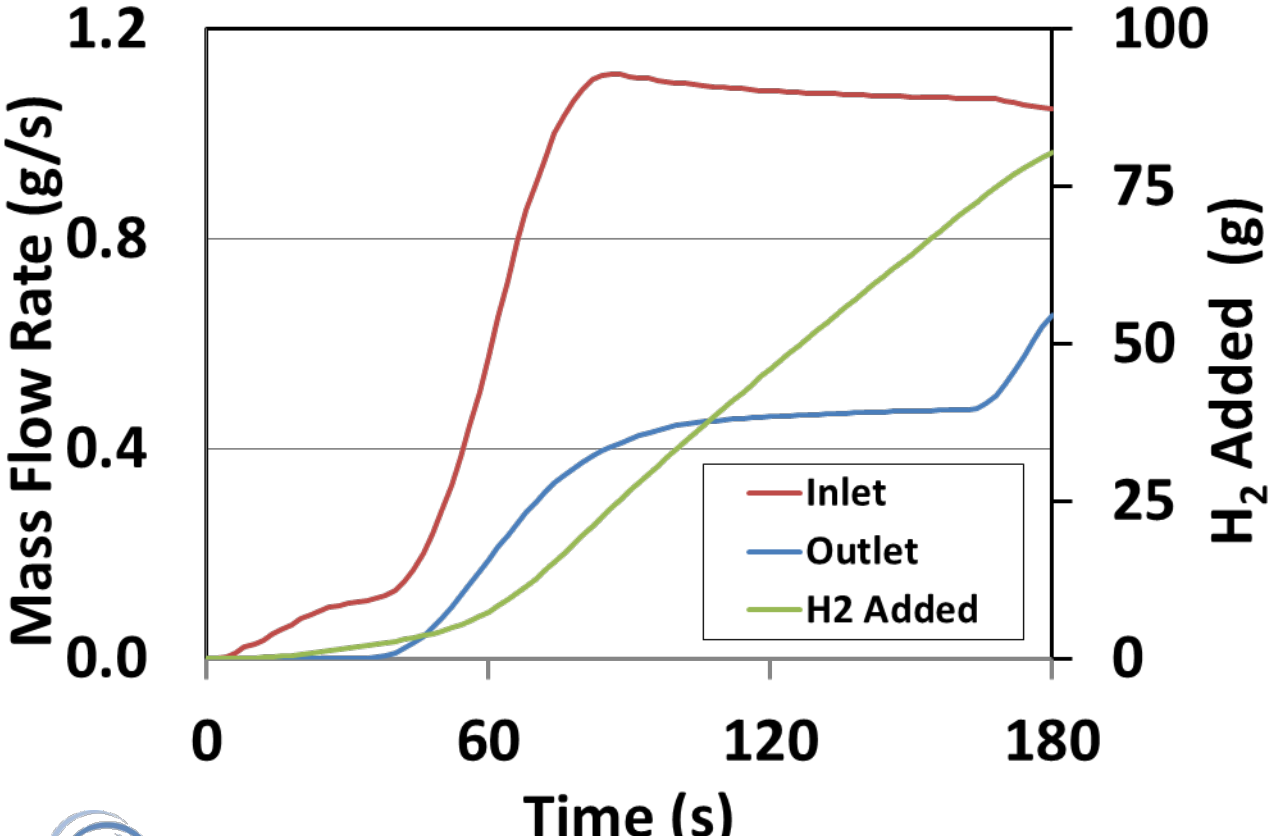




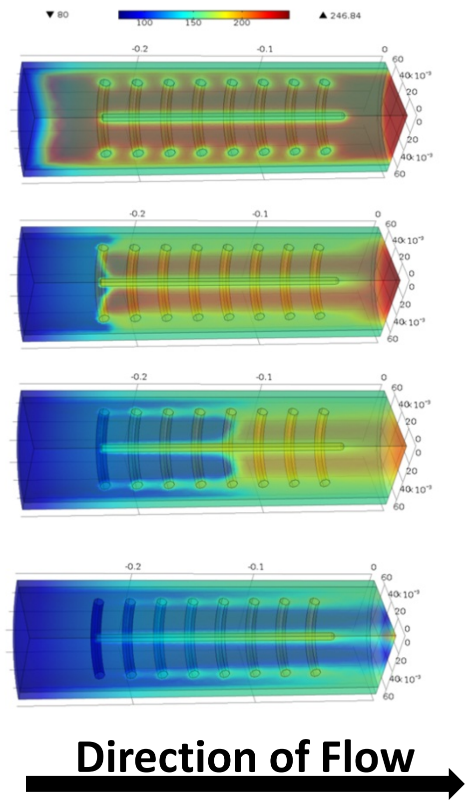
- Variable inlet and outlet flow rate up to 0.5 g/s (332 LPM)
- Test vessel vacuum chamber for adiabatic conditions
- Vessel adsorbent bed volume = 3 L
- Bed sealed on each end with porous metal disks (nominal pore size = 2 microns)
- Up to 22 axial positions for temperature measurements with adjustable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

MOF-5 Powder Adsorption Model Validation: Ideal Adsorption Model

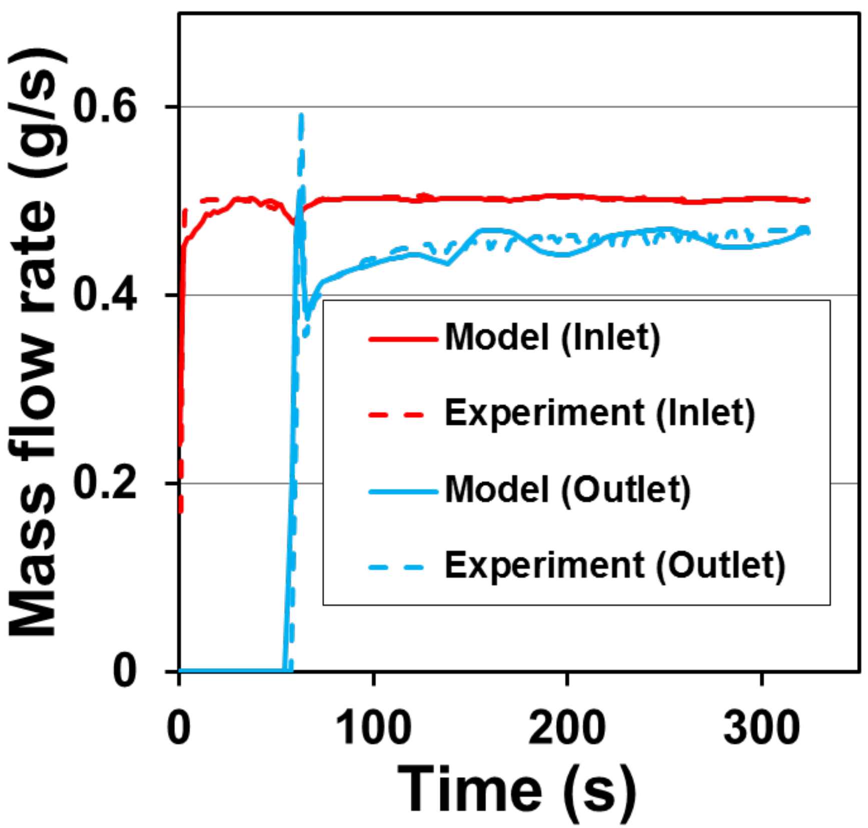
- Ideal model indicates inlet flow of 1.2 g/s required to meet 3 minute refueling milestone condition of T 150 – 80 K
- Model inlet flow exceeds experimental limitations (0.5 g/s)

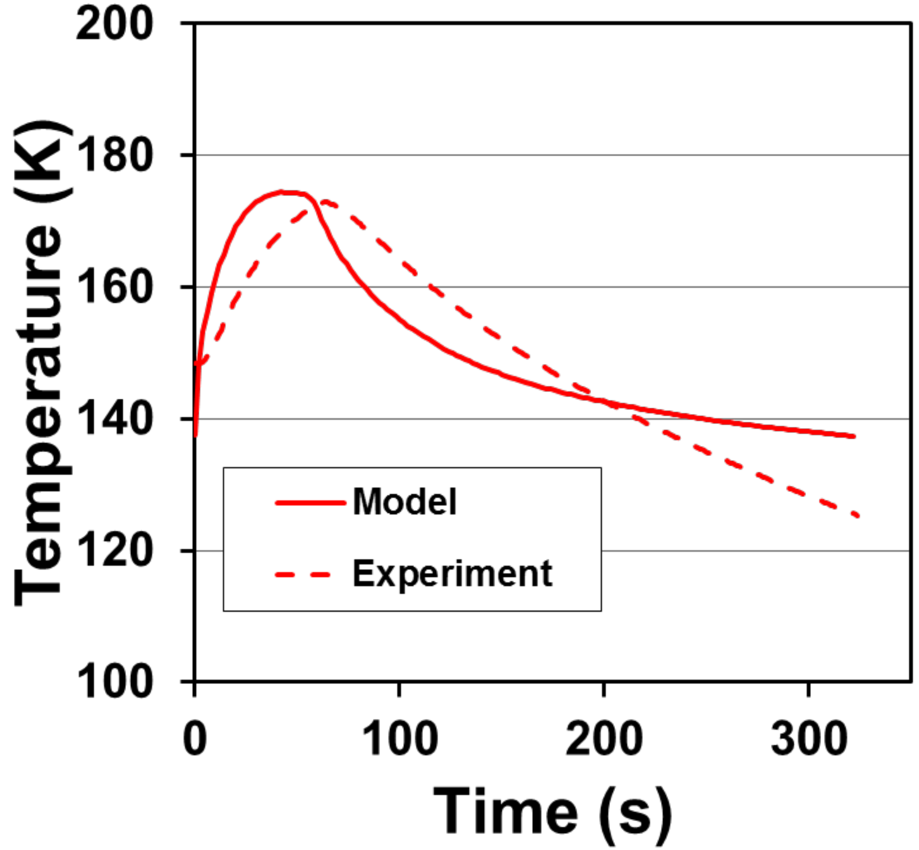


Vessel Temperature Profile

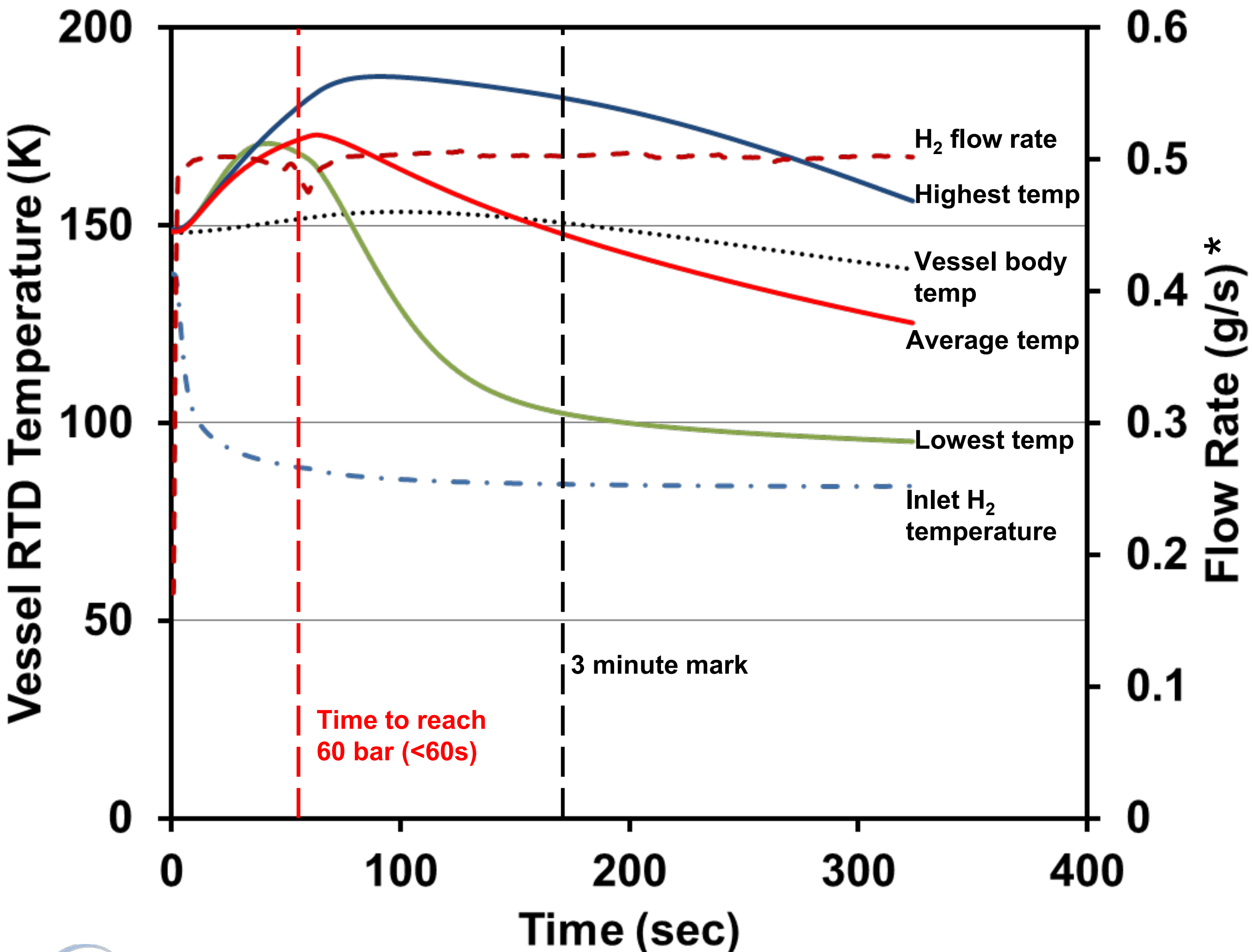


MOF-5 Powder Adsorption Model Validation: Model Simulation within Experimental Limits





MOF-5 Powder Adsorption Experiment: Cryo-adsorption within Apparatus Limits



<u>At 3 minutes</u>

- Highest temperature = 181 K
- Lowest temperature = 101 K
- Average temperature = 146 K

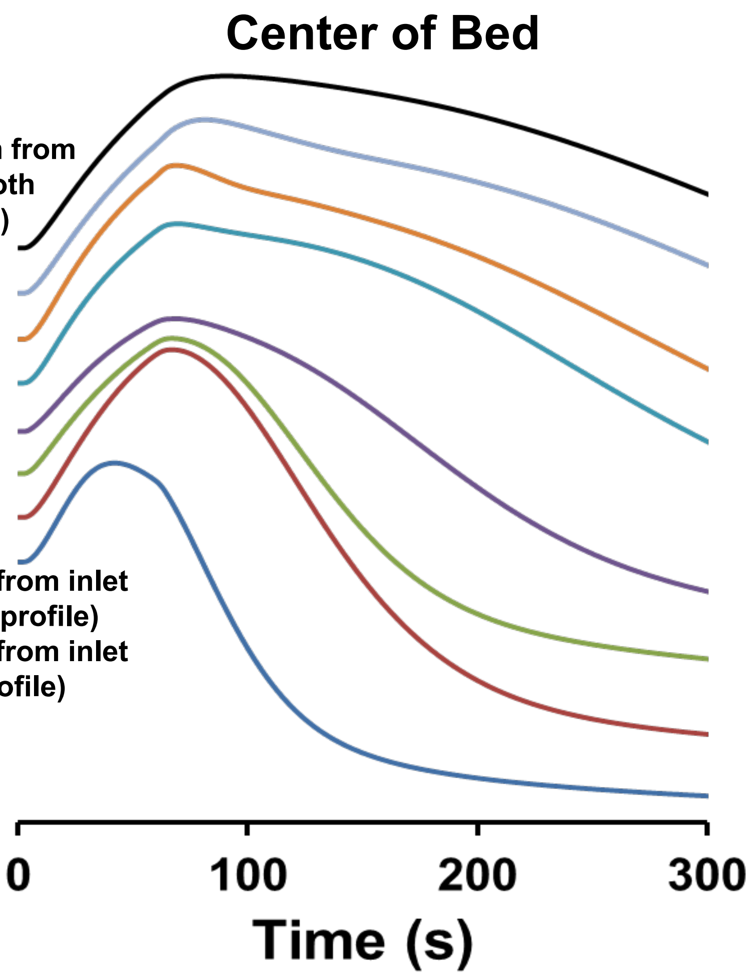
<u>Vessel Body Temperature</u>

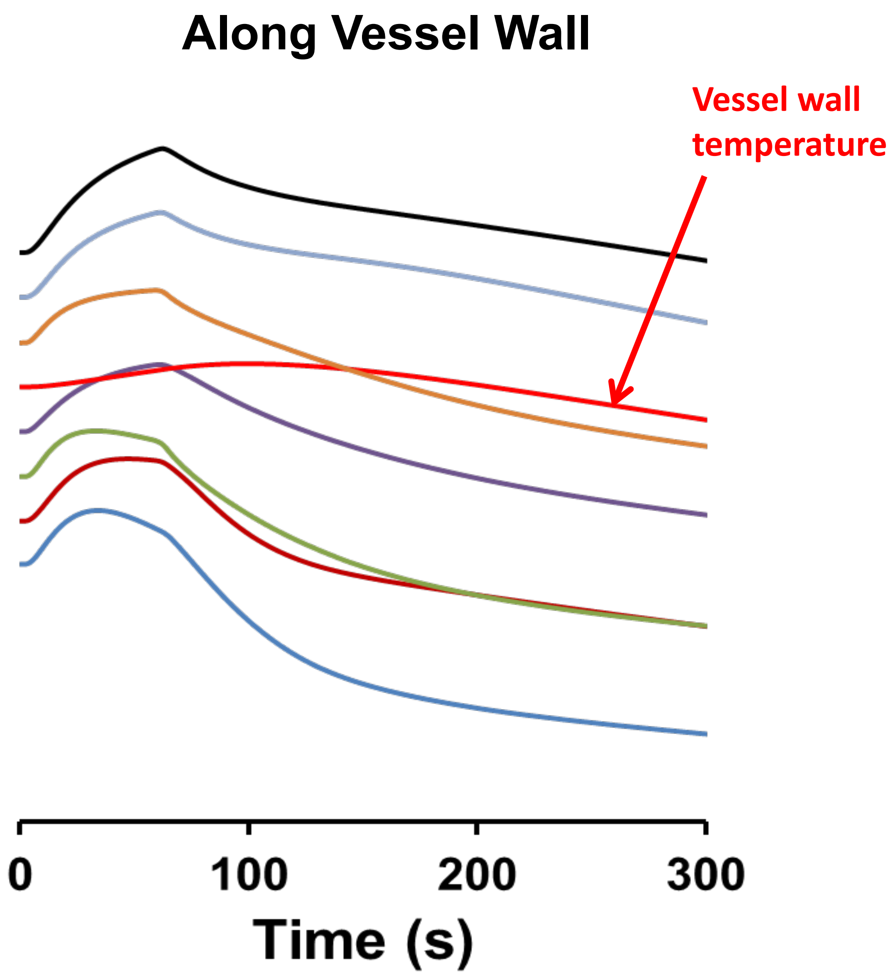
- Large thermal mass of vessel body adversely effects cooling of bed
- Vessel body cools by only 10 – 15 K over 5 minutes

* Running with a constant out flow of 0.05 g/s improved bed temperatures by only a few degrees

MOF-5 Powder Adsorption Experiment: Cryo-adsorption Powder Bed Temperature Profile*

- 270 mm from inlet (both profiles)
- 68 mm from inlet (center profile)
- 63 mm from inlet (wall profile)





* Temperature data profiles offset for clarity

Accomplishment II. Hydrogen Desorption in MOF-5 Storage System: Helical Coil Resistance Heater Performance in 200L and 3L Vessels

	3 L Steel Test Vessel[1]	200 L Aluminum Vessel[2]
Bed Diameter	0.114 m (4.5 in)	0.5 m
Bed Height	0.303 m (11.9 in)	1.02 m
Bulk Density of MOF-5 in bed	180 kg/m^3 (calculated)	150 kg/m^3
Mass of MOF-5 in bed	0.53 kg (measured)	30 kg
Total mass of adsorbent bed + wall	10.8 kg	74.4 kg
Total volume of adsorbent bed + wall	4.3 L	216.4 L
Pitch of the helical coil[3]	0.025 m	0.075 m
Diameter of the helical coil[4]	0.08 m	0.35 m
# of turns in the coil	8.4	12.4
Length of the coil	2.12 m	13.63 m
Height of coil (and center rod)	0.21 m	0.93 m
Outer diameter of tube, center rod	8.1 mm	30 mm
Volume of coil + rod	0.12 L	10.3 L

[1] Based on physical stainless steel cryogenic test vessel
[2] Based on modeling results for 200 L aluminum vessel
[3] Optimized to obtain uniform temperature distribution throughout MOF-5 bed. For 3 L, 0.025 is optimum.
[4] Simulations show that coil diameter that is approximately 70% of vessel internal diameter is optimum.

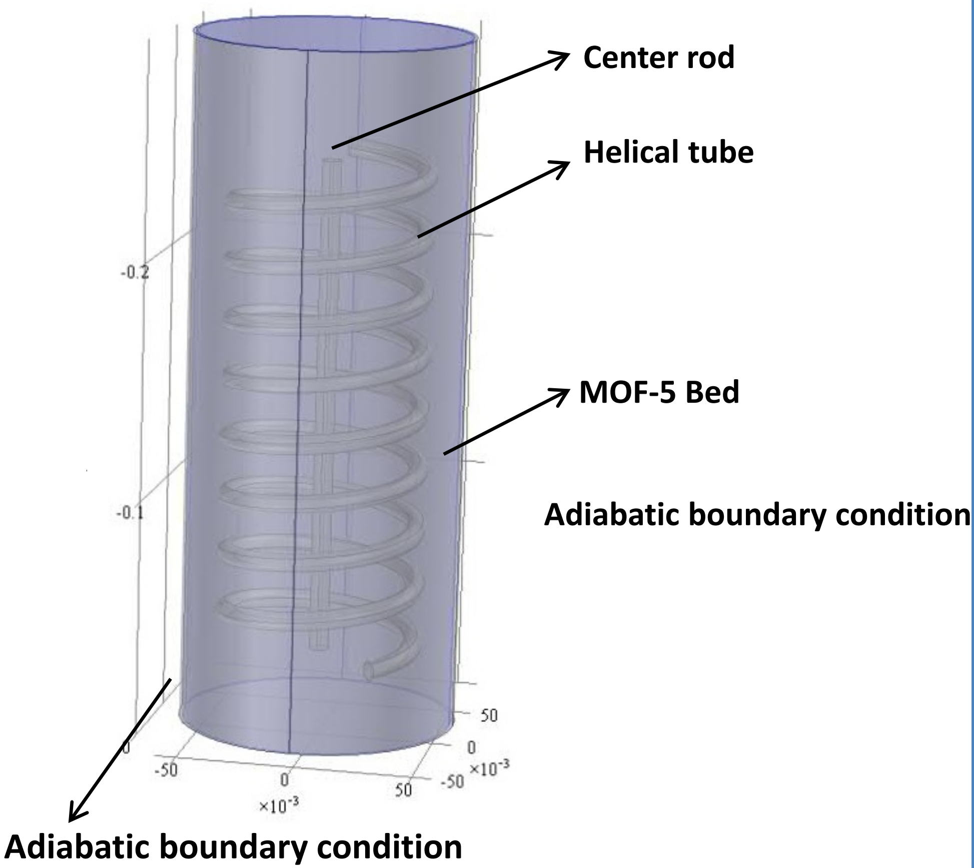
Heat Exchanger Design and COMSOL Model

- 3-D COMSOL model includes a cylindrical bed, adsorbent, and a helical coil heat exchanger/center rod within the MOF-5 bed.

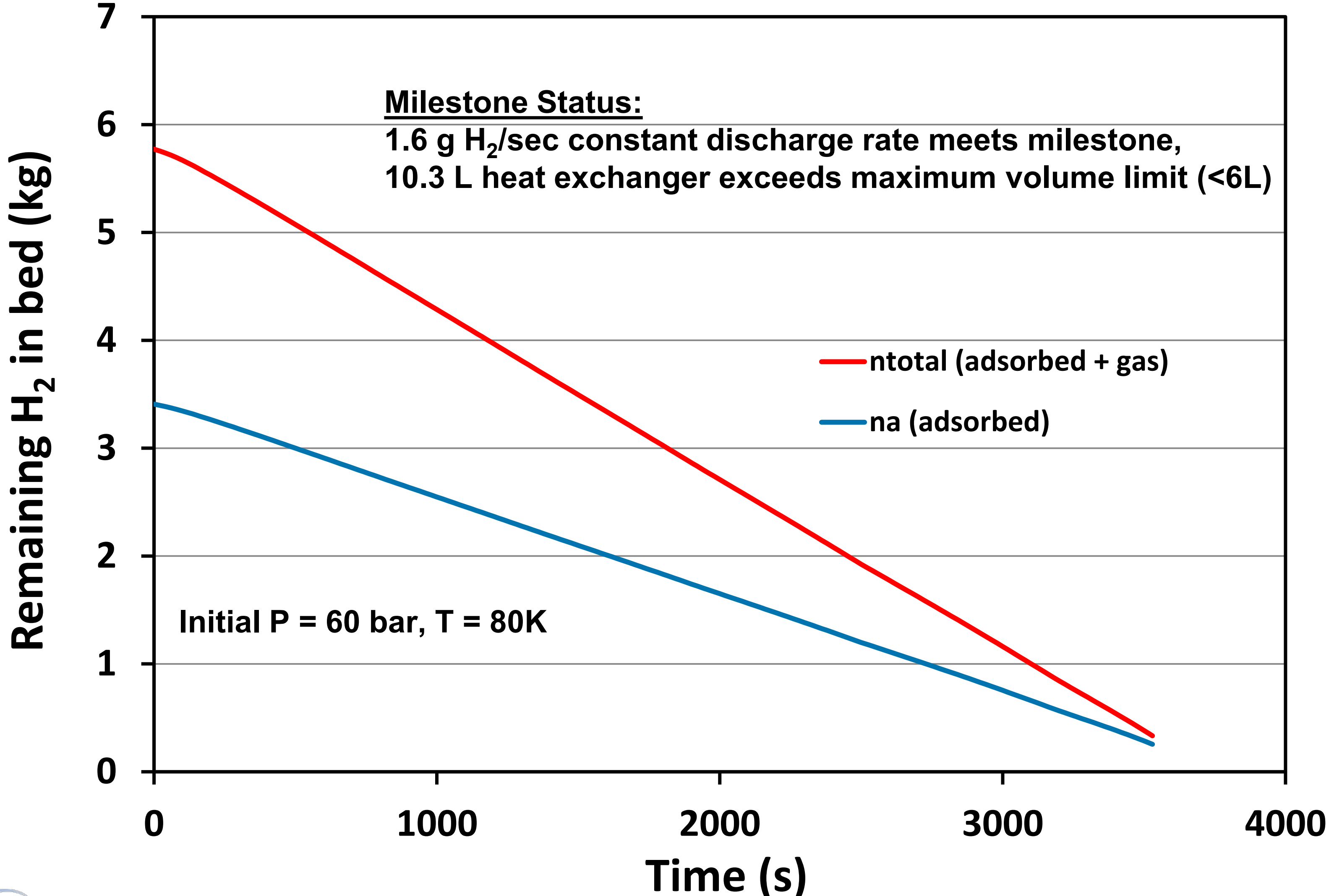
- 8 coil turns included in the 3 Liter vessel simulations

- 3D model includes mass and energy balance, Darcy's law for pressure variation in the bed and a modified Dubinin-Astakhov hydrogen adsorption isotherm (parameters from Ford)

- Hydrogen properties and additional parameters obtained from SRNL (B. Hardy)



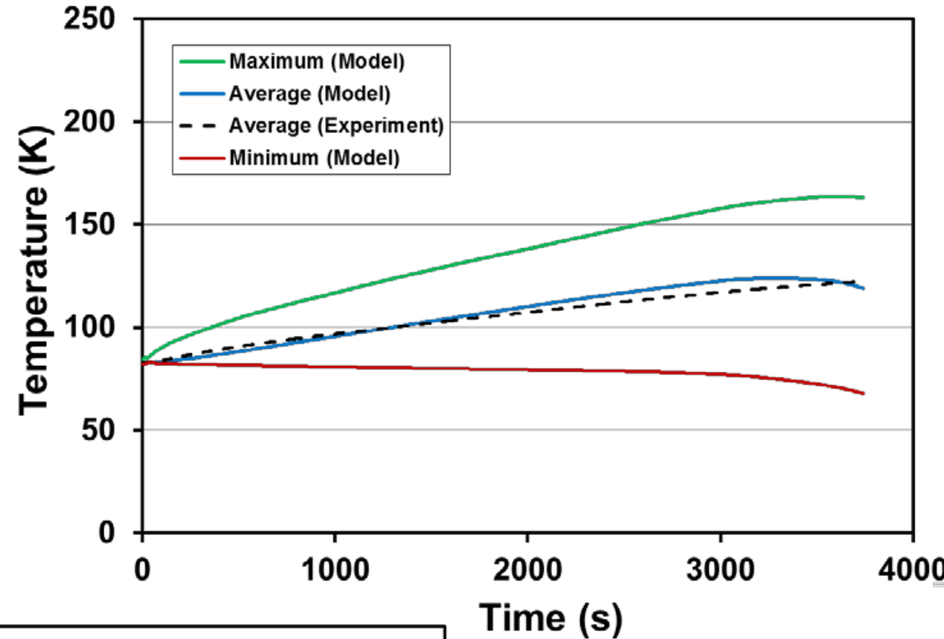
Discharge Simulation for 200 L MOF-5 bed: H_2 Release Rate and Heat Exchanger Milestones



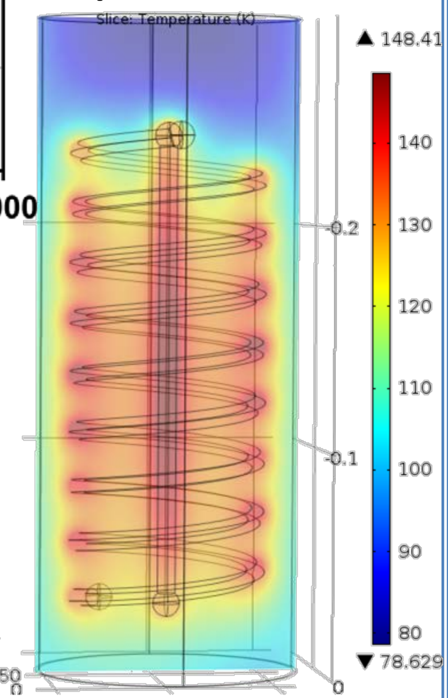
3L Vessel Desorption Run 1: Model & Experimental Results

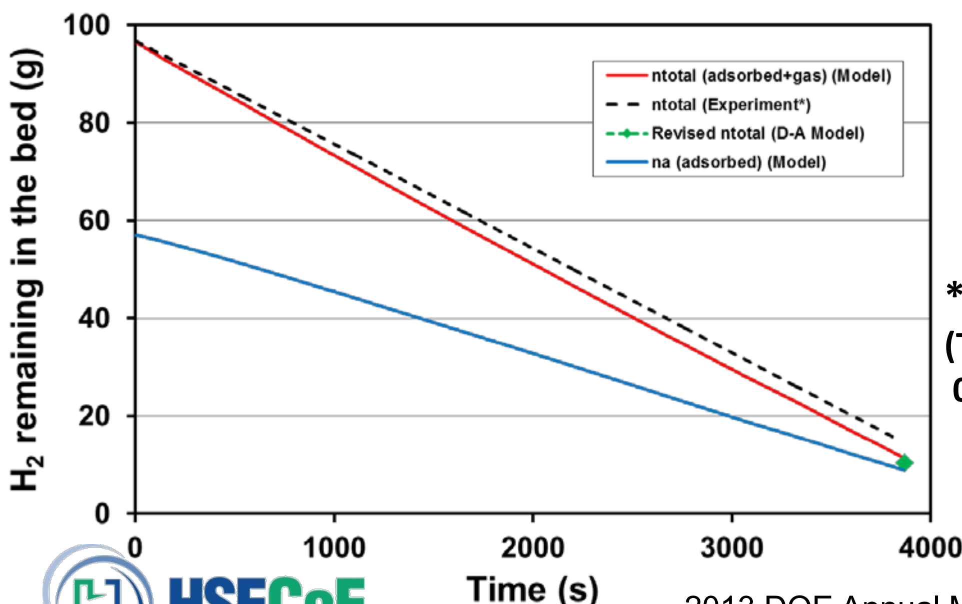
Helical Coil Heat Flux:
678 W/m^2

Discharge rate:
0.02 g H_2/sec



Temperature profile at 2500 s



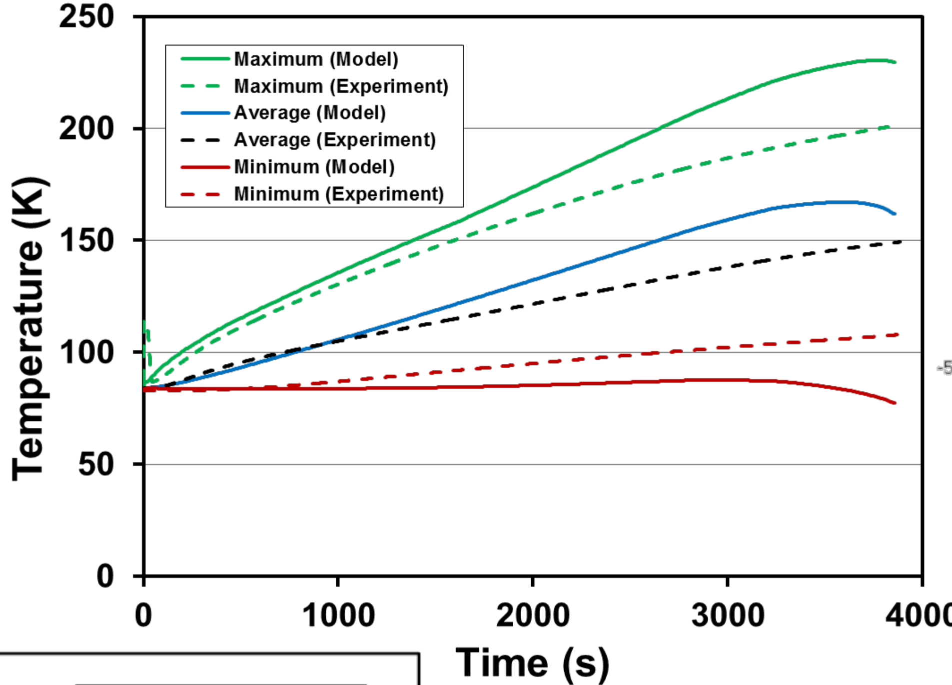


***Based on D-A Model** **(T_o = 83K, P_o= 60 bar) and 0.02 g H_2/sec mass flow rate.**

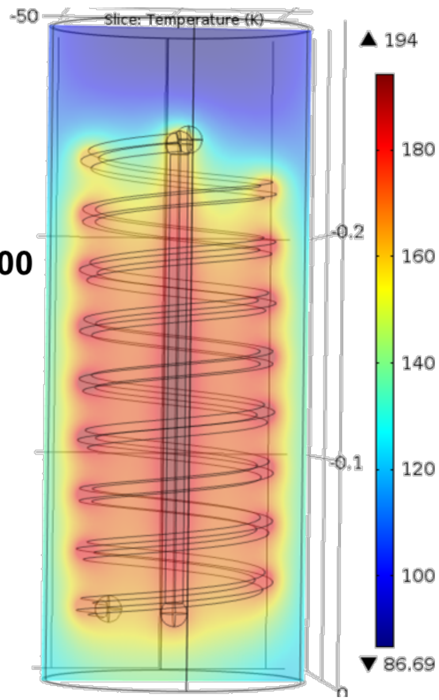
3L Vessel Desorption Run 2: Model & Experimental Results

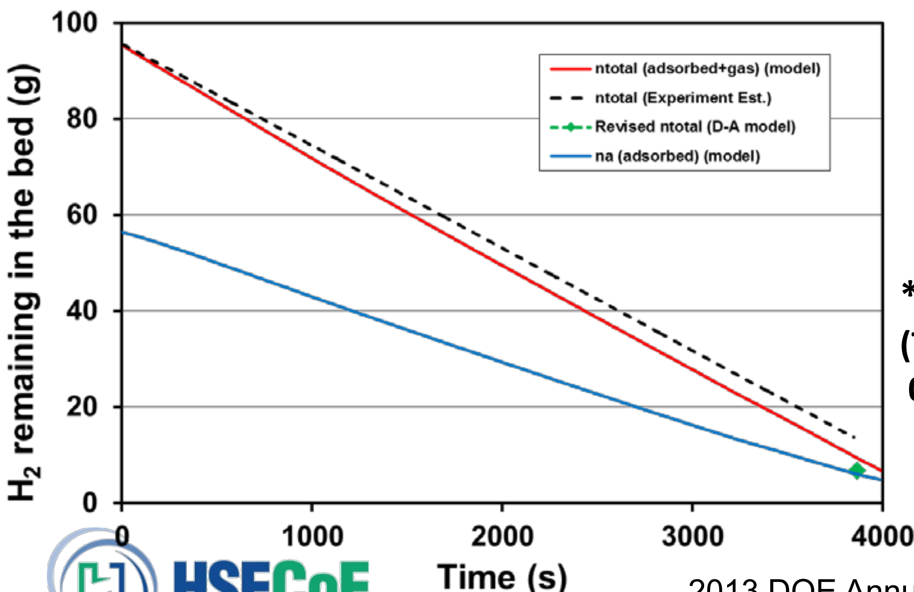
Helical Coil Heat Flux:
978 W/m^2

Discharge rate:
0.02 g H_2/sec



Temperature profile at 2500 s

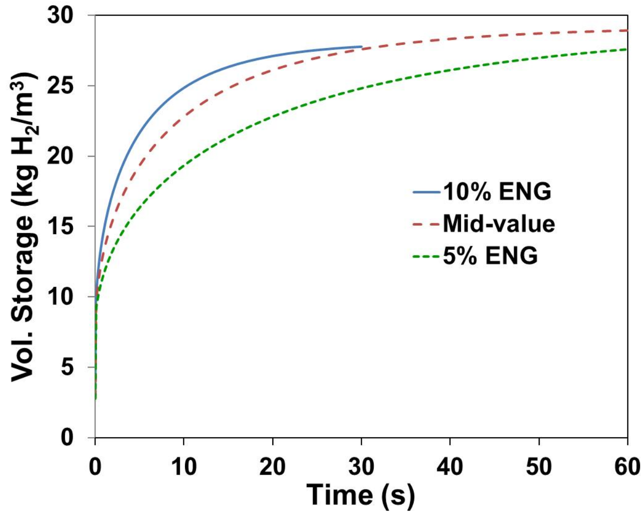




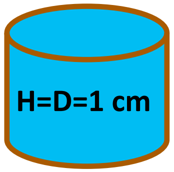
*Based on D-A Model (T_o = 84K, P_o= 61 bar) and 0.02 g H_2/sec mass flow rate.

Accomplishment III. Hydrogen Adsorption in MOF-5 Cylindrical Pellets: Thermal Conductivity Effects on Refueling

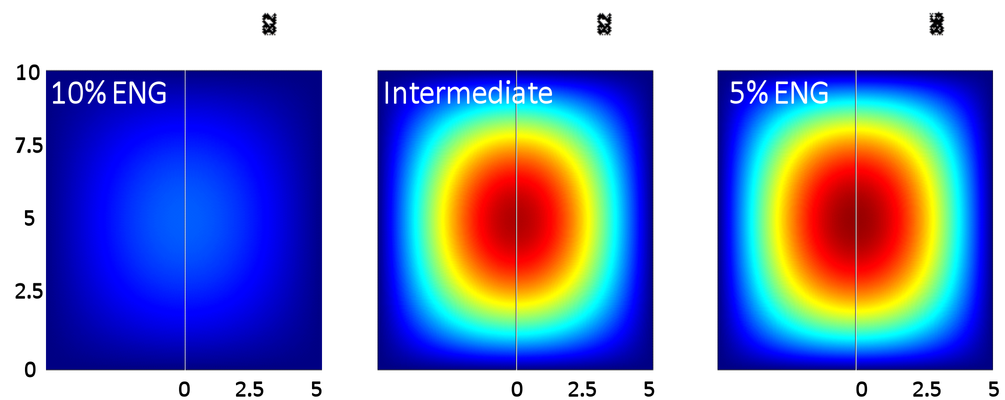
Pelletization offers the potential to increase volumetric storage capacity, but the mass and heat transport in pellets affect the rate of adsorption and cause difficulties in meeting the refueling time targets. Increasing the pellet thermal conductivity with the additive ENG accelerates cooling within the pellets, thus decreasing refueling time.



Net volumetric storage of hydrogen vs. time for the three values of thermal conductivity. (k = 0.55, 0.32, and 0.16 W/m-K for 10%, Mid-value, and 5% ENG, resp., at 110 K)



A pellet compacted to 0.51 g/cm^3 at 140 K and 4 bar (empty) is enveloped in H_2 gas at 80K and 30 bar (refueling)

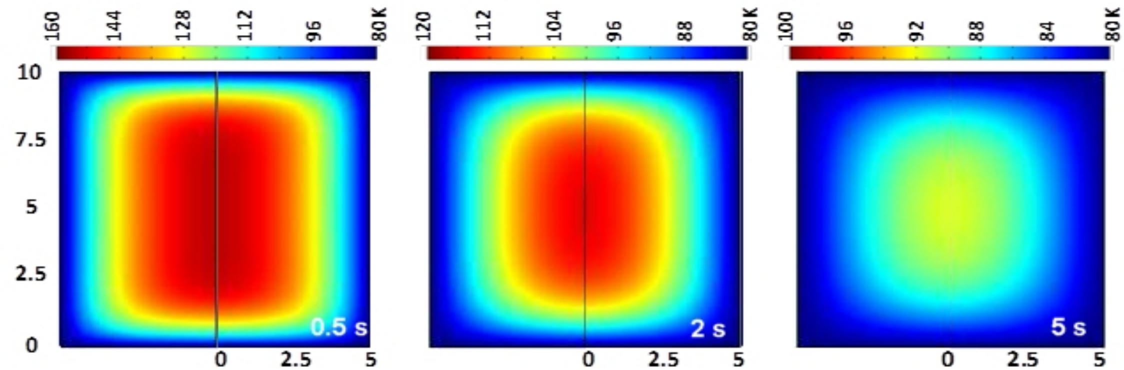


Temperature contours within a 1x1 cm pellet for three different thermal conductivity values at 25 seconds. Refueling is completed for the first case, nearing completion for the second case, but significant temperature gradients exist for MOF-5 with 5% ENG.

Hydrogen Adsorption in MOF-5 Cylindrical Pellets: Anisotropic Thermal Conductivity and Optimal Pellet-Sizing

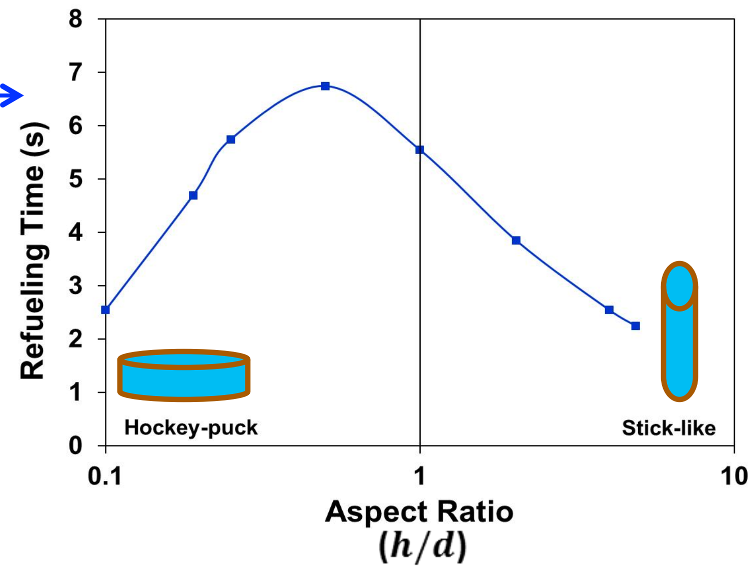
Experimental data indicates that the in-plane (radial) value of thermal conductivity can be 5 times greater than the axial thermal conductivity. This anisotropy is due to the peculiar alignment of ENG in compacted pellets.

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



Optimal Pellet-Sizing

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.

Future Plans

- Document the material and system modeling results and provide the gap analysis to DOE HSE CoE.
- Polish and upload all GM developed adsorption/desorption models onto DOE HSE CoE's web site for sharing and feedback.
- Complete the experimental data collection and prepare cryo-adsorbent test apparatus plus associated instrumentation for continued usage by the DOE HSE CoE as needed in phase III.
- General Motors will continue to participate the DOE HSE CoE Phase III of the program as an OEM consultant and provide the center with vehicle level performance requirement.

Summary

- **Accomplishment 1: Hydrogen Adsorption in MOF-5 Storage System**
  a) Cryo-adsorption test apparatus installed & modified for improved performance.
  b) Adsorption model indicates cooling bed to 80K for 3 minute refueling of 3 L vessel, within milestone parameters, requires a flow rate that exceeds test apparatus limits.

- **Accomplishment 2: Hydrogen Desorption in MOF-5 Storage System**
  a) Configuration of resistance heater optimized. Scaled version for 3 L cryogenic test vessel installed for experimental desorption validation.
  b) Discharge experiments show the helical coil heater is effective at desorbing sufficient H_2 to maintain desired flow rates.
  c) Agreement found between experimental results and desorption model.

- **Accomplishment 3: Hydrogen Adsorption in MOF-5 Cylindrical Pellets**
  a) 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.
  b) "Stick-like" and "hockey-puck" pellets may be suitable for fast refueling.

Collaborations: Center Partners

Industrial Collaborators

Ford → **MOF-5 characterization, pure and thermally enhanced, material liaisons to BASF for Center, Unilan adsorption model fit parameters**

United Technologies Research Center → **Modeling Framework (integration of hydrogen storage modules)**

BASF The Chemical Company → **Metal Organic Framework (MOF-5) supplier (synthesis and processing)**

National Laboratory Collaborators

SRNL Savannah River National Laboratory → **Center management, transport model equations and H_2 properties**

Pacific Northwest National Laboratory → **Optimized resistive heater for material desorption and system cost modeling**

Academic Collaborators

UQTR Université du Québec à Trois-Rivières → **Adsorbent materials member, experimental apparatus and procedure**

OSU Oregon State University → **Adsorbent materials member, experimental approach and test vessel design**

Technical Back-up Slides

COMSOL Model Equations: Thermodynamics

Modified Dubinin-Astakhov Isotherms

Absolute adsorbed hydrogen: $n_a = n_{\max} \exp\left[-\left[\frac{RT}{\alpha + \beta T} \right]^2 \ln^2 \frac{P_0}{P} \right]$

Total adsorbed hydrogen : $n_{total} = n_a + \rho_g (V_v - V_a)$

Internal energy of the condensed phase : $U_a = \Delta U_a + u_o n_a$

where $$\Delta U_a = -\frac{n_{\max} \alpha \sqrt{\pi}}{2} \left[1 - erf\left(\sqrt{-\ln\left(\frac{n_a}{n_{\max}} \right)} \right) \right] + n_a \left[RT - \alpha \sqrt{-\ln\left(\frac{n_a}{n_{\max}} \right)} \right]$$

COMSOL Model Equations

Mass and momentum balance

$$\frac{\partial}{\partial t}(\rho\varepsilon)+\nabla.(\rho u)=S_o$$

where, Mass source term $S_o=-M_{H_2}*\rho_C*\frac{\partial n_a}{\partial t}$

Darcy's Equation $u=-\frac{\kappa}{\mu}\nabla p$ permeability $\kappa=\frac{1}{\left(\frac{150*(1-\varepsilon)^2}{\varepsilon^3*D_p{}^2}\right)}$

Final mass balance coupled with Darcy's law:

$$\frac{\partial}{\partial t}(\rho\varepsilon)+\nabla.\left(\rho\left(-\frac{\kappa}{\mu}\nabla p\right)\right)=S_o$$

COMSOL Model Equations

<u>*Energy balance*</u>

$$\underbrace{\rho_b C_{pb} \frac{\partial T}{\partial t} + \rho_g C_{pg} \frac{\partial T}{\partial t}}_{Conduction\ \ term} - \nabla . k_b \nabla T$$

$$= \underbrace{\rho_g C_{pg} \vec{u} . \nabla T}_{Convection\ \ term} - \underbrace{\gamma T \left[\varepsilon_b \frac{\partial p}{\partial t} + (\vec{u} . \nabla) p \right]}_{Compression\ \ source\ \ term} - \underbrace{\left(\frac{S_o}{M_{H_2}} \right) \Delta H}_{Adsorption\ \ heat\ \ source} - \rho_b \left(\underbrace{\frac{\partial \Delta U_a}{\partial t} + \frac{\partial (u_o n_a)}{\partial t}}_{Sorption\ energy} \right)$$