Testing and Modeling of a Cryogenic Hydrogen Storage System with a Helical Coil Electric Heater

Mei Cai – P.I.

Peter Hou, Jerry Ortmann, Martin Sulic

General Motors Company

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Project ID: ST009

Overview

Timeline

- Project Start Date: February 2009
- Project End Date: June 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*: $2,311,512

*as of 3/31/14

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

Michigan

Los Alamos National Laboratory

Hexagon Lincoln

HRI UQTR

Objectives and Approach

HSECoE Technical Objectives addressed:

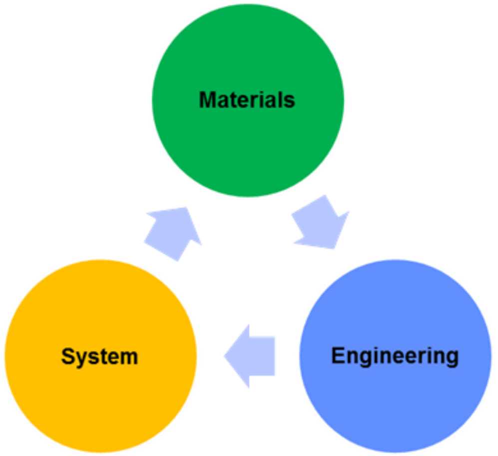
Design, build and evaluate subscale prototype systems to assess the innovative storage devices and subsystem design concepts, validate models, and improve both component design and predictive capability.

Experimental Validation of Models 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)*
- Installation and testing of a highly-instrumented cryo-adsorbent apparatus containing MOF-5 powder to validate adsorption and desorption models
- Experimental validation of desorption model with helical coil resistive heater in cryo-adsorbent apparatus
- Experimental validation (with cryo-adsorbent apparatus) of flow-through cooling of MOF-5 powder bed during charging
- Determine status towards S*M*A*R*T milestones for charging and discharging both experimentally and with simulation models

Other Tasks (with HSECoE partners):

- Prioritization of DOE Technical targets (OEMs)
- Development of an integrated framework including the vehicle, fuel cell, and H_2 storage system models (UTRC, NREL, Ford, SRNL,PNNL)



Progress Towards 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

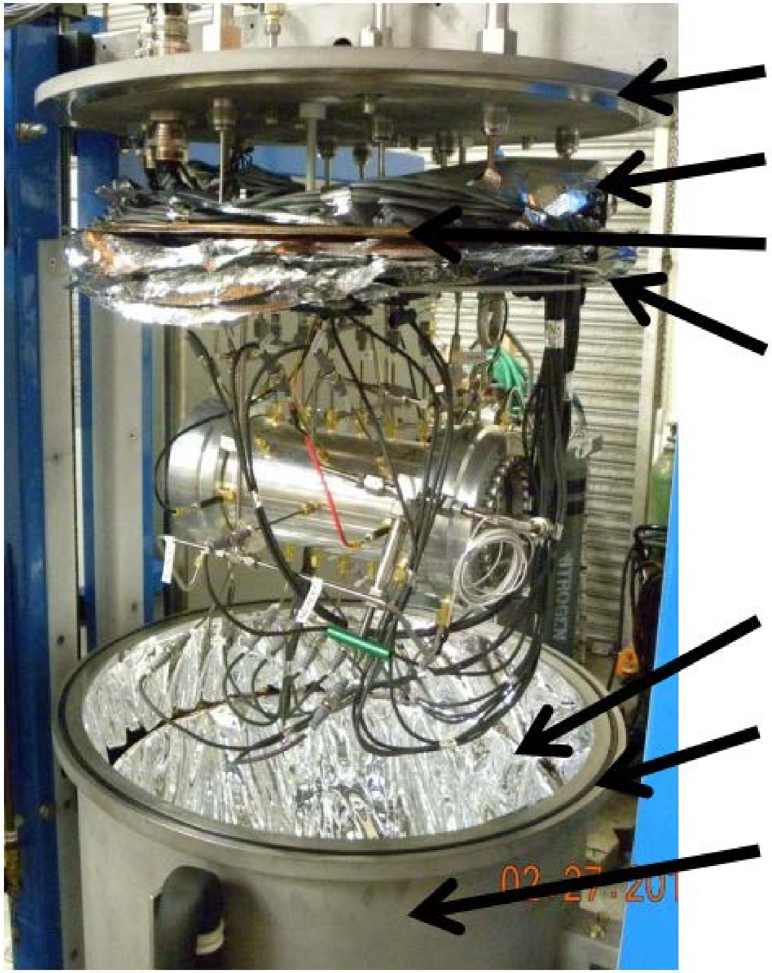
- Milestones: Design and demonstrate an internal heat exchanger capable of achieving a scaled release rate of 0.02 g H_2/(sec. kW) at P = 60 – 5 bar and T = 80 – 160 K, with a mass less than 6.5 kg and a volume less than 6 liters. Validate MOF-5 powder bed having a total hydrogen density of: 18 g H_2/(100 g MOF) and 24 g H_2/(liter MOF).
  - ❑ Discharge experiments with helical coil resistive heater and desorption model show the scaled release rate milestone can be met and 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 < 6L

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. Hydrogen Desorption in MOF-5 Storage System: Cryogenic Test Apparatus Experiments and Model Simulations

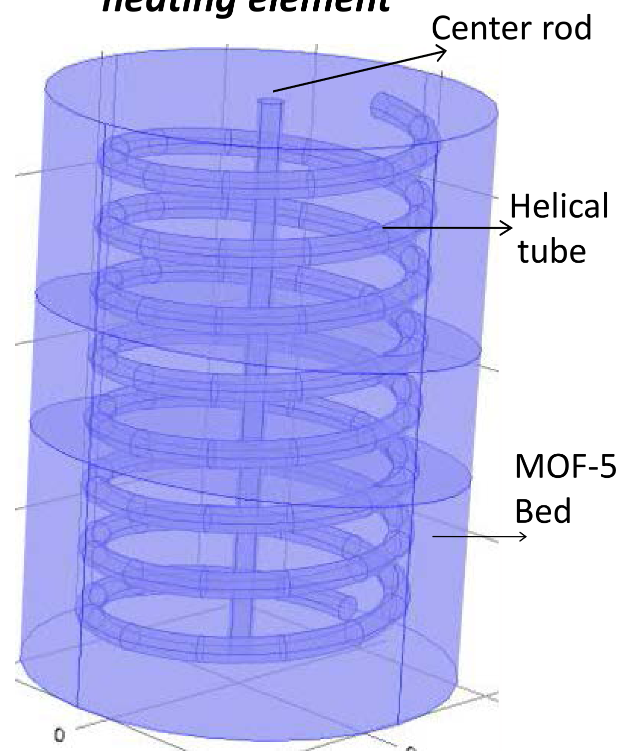
- **Variable inlet and outlet flow rates up to 0.5 g/s (332 LPM)**
- **Test vessel vacuum chamber for adiabatic conditions**
- **Vessel adsorbent bed volume = 3 Liters**
- **Bed sealed on each end with porous metal disks (nominal pore size = 2 microns)**
- **Up to 22 axial positions for temperature measurements 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)**



Desorption model with Helical Coil Electric Heating

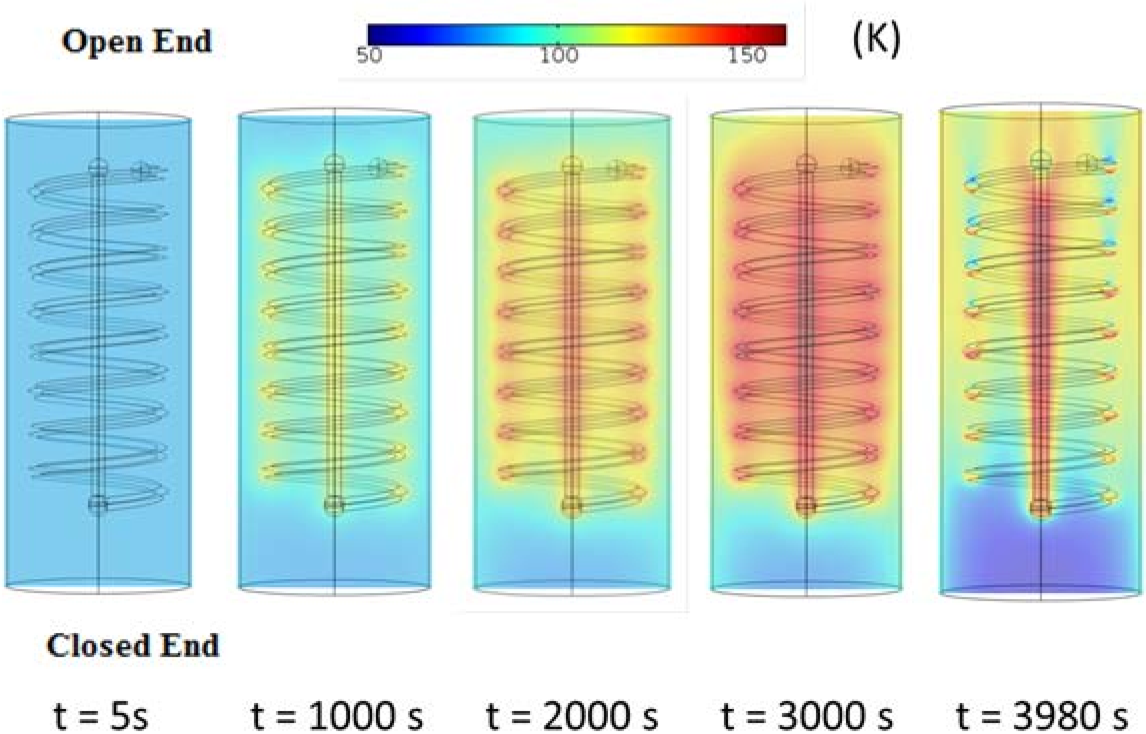
- 3-D COMSOL® model of the cryogenic test vessel includes a 3 Liter cylindrical bed, adsorbent, and a helical coil heat exchanger/center rod within the MOF-5 bed.
- Model equations include mass and energy balance, Darcy's law for pressure variation in the bed and a modified Dubinin-Astakhov (D-A) hydrogen 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



Desorption Model Temperature Profiles During Discharging

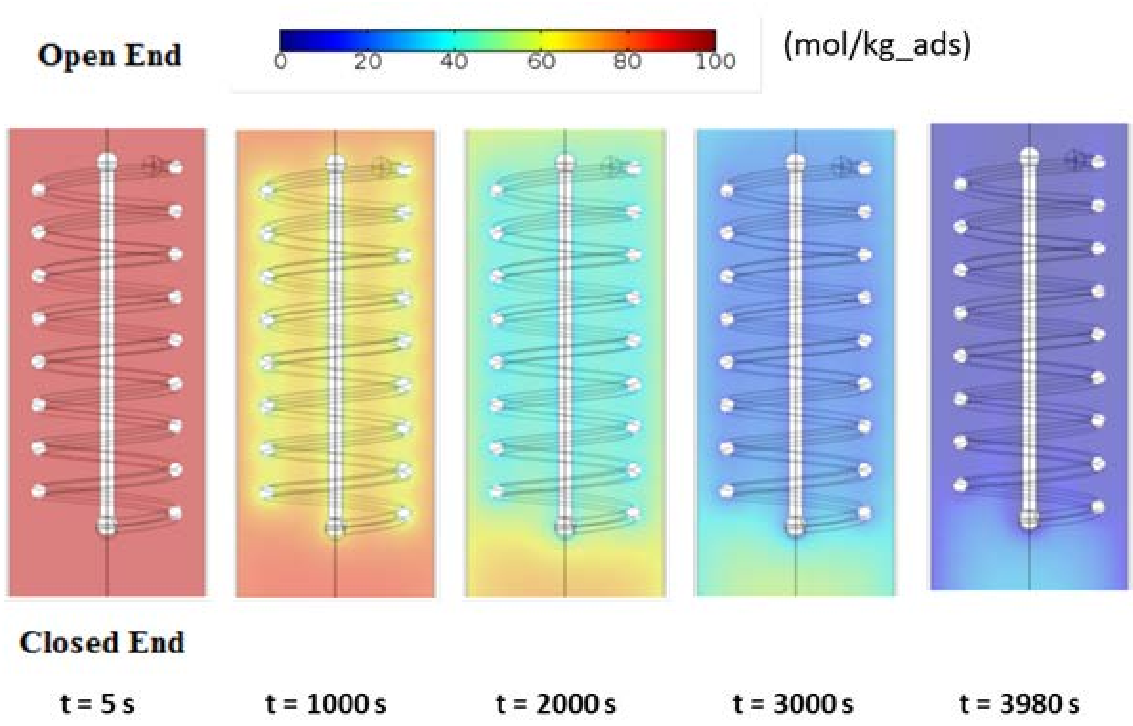
T_o = 83 K, P_o = 60 bar, outlet mass flow rate = 0.02 g/s, Supplied power = 39 W



By end of discharge average bed temp = 120 K, minimum = 100 K, and maximum = 160 K

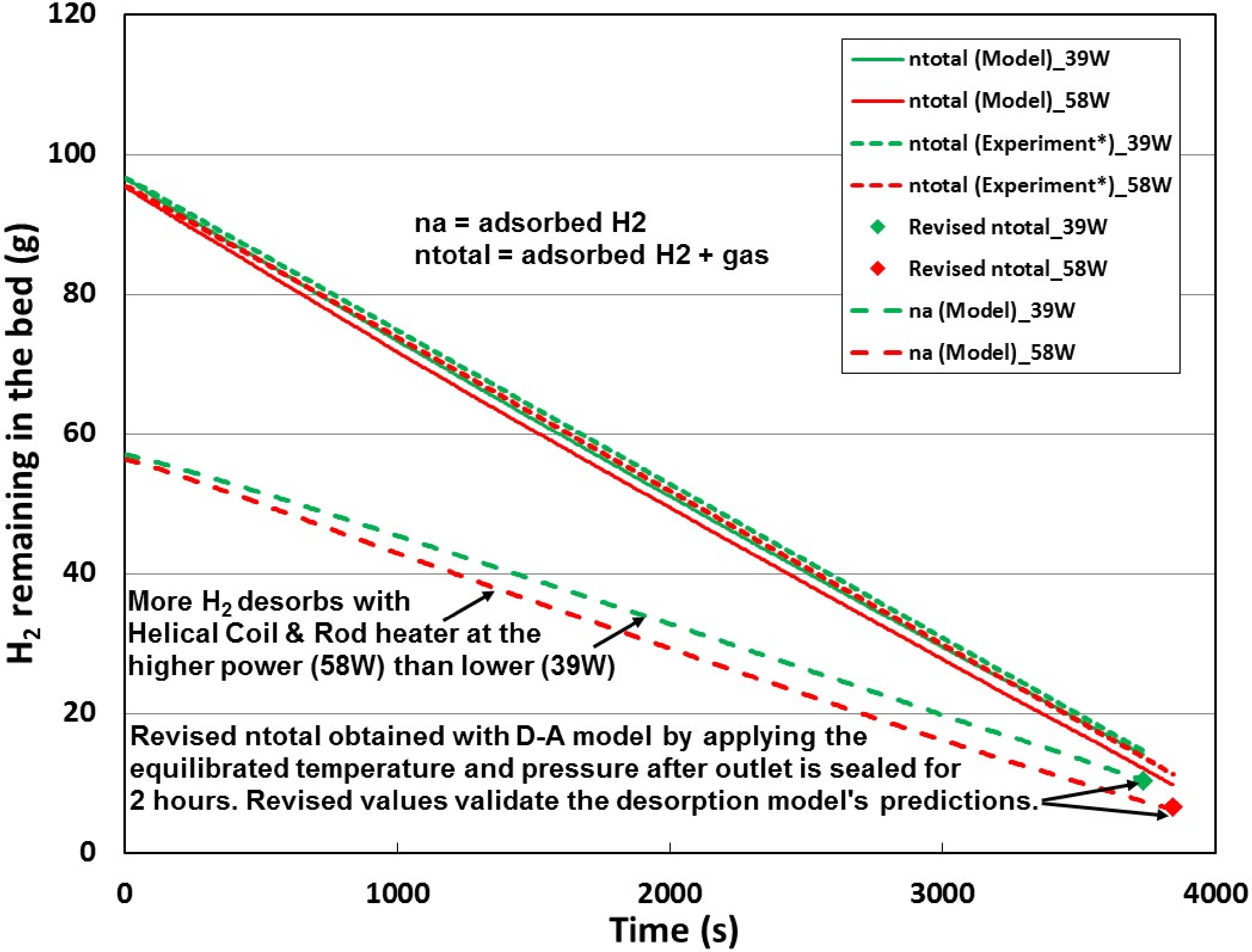
Desorption Model n_{total} (adsorbed H_2 + gas) During Discharging

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



Helical coil & rod heater successfully maintain discharge rate to reach release rate milestone

Heating Power Effects on Hydrogen Storage During Discharging



Accomplishment II. Flow-through Adsorption in MOF-5 Hydrogen Storage System: Experiments and Simulations

Several experimental approaches were considered for improving thermal management to reach milestones and validate the flow-through adsorption model:

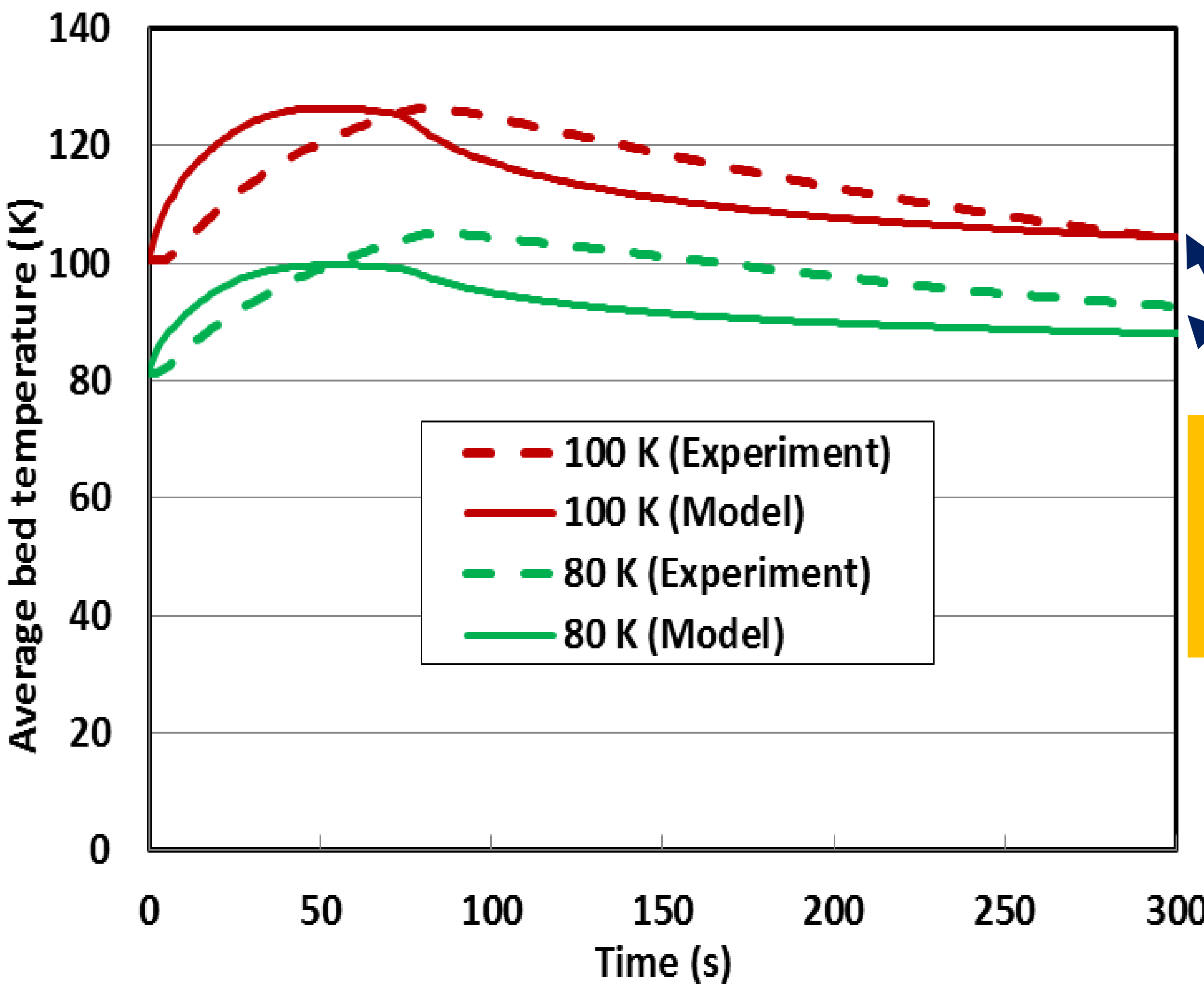
1. **Varying initial bed temperature**
2. **Increasing vessel powder density**
3. **Varying outlet opening time**
4. **Varying outlet flow rates**

(Set inlet flow rate of 0.5 g/s (330 LPM) and gas temperature of ~80 K for all tests)

<u>Beyond Project Scope</u>:

•Additional experimental techniques for cooling of the MOF-5 bed were conducted to evaluate alternatives to flow-through cooling
•Vertical flow-through cooling was examined to determine if this vessel orientation produces different results than horizontal

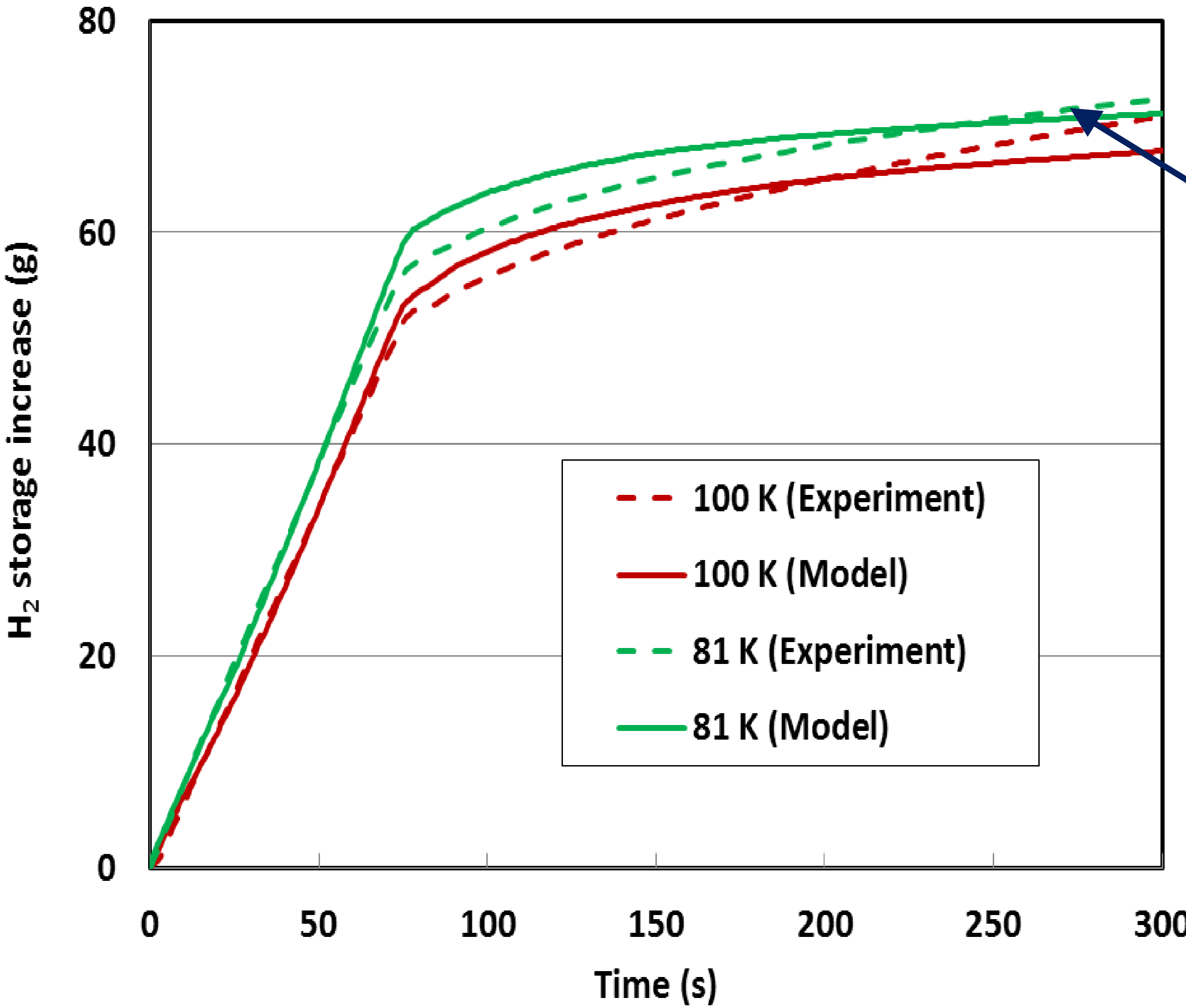
Effect of Initial Temperature on Flow-through Cooling During Charging



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

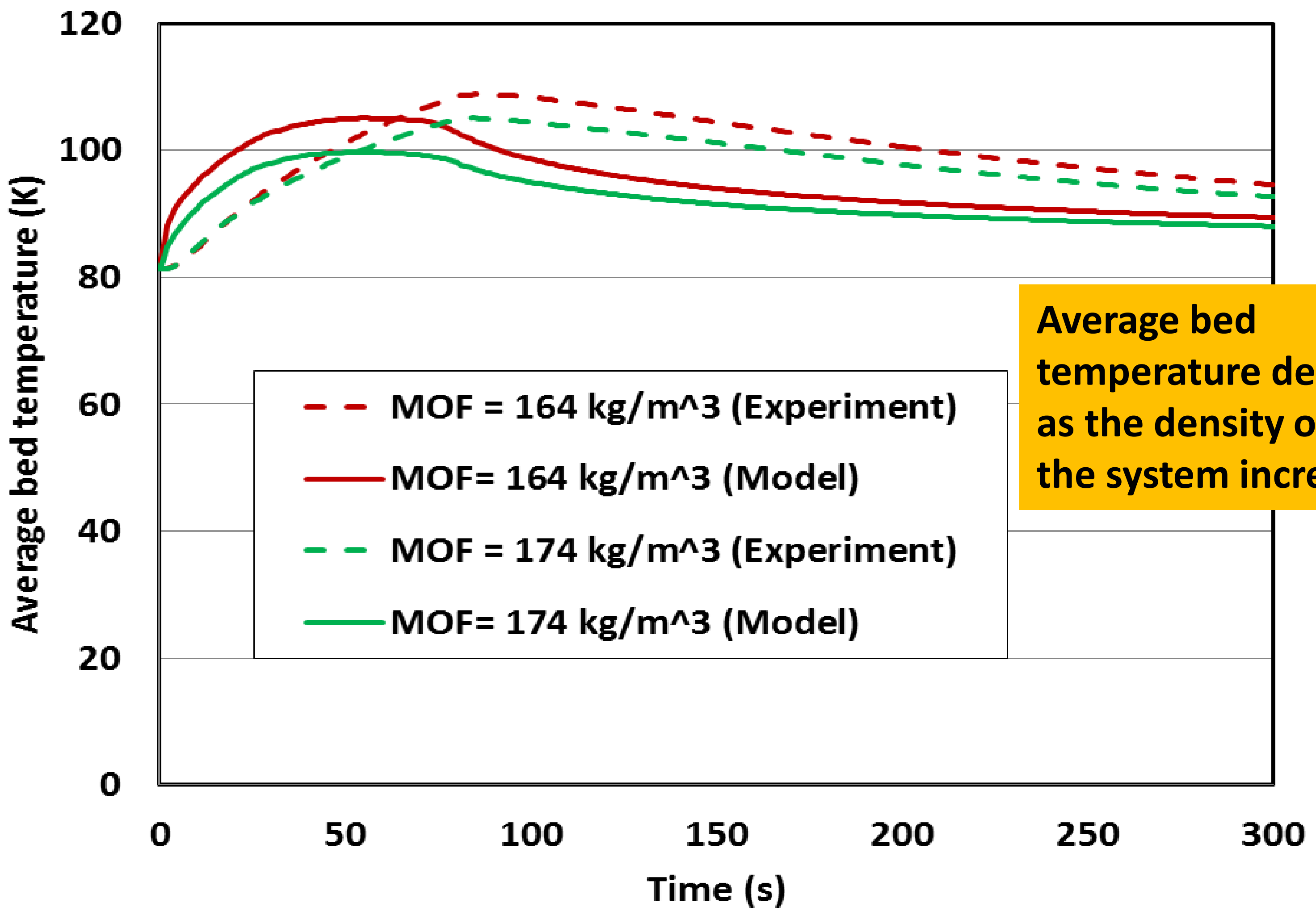
Effect of Initial Temperature on H_2 Storage



Colder starting temperature gave colder final bed temperature, correlating to more gas adsorbed in the system, as expected.

Effect of Powder Density on Flow-through Cooling

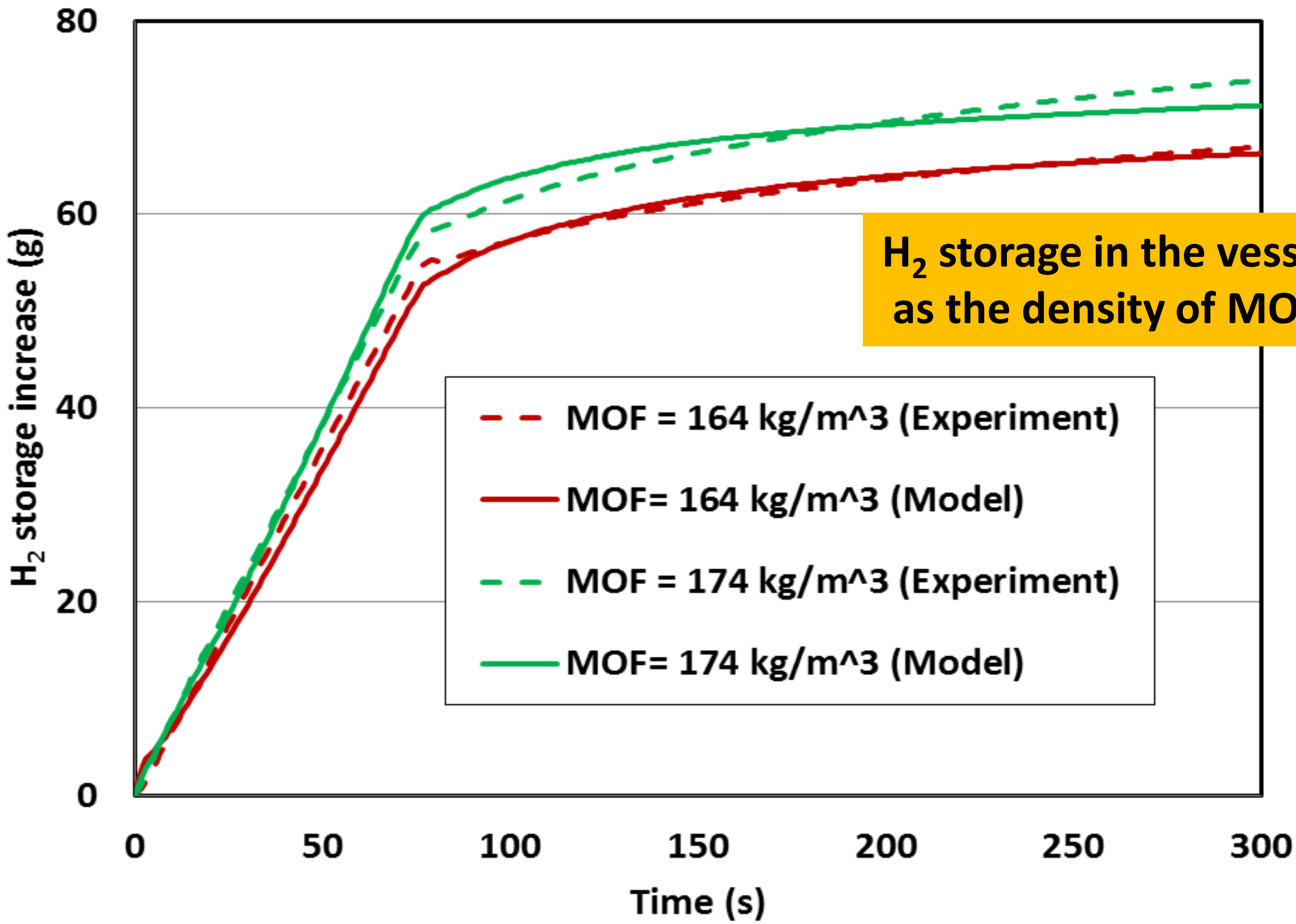
- Added 6% more powder (≈ 30 g) and compressed
- Increased powder density from 164 kg/m^3 to 174 kg/m^3
- Pressure ramped from 5 to 60 bar within 75 seconds, outlet then opened



Average bed temperature decreases as the density of MOF in the system increases

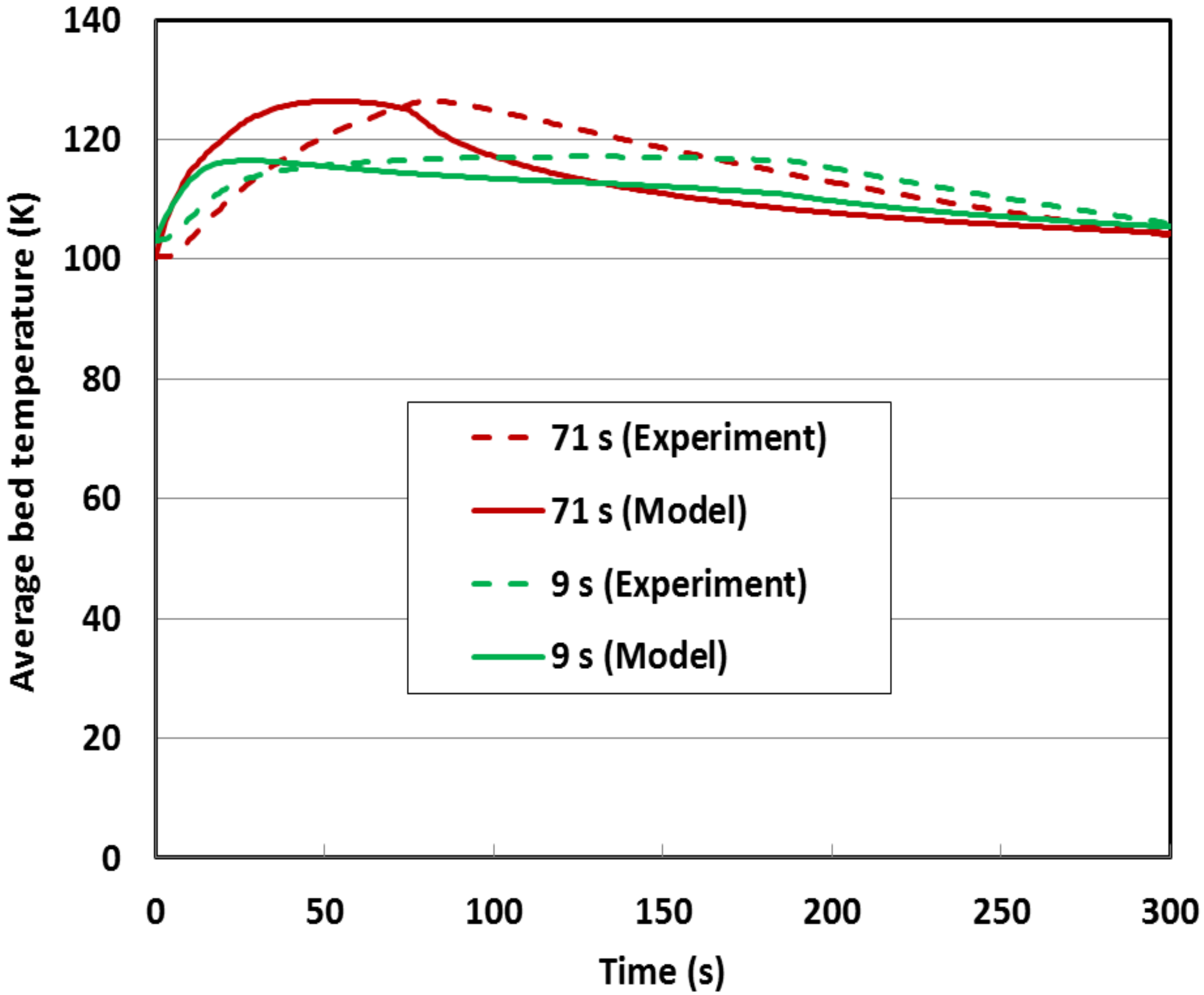
Effect of Powder Density on Storage Capacity

- Model and experimental data shown for starting bed temperature of 150 K, experimental for 80 K
- At 3 and 5 minutes, amount of hydrogen added to system, at each temperature, less than theoretical



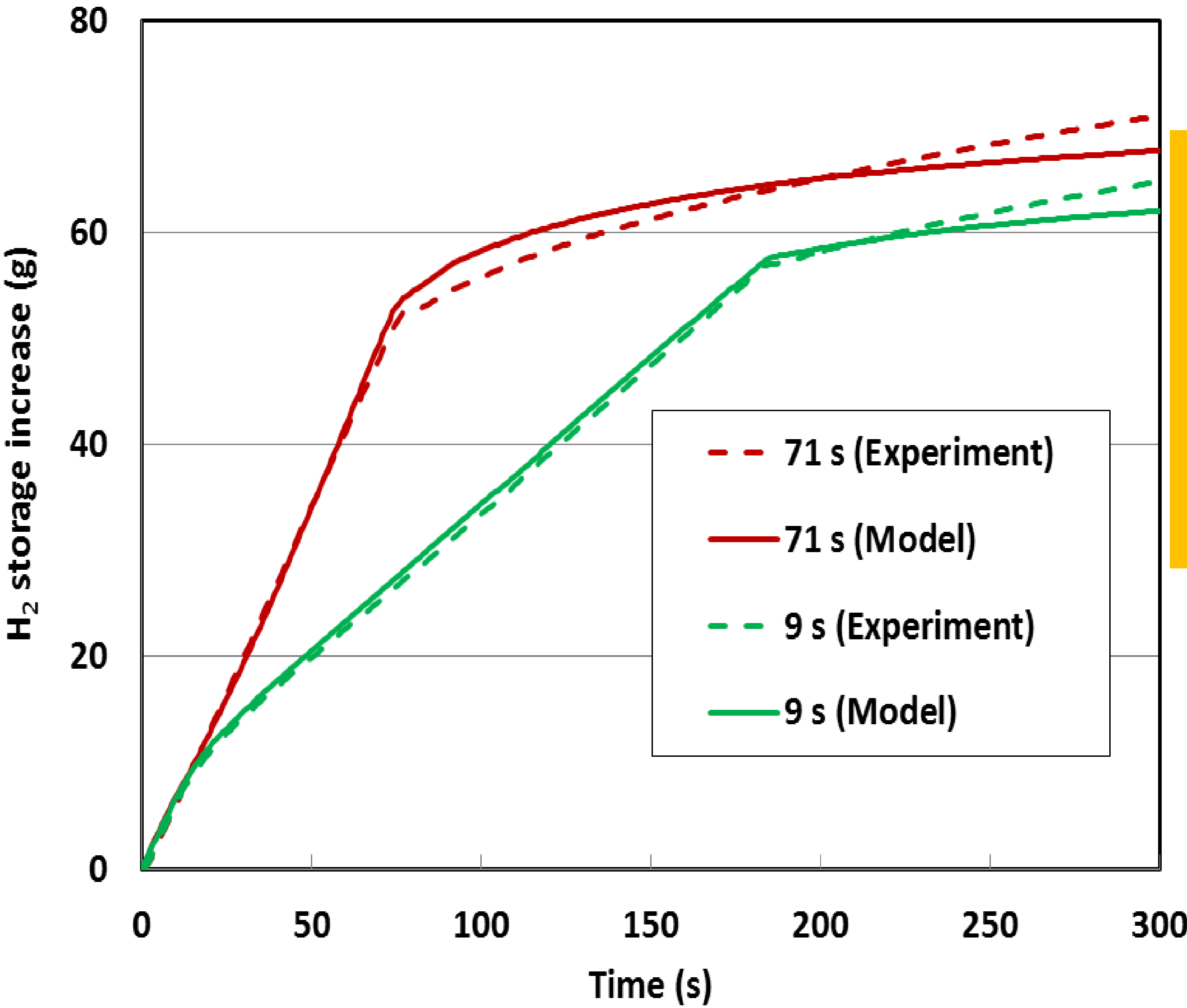
H_2 storage in the vessel increases as the density of MOF increases

Effect of Outlet Opening Time on Flow-through Cooling



- H_2 cooled to 80 K initially
- Continuous flow-through once 60 bar reached
- With same starting temperatures, similar average bed temperatures in less than 200s

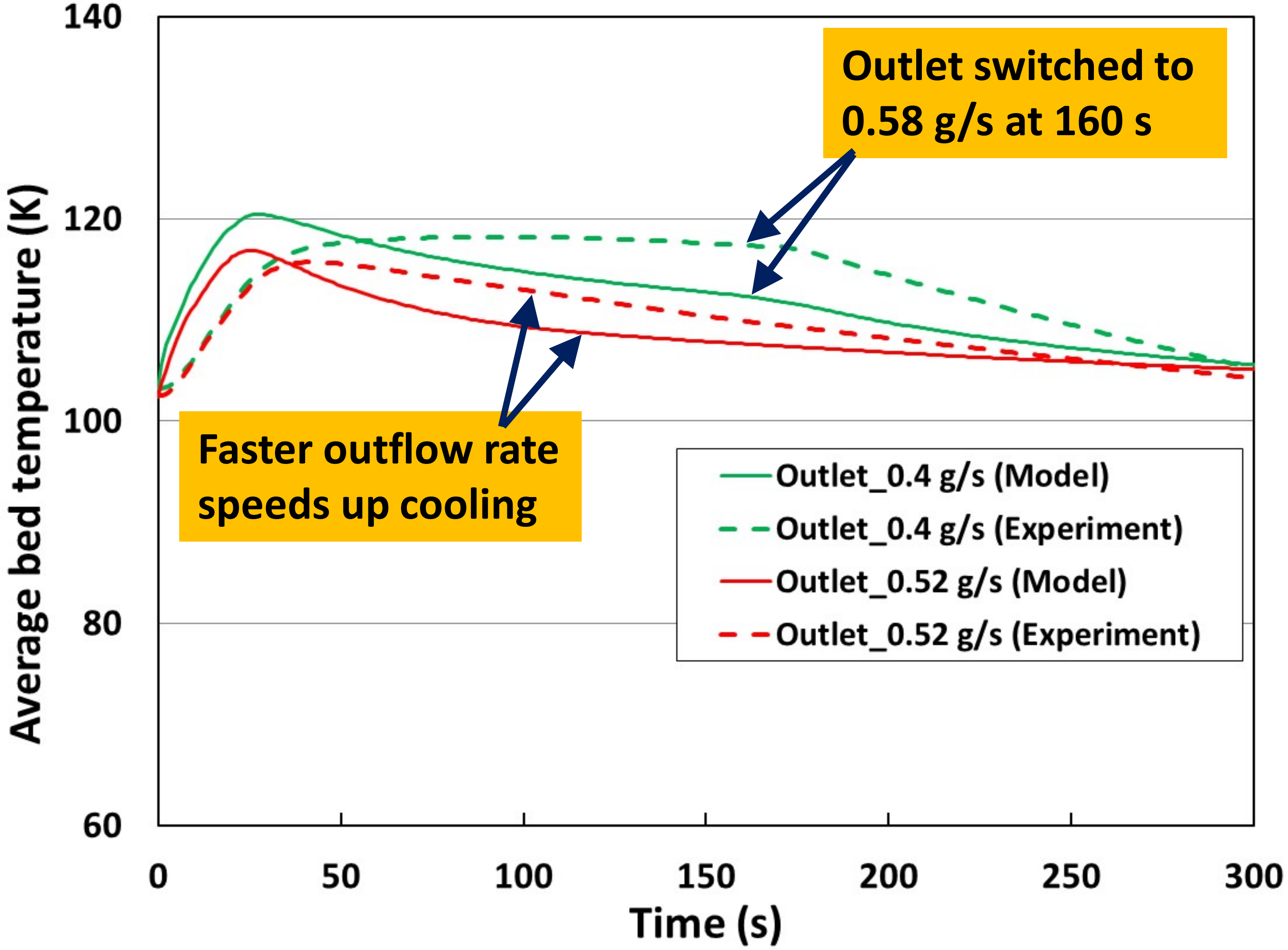
Effect of Outlet Opening Time on H_2 Storage



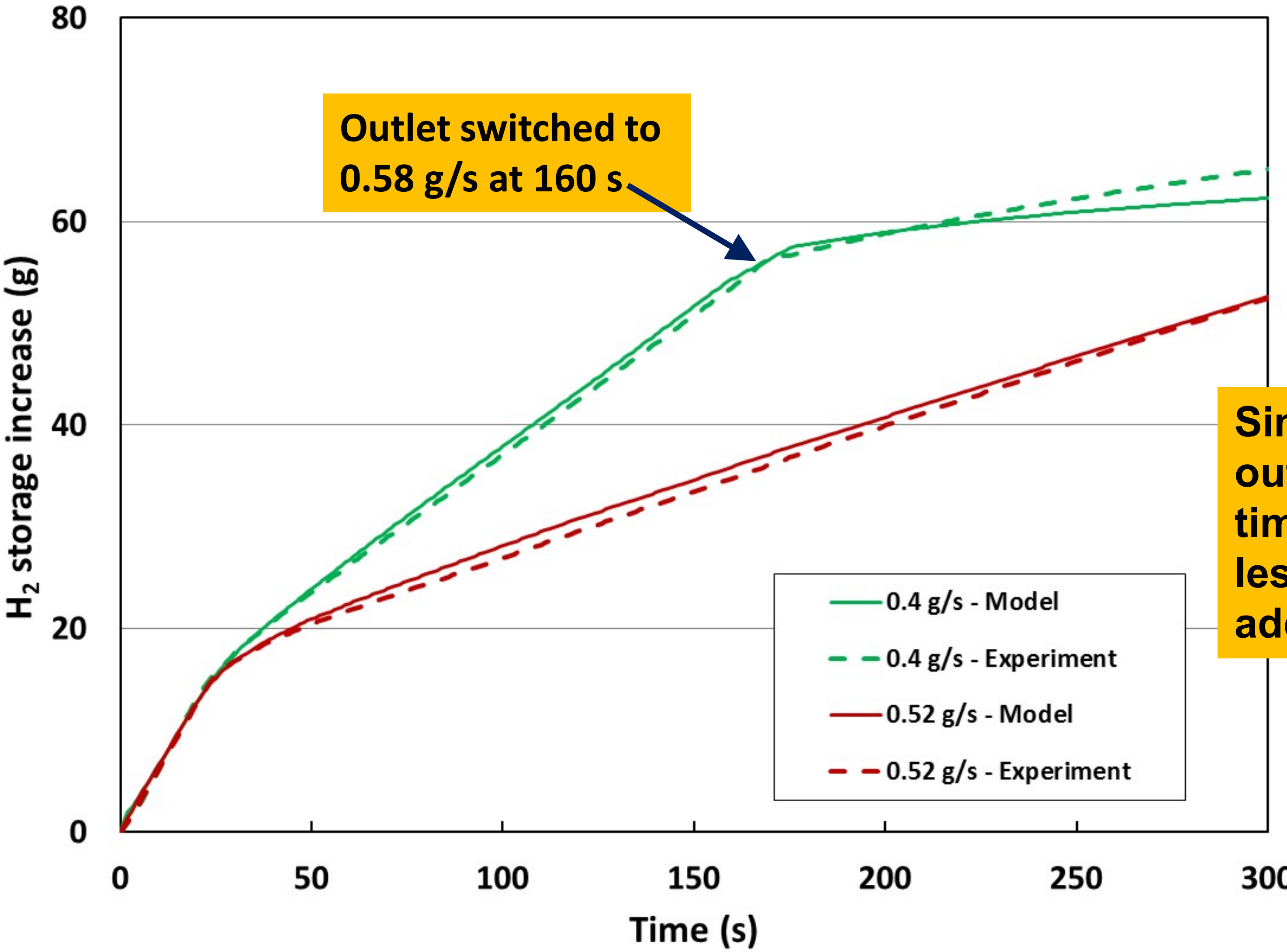
- **Faster opening time = less gas added to system**
- **60 bar reached at 180 s when outlet opened at 9 s (110 s longer than when sealed)**

Effect of Outlet Flow Rate on Flow-through Cooling

- Initial bed temperature 100 K
- Outlet flow rates 0.4/0.58 and 0.52 g/s, fixed opening time
- Inlet flow rate 0.5 g/s



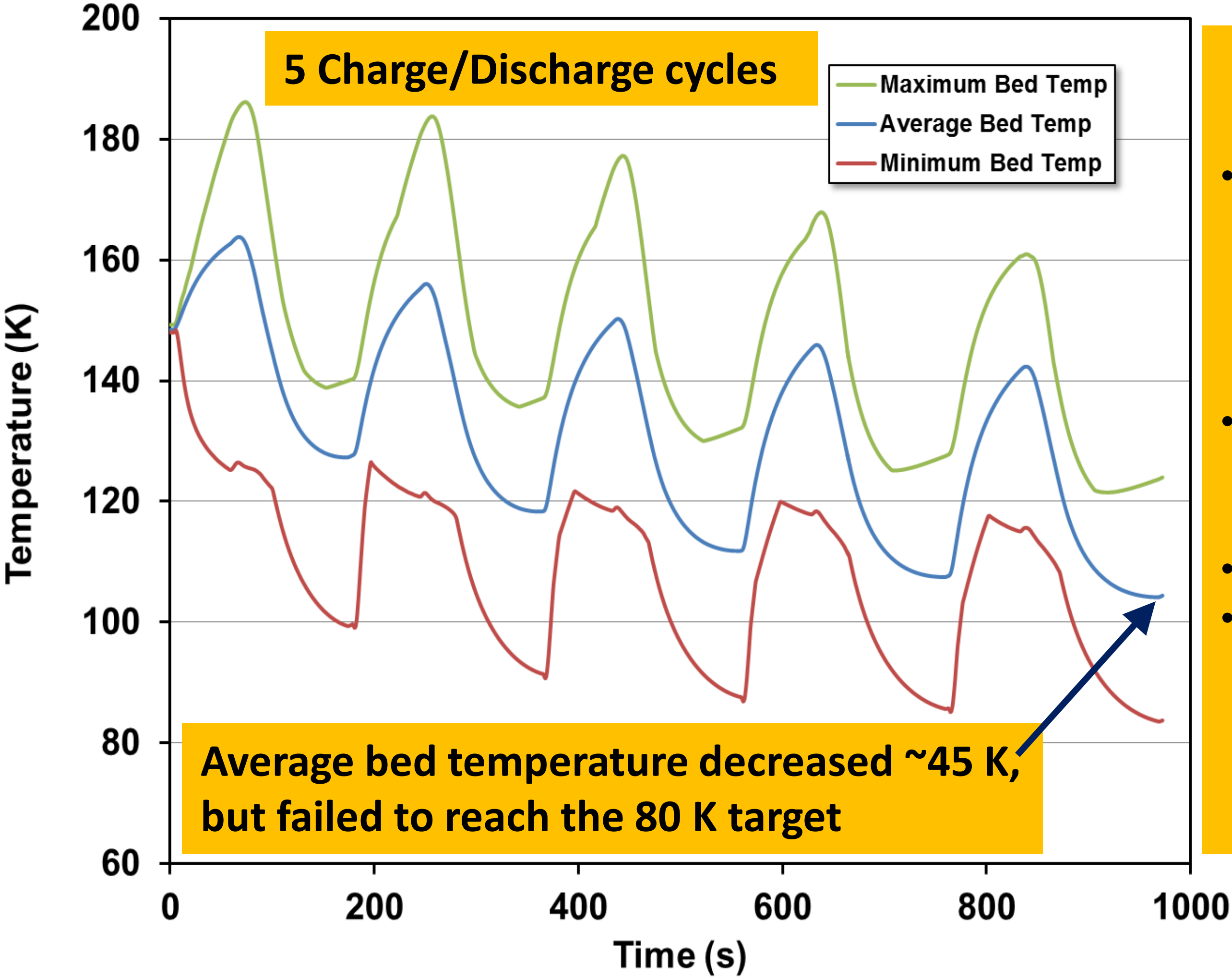
Effect of Outlet Flow Rate on H_2 Storage



Similar results as outlet opening time varied (i.e. less hydrogen added to system)

Achieving Bed Temperature of 80 K – Rapid Cooling

Starting bed temperature of 150 K

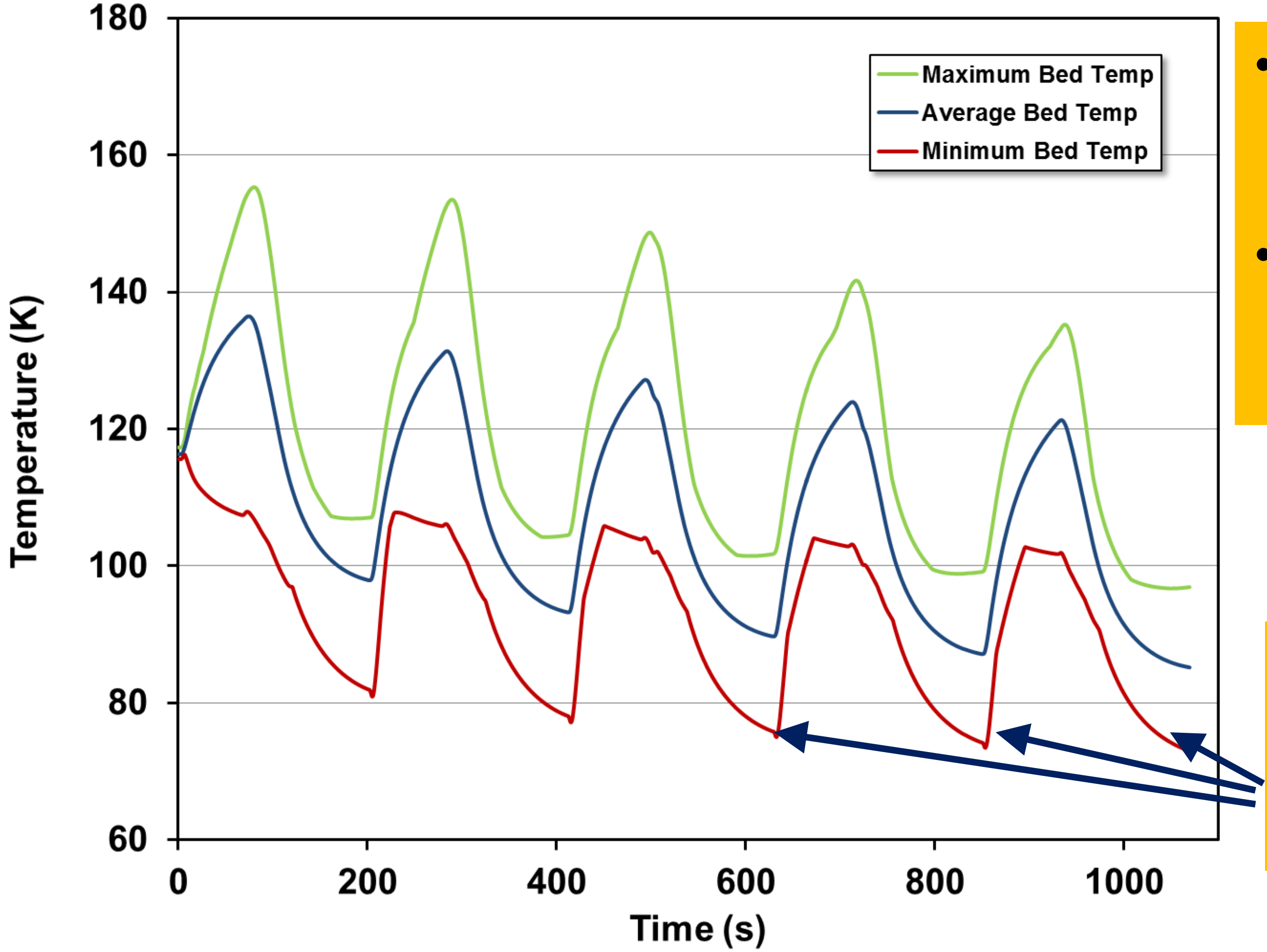


Rapid Charge/Discharge Cycling Method:

- Vessel discharged as fast as possible (within instrument's safety limitations) to release heated H_2, depressurize
- High temperature of 120 K, low of 84 K, avg. of 100 K
- After 300 s avg. of 125 K
- Hybrid cooling attempted (constant outflow during discharge; no better than with no outflow)

Achieving Bed Temperature of 80 K – Rapid Cooling

Starting bed temperature of 115 K

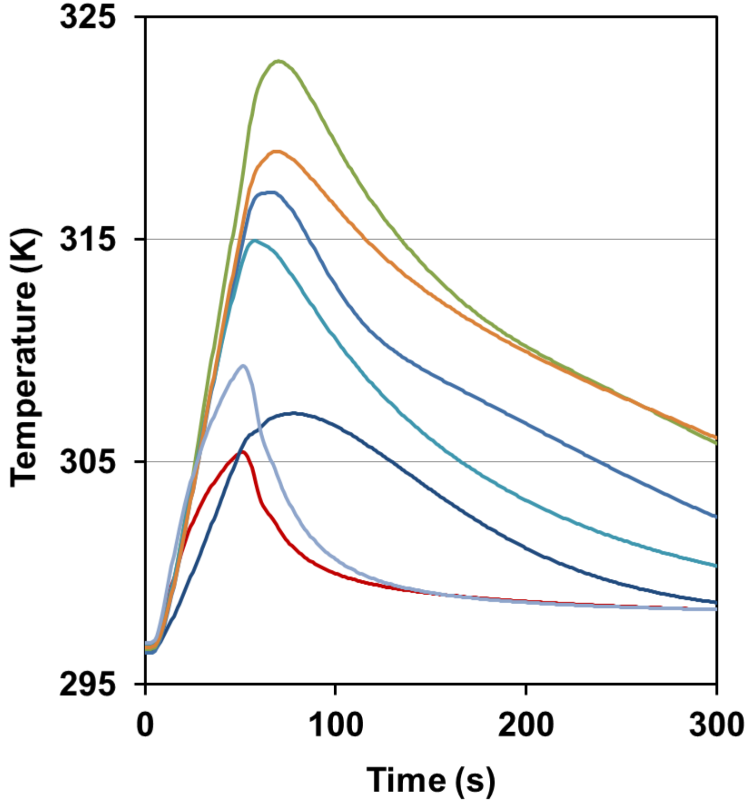


- **More than half of RTDs read below 90 K**
- **High temperature of 96 K, low of 73 K, avg. of 85 K**

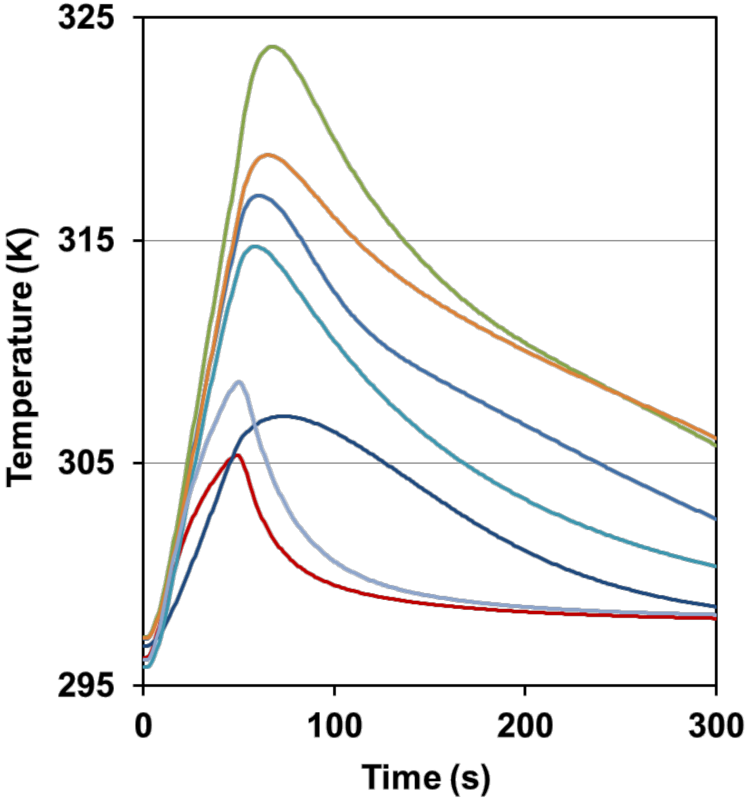
Certain regions of the bed cooled to a lower temperature than the inlet H_2 (80 K)

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.

Summary

- **Accomplishment 1: Hydrogen Desorption in MOF-5 Storage System**
  a) Designed, built, and tested a cryo-vessel with a helical coil heater and automated control instrumentation
  b) Discharge experiments and desorption model results show the scaled release rate milestone and the gravimetric and volumetric milestones can be met.
  c) Experimental results with helical coil resistive heater validate the accuracy of the desorption model.

- **Accomplishment 2: Flow-through Adsorption in a MOF-5 Hydrogen Storage System**
  a) Conducted experiments and model simulations while varying several operating conditions to improve flow-through cooling of MOF-5 bed.
  b) Determined that a flow rate of 1.2 g/s (800 LPM) is required to refuel the 3L test vessel in less than 3 minutes, which exceeds our instrumentation's limit of 0.7 g/s flow rates.
  c) Verified with experiments that vertical orientation of the vessel produces results in close agreement with horizontal placement.

Future Plans

- General Motors will continue to participate in the DOE HSECoE Phase III of the program as an OEM consultant and will provide the center with vehicle level performance requirements.
- Test and evaluate Framework model and other models to be published on the WEB.
- Participate in Center Face-to-Face meetings and Coordinating Council Telecons; indicate technical or programmatic areas the Center should be pursuing with more emphasis.

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**

Responses to Previous Year's Reviewer Comments

Comment 1 : MOF-5 will likely not be able to meet the DOE targets for hydrogen storage. Will the work conducted on this project be fully transferable to another, more suitable, material if/when it is identified?

Response: Previous modeling work did in fact include both AX-21 and MOF-5: see Chakraborty A, Kumar S, *Thermal management and desorption modeling of a cryo-adsorbent hydrogen storage system, International Journal of Hydrogen Energy* (2012). The Center selected MOF-5 as the adsorbent material to test, with the intent that other materials could be substituted in all models in the future.

Comment 2: The modeling results appear to be approximations in some cases. The functional forms of the model curves do not always match the experimental curves. It is not clear how serious an issue this is. Thermal energy flow, in particular, is often hard to model.

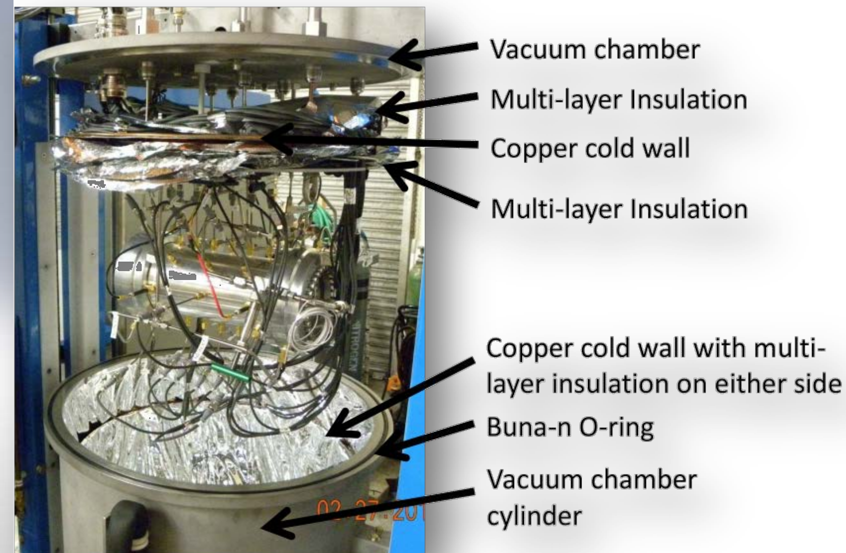
Response: Comparing the finite element model results to the relatively small number of temperature measurements that were possible did prove to be challenging. Ideally, having measurements at a finer set of grid points within the vessel would better capture the moving adsorption front one would expect to see in a charging experiment. Another issue we found was that the model can't account for the channeling effect, which may be particularly significant in the flow through tests.

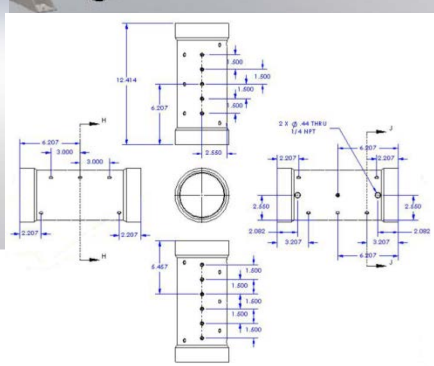
Comment 3: Papers should be prepared and submitted for publication reporting on cryogenic testing of the prototype beds and MOF-5 adsorbent properties. Prior modeling and test results should be fully shared with other HSECoE partners.

Response: An internal paper detailing the testing performed with the cryogenic apparatus and the modeling of these tests is in the review process, and will subsequently be submitted for publication. All of our previous work is presented to our HSECoE partners at F2F meetings, and these presentations are also shared on the Center's web site.

Technical Back-up Slides

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;**

Helical Coil Resistance Heater and 3L Vessel Dimensions

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

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

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

Energy balance

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

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