Thermal Management of On-Board Cryogenic Hydrogen Storage Systems

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General Motors Company

Project ID: ST009

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Overview

Timeline

- Project Start: Feb 2009
- Phase I end: Mar 2011
- Phase II end: June 2013
- Project end: June 2014
- % complete: 55%

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 in FY 11: $380,000
- Funding for FY 12: $480,000

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

System Simulation Models and Detailed Transport Models for Metal Hydrides *(with UTRC, SRNL, PNNL,NREL)*

- Novel heat exchanger designs and optimization
- System simulation models and detailed 2-D models to include heat transfer, chemical rxns to guide system models
- Test simulation models for system performance, performance metrics in relation to DOE targets

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

- Binders and additives for pelletization of AX-21
- *Adsorption isotherms and low temperature thermal conductivity for MOF-5 pellets*
- *Anisotropic thermal conductivity measurements for MOF-5 pellets*

Transport Models, System Simulation Models and Experimental Model Validation for Adsorbent Systems:

- Construct and test system simulation models for adsorbent systems and identify operating conditions for meeting DOE goals *(with SRNL)*
- *Detailed transport models to include adsorption and heat transfer to guide system models (with SRNL)*
- *Design of heating system for desorption*
- *Non-isothermal adsorption in pellets of various shapes/sizes*
- *Experimental validation of adsorption and desorption strategies*

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)*
- FMEA Analysis of the adsorbent System (most HSECoE partners)

Milestones and Progress Towards:

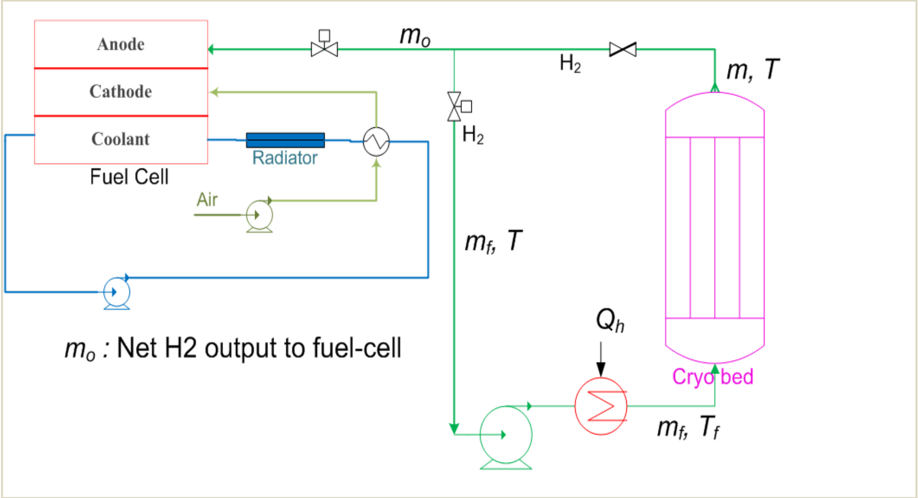
1. **Discharge thermal management for adsorbent systems**
   - Design and modeling of adsorbent bed with a resistance heater
   - Determination of bed thermal conductivity necessary for hydrogen discharge
   - Additional design investigations ongoing
2. **Hydrogen adsorption in pellets (bed design)**
   - 2-D analysis of thermal effects, isotropic thermal conductivity ($k_r = k_z$)
   - Cylindrical pellets with H/D =1, short hockey puck shape (H/D << 1), and long stick shaped (H/D >> 1) pellets
   - Anisotropic thermal conductivity effect ($k_r > k_z$) work ongoing
3. **Engineering properties measurement**
   - Low temperature (4-355 K) thermal conductivity measurement of MOF-5 pellets of varying densities. Results presented by Ford
   - Validation of MOF-5 hydrogen adsorption measurements
   - Preliminary work done; work continuing on anisotropic thermal conductivity measurements in pellets
4. **Design and fabrication of a 3-L vessel for MOF-5 charging and discharge experiments – Model validation**
   - Design and fabrication completed
   - Vessel received at GM in March
   - Model validation experiments in coming months

Accomplishment I. Hydrogen Desorption in a Cryo-adsorbent Bed

Bed temperature must be raised to extract a high fraction of the adsorbed H_2

Hot Gas Recirculation

- Hot gas recirculation is an efficient way to supply the thermal energy to the bed
- High H_2 side-stream flow rate and a cryogenic pump needed to deliver this H_2 to the bed
- Therefore, alternatives to hot gas recirculation needed to supply thermal energy to the bed.



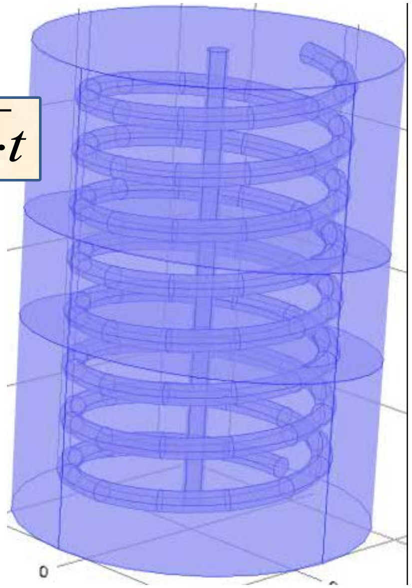
Cryo-adsorption Discharge Schematic Diagram with Hot Gas Recirculation

Electric Heating with a Helical Coil

- Electric heat is a good option
- However, because of low k_{th} of AX-21 and MOF-5, design of an electric heater is a challenge; `<u>thermal penetration thickness</u>' δ_T is very small.
- Helical coil heater is an efficient way of distributing heat; a center element was needed
- Coil pitch and radius can be easily changed to ensure uniform distribution of heat

$$\delta_T \cong \sqrt{\alpha \cdot t}$$

Schematic of a helical coil with central heating element



- Model developed for H_2 extraction from AX-21 bed by desorption using a helical coil electrical heater
- Two scenarios explored: Storage system at (a) 60 bar, and at (b) 200 bar
- Simulations with the goal of selecting thermal conductivity (k_{th}) that allows fairly uniform temperature distribution through the bed and desorption of most of H_2

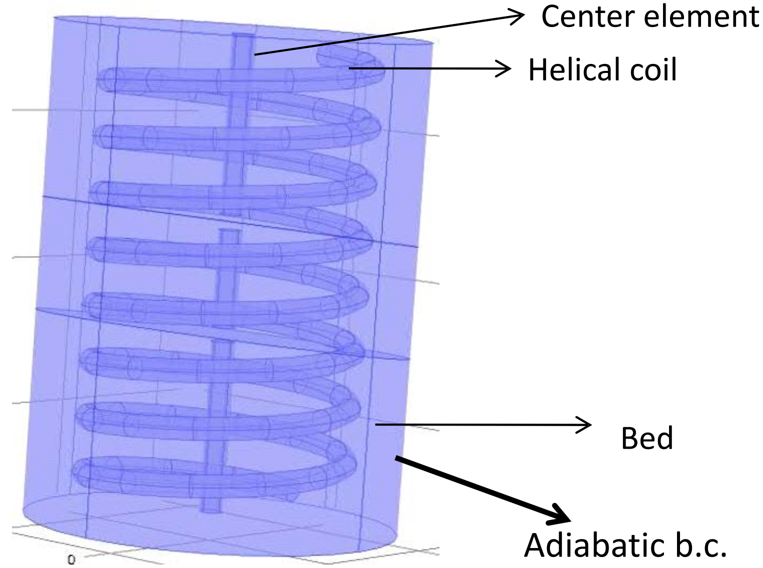
Heater Design and COMSOL Model

- Simulations include mass and energy balance, Darcy's law for pressure variation in the bed and a modified Dubinin-Astakhov hydrogen adsorption isotherm

- 3-D model includes a cylindrical bed, adsorbent, and a helical coil heater in the bed.

- 8 coil turns included in the simulation

- 240,000 hexahedral cells were used for meshing the geometry. Solution accurate in the middle domain.



Simulations for k=0.1- 0.5 (W/m.K), Selected two scenarios

Scenario 1
Initial Pressure = 60 bar, Temp = 80 K

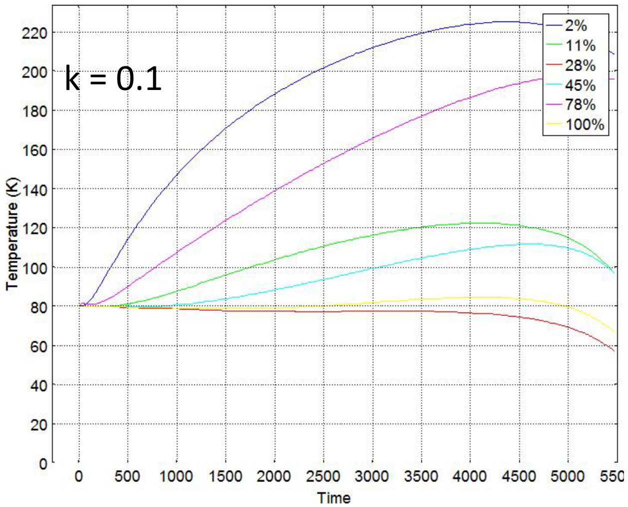
- Case 1: k = 0.3
- Case 2: k = 0.5

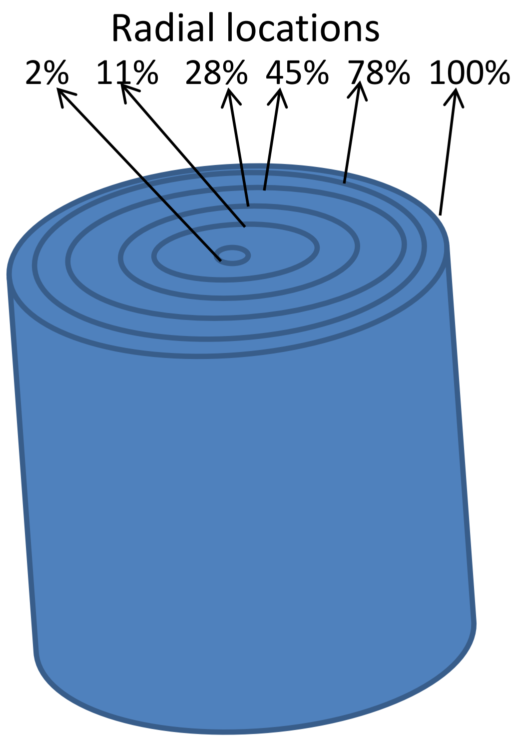
Scenario 2
Initial Pressure = 200 bar, Temp = 80 K

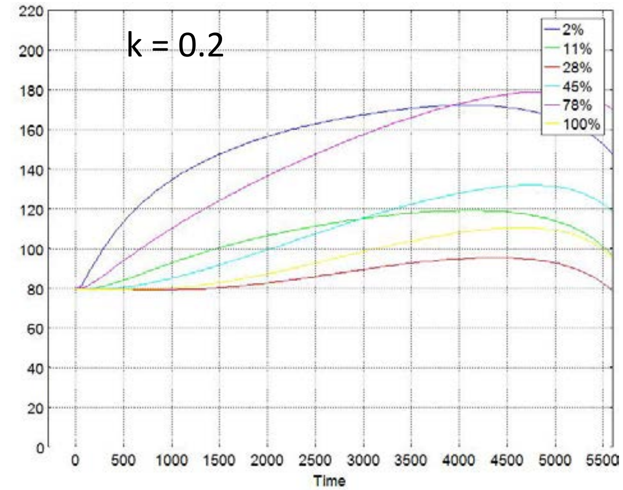
- Case 1: k = 0.3
- Case 2: k = 0.5

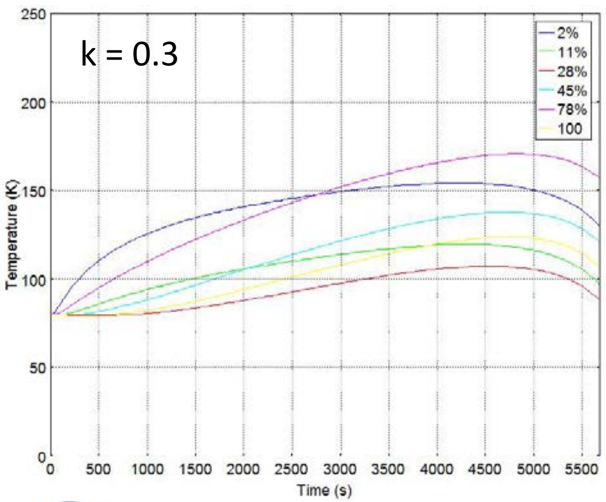
Bed temperature as a function of time for various values of k (W/m.K)

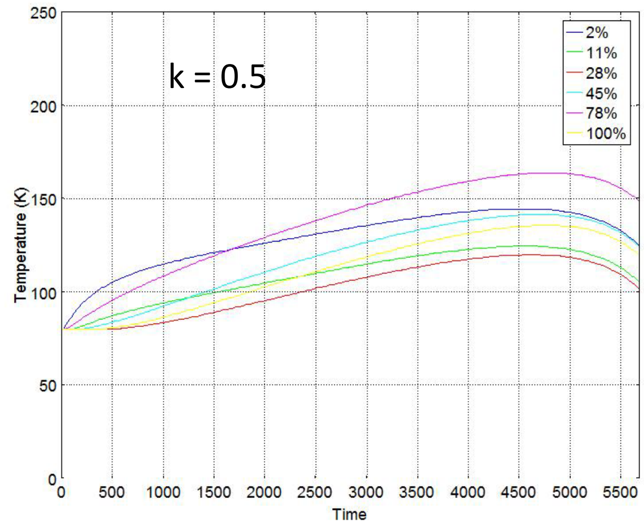
Initial bed pressure of 200 bars and temperature of 80 K





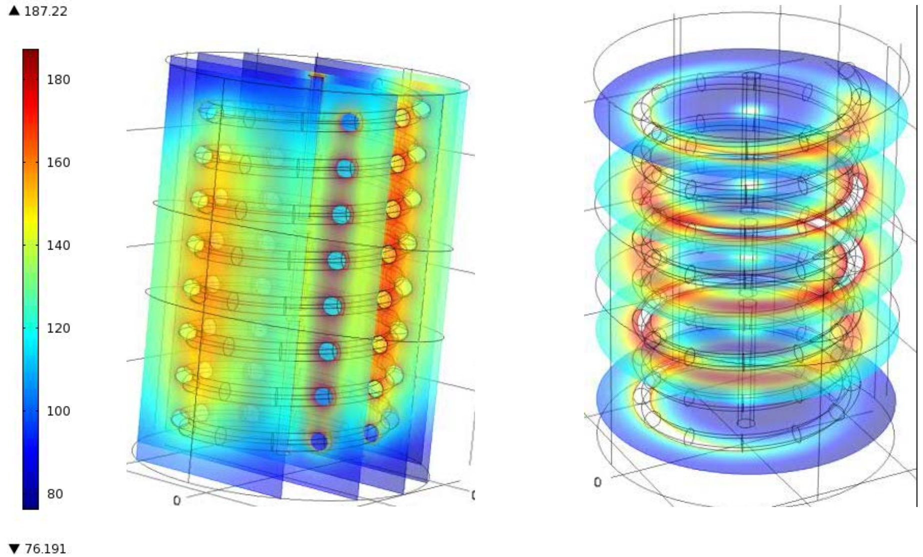




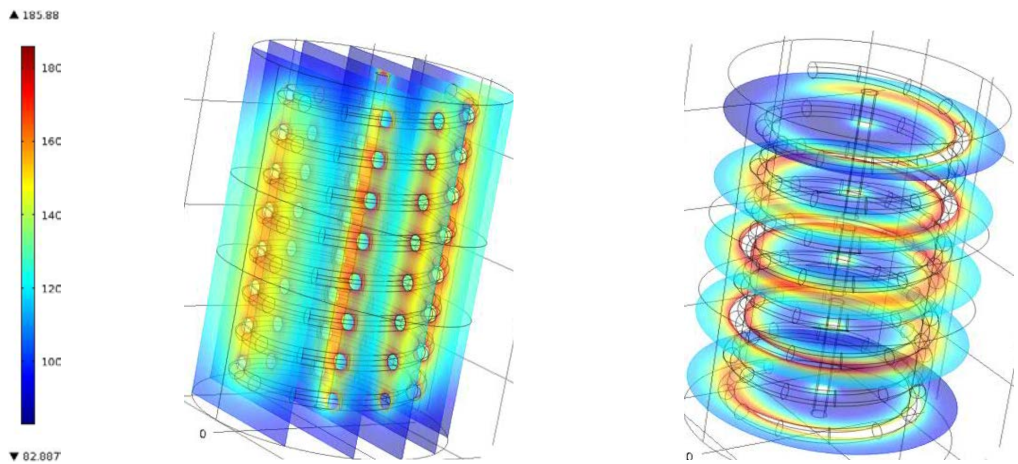


Temperature (K) distribution for two cases (k=0.5 W/m.K)

Case 1: Initial Pressure 60 bar

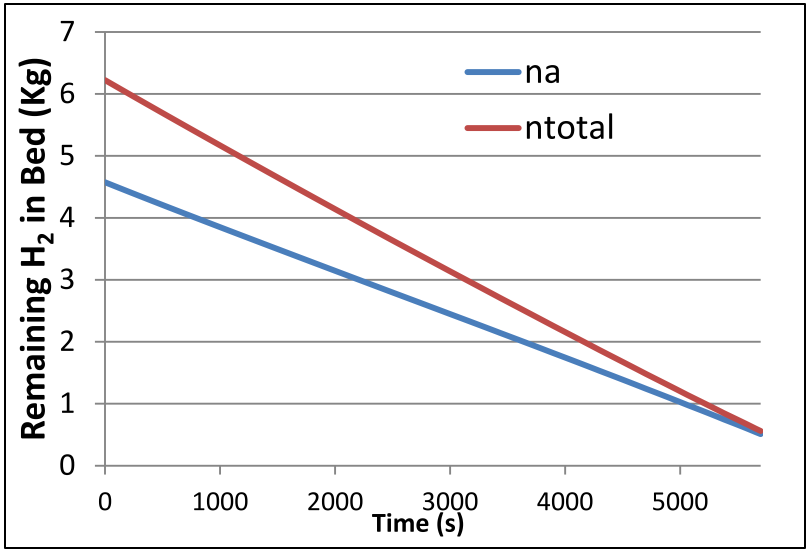


Case 2: Initial Pressure 200 bar

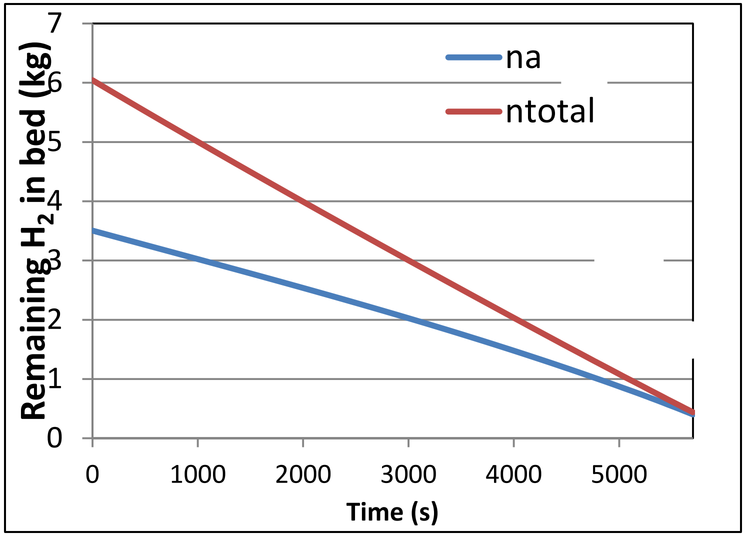


Total and adsorbed hydrogen in the bed

Case 1: Initial Pressure: 60 Bar



Case 2: Initial Pressure: 200 Bar



Hydrogen Available for Extraction: Full (80K, 60 or 200 bar)→Empty (4 bar, 150K)				
Case	Pressure (bar)	Heat (W)	k = 0.5 W/m.K % extracted N_{total}	k = 0.3 W/m.K % extracted N_{total}
1	60	1760	91.8%	90.7%
2	200	1374	92.6%	92.2%

Design parameters for 5.6 kg of deliverable hydrogen

	Initial Pressure: 200 bars, Initial Temperature: 80K, Final Temperature: 150K, Final Pressure: 4 bars	Initial Pressure: 60 bars, Initial Temperature: 80K, Final Temperature: 150K, Final Pressure: 4 bars
Hydrogen delivered (g)	5600	5600
Hydrogen in the bed before discharge (g)	6050	6102
Hydrogen in the bed after discharge (g)	450	502
Bulk density of AX-21 (kg/m^3)	300	300
Thermal conductivity of AX-21	0.5	0.5
Diameter of the bed (m)	0.5	0.5
Height of the bed (m)	0.61	1.027
Height of the helical coil m)	0.57	0.93
Pitch of the coil (m)	0.075	0.075
# of turns of the coil	8	13
Diameter of the coil (m)	0.35	0.35
Total coil length (m)	8.35	13.69
Diameter of the heating element (m)	0.03	0.03
Total required heat (W)	1374	1760

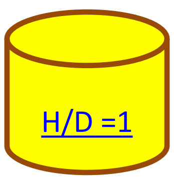
Design also completed for MOF-5; results not presented because of time constraints

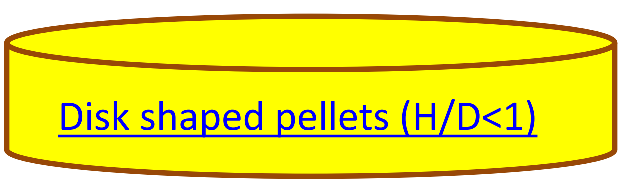
Accomplishment II. Hydrogen Adsorption in Cylindrical Pellets - Thermal effects

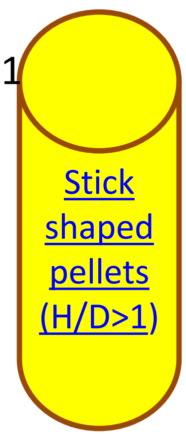
Pelletization offers the opportunity for increasing volumetric storage density. However, two issues:

- ***Decrease of hydrogen adsorption capacity in adsorbents pellets***
- ***Mass and heat transport in pellets can affect the rate of adsorption and thus cause difficulties in meeting the refueling time targets***
- ***Therefore, important to understand the effect of pellet shape and size on refueling***

- Short cylindrical pellets, H/D =1
- Flat disk pellets, H/D < 1
- Stick shaped pellets, H/D>1



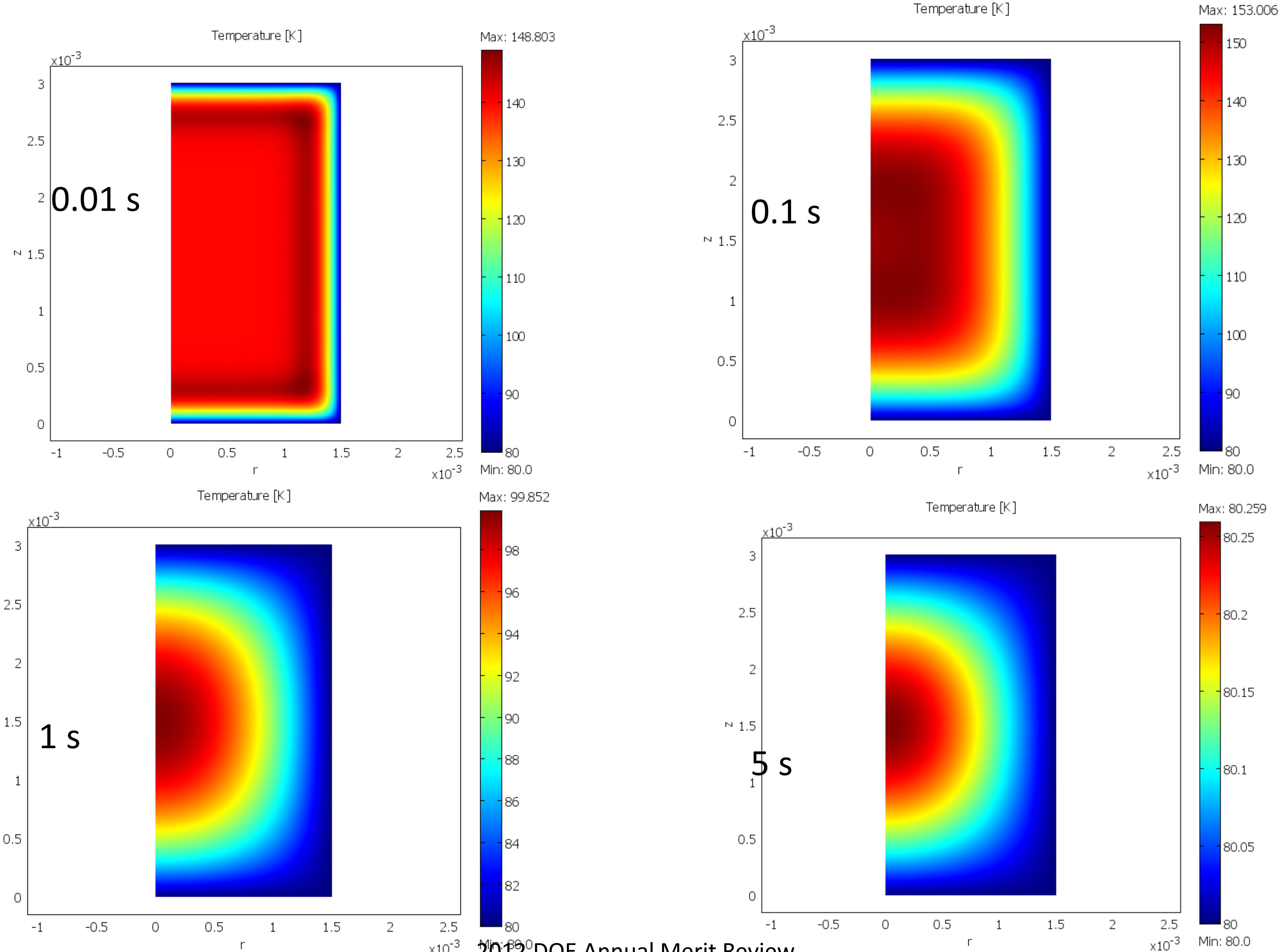




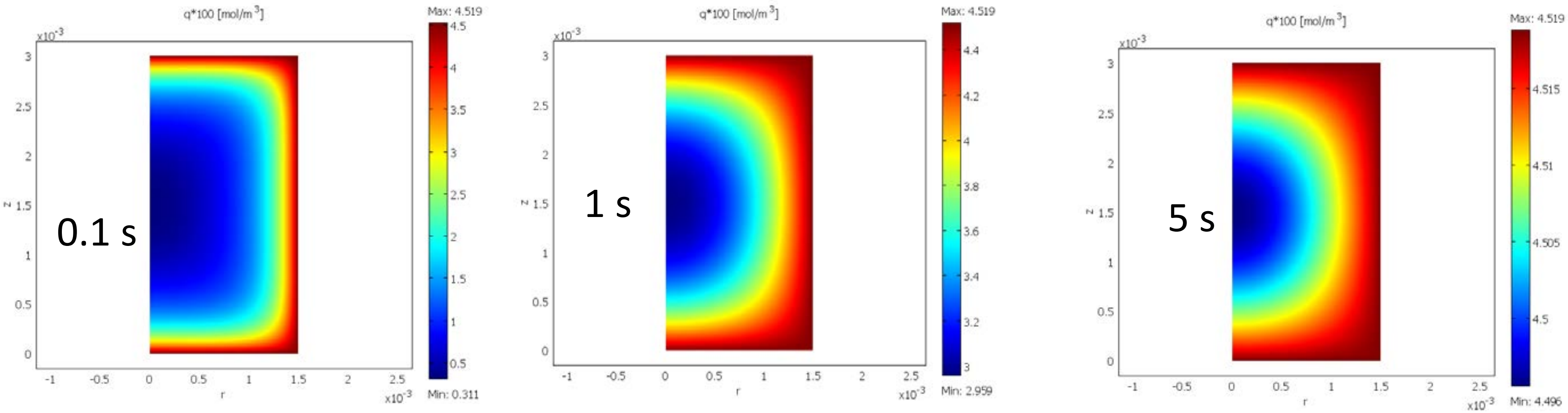
In the following slides, results shown are for cylindrical pellets with H/D = 1

- A pellet at 140 K and 4 bar (empty) enveloped in H_2 gas at 80K and 30 bar (refueling)
- The results are axisymmetric. Hence, only the right half of the cylindrical pellet is shown in the following 2-D images.

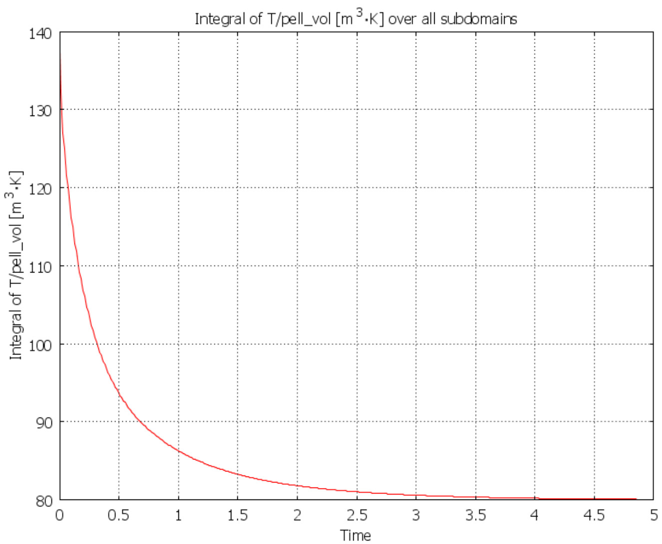
Temperature evolution - 3 mm pellet results

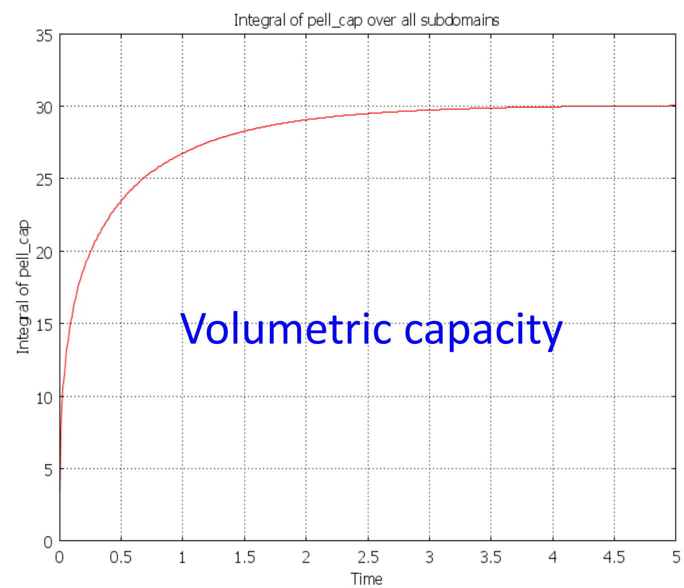


Adsorbate concentration evolution - 3 mm pellet results

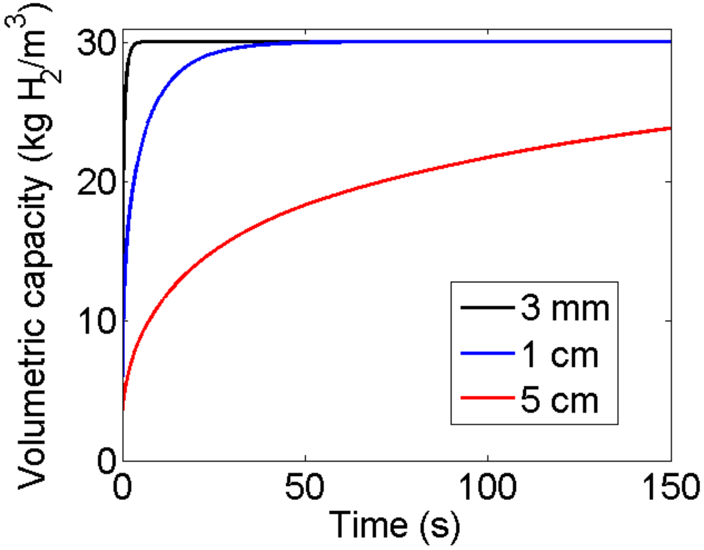


Volume averaged evolutions - 3 mm pellet results





Effect of pellet size on transient volumetric capacity



For short cylindrical geometry (H=D) pellets:

- As size increases, a pellet takes longer time 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 many minutes. In a conventional packed bed, it may not be possible to achieve a 3 minute refueling with pellets larger than 1 cm

Effect of pellet shape

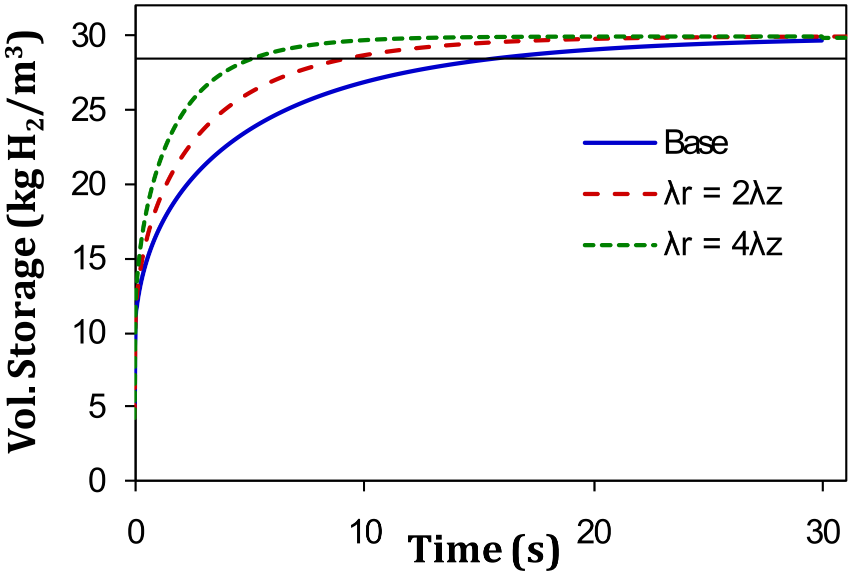
- Analysis also performed for flat cylindrical disk shaped (hockey-puck like) compacts and long stick-like pellets (H/D << 1 and H/D >> 1)
- Adsorption rate appears to depend on the shrink wrap surface area. Results indicate that adsorption rate for:
  short cylindrical pellets > stick-like pellets > disk shaped pellets
- In addition, stick-like pellets can achieve high packing density in a structured bed
- Bed design should take into account both the packing density and adsorption capacity

Anisotropic Thermal Conductivity in Pellets

- Recent experiments suggest that for pressed pellets thermal conductivity is anisotropic
- UTRC measurements suggest $k_r > k_z$ by a factor of 5
- Thermal conductivity measurements underway at GM

Simulations for 1 cm cylindrical pellets:

- Axial value of λ was kept constant; radial value was varied
- Increasing k_{radial} resulted in faster refueling times
- 95% volumetric capacity was reached in 5.1 seconds



Simulations underway to combine the pellet shape and size effect and anisotropic thermal conductivity

Accomplishment III. Cryo-adsorption Test Vessel

- A 3-L cryogenic adsorption vessel has been designed and built. Set-up and experiments to start in Q2 2012.
- MOF-5 powder acquired
- The vessel will be used to measure the bed capacity under dynamic conditions and test heater design for efficient hydrogen desorption
- Vessel enclosed in a vacuum jacket, will be able to achieve adiabatic wall conditions
- Instrumentation:
  - Flow rates in and out of the bed
  - Temperatures within the bed at multiple locations
  - Pressure in and out
  - Control of flow rate out of the vessel to maintain bed pressure

Other Accomplishments:

1. Completed and wrapped up metal hydride work
2. Measured low temperature (T= 4 to 350 K) thermal conductivity for pellets of various densities and various % ENG content. Results will be presented by Ford.
3. Supported adsorbent system FMEA Analysis performed by the HSECoE team – Results presented by Ford
4. Anisotropic MOF-5 pellet thermal conductivity measurements to complement UTRC measurements

Collaborations:

- Thermal conductivity measurements for pellets (UTRC and Ford)
- Adsorbent system – system and transport modeling (SRNL)
- Adsorbent system refueling and discharge experiments (SRNL and UQTR)
- Metal hydride work wrap-up (UTRC, SRNL, NREL, and PNNL)
- FMEA Analysis (All partners)

Summary

Discharge thermal management:

- A helical coil heater along with a center heating element proposed to supply the heat during discharge, and the discharge process modeled for the adsorbent bed
- Two pressure cases studied: Initial bed pressure 60 bars and 200 bars
- Thermal conductivity of the bed in the range 0.3-0.5 W/m-K provides fairly uniform temperature distribution throughout the bed; simulations show that over 90% of the H_2 in the bed can be extracted these two cases
- Power requirement for the 200 bar case is 1374 W. For the 60 bar case (for 5.6 kg deliverable H_2 , we have less H_2 in gas-phase and correspondingly higher amount of adsorbed hydrogen) the power requirement is 1760 W.

Pellet Adsorption :

- In the beginning, as adsorption is occurring near the surface of the pellet, desorption is occurring within the pellet due to heat effects.
- For small pellets, temperature equilibration is fast because a high rate of cooling is achieved due to the small size of the pellet. Larger pellets take longer time to cool and reach the equilibrium adsorbate concentration due to higher thermal resistance
- Stick-shaped pellets offer one way to increase the packing density without undue reduction in refueling time
- Higher thermal conductivity in the radial direction reduces the time necessary for the pellets to reach equilibrium
- Further thermal conductivity *measurements and simulations* underway to optimize the bed structure

Experimental Validation of Refueling and Discharge Strategies:

- Apparatus designed, fabricated, and received. Set-up and experimental work starting.

Future Plans

- **Determine optimal pellet size and shape for fast refueling for the case of non-isotropic thermal conductivity**
  - For a single pellet
  - For a bed filled with pellets
- **Improve resistance heater design for desorption**
  - Coil heater
  - Other designs
- **Design and modeling of heat exchanger**
  - Liquid N_2 cooling during adsorption
  - FC waste heat for desorption
- **Measurement of MOF-5 engineering properties**
  - Measure RT thermal conductivities of MOF-5 pellets, with a laser-flash apparatus, in radial and axial directions to confirm and complement UTRC measurements
- **Cryo-adsorption test vessel**:
  - Installation and testing
  - Measure dynamic capacity of the MOF-5 powder bed
  - Validate convection cooling concept
  - Test resistance heater design

Acknowledgements

- DOE for funding the project
- Ned Stetson and Jesse Adams of DOE for project direction
- All Center partners for great cooperation
- GM management for support

Technical Back-up Slides

Technical Obstacles and Engineering Challenges

A cryogenic adsorbent system faces many challenges. We plan to address these challenges.

High system cost : Focus is on low cost system design including a low pressure vessel and low cost heating element

Flow-through cooling requires that some of the H_2 passing through the vehicle storage tank be cooled at the station for refueling subsequent vehicles. We are designing a low-cost heat exchanger system that will do double duty - use liquid N_2 for cooling the tank and the FC waste heat to supply energy for desorption.

Low volumetric density: The low density powder adsorbents can be compacted to increase the volumetric density. However, the compaction may lead to higher refueling times. Effect of compacted pellet size and shapes on refueling times is under study.

Low temperature properties data: we are working with Ford and UTRC to measure engineering properties of these materials

Low Temperature k Measurements

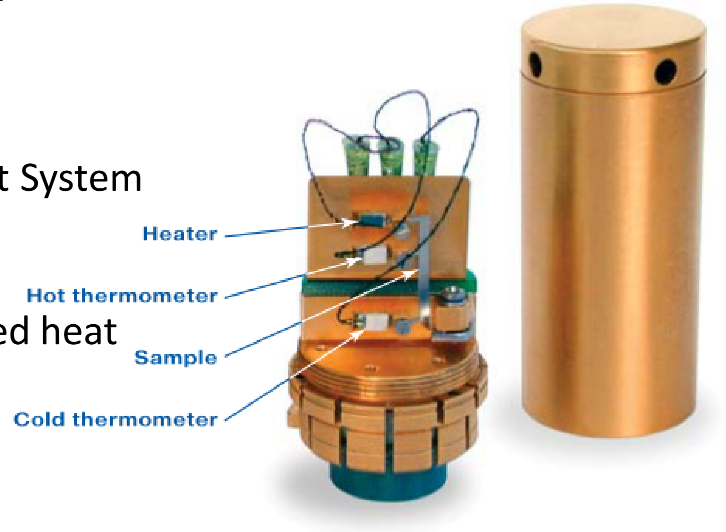
Series of MOF-5 pellets at 0.3 and 0.5 g/cm^3 with 0, 5 and 10 wt% expanded natural graphite provided by Ford (ongoing).

Pellet Characteristics:

- 0.3 g/cm^3 very fragile at all levels of ENG added, difficult to handle.
- 0.5 g/cm^3 more rigid, but fragility increases with increased levels of ENG.
- Pellets structural integrity dependent on instrument cool down rate, pellets have tendency to crack and fall apart if cooled too quickly.

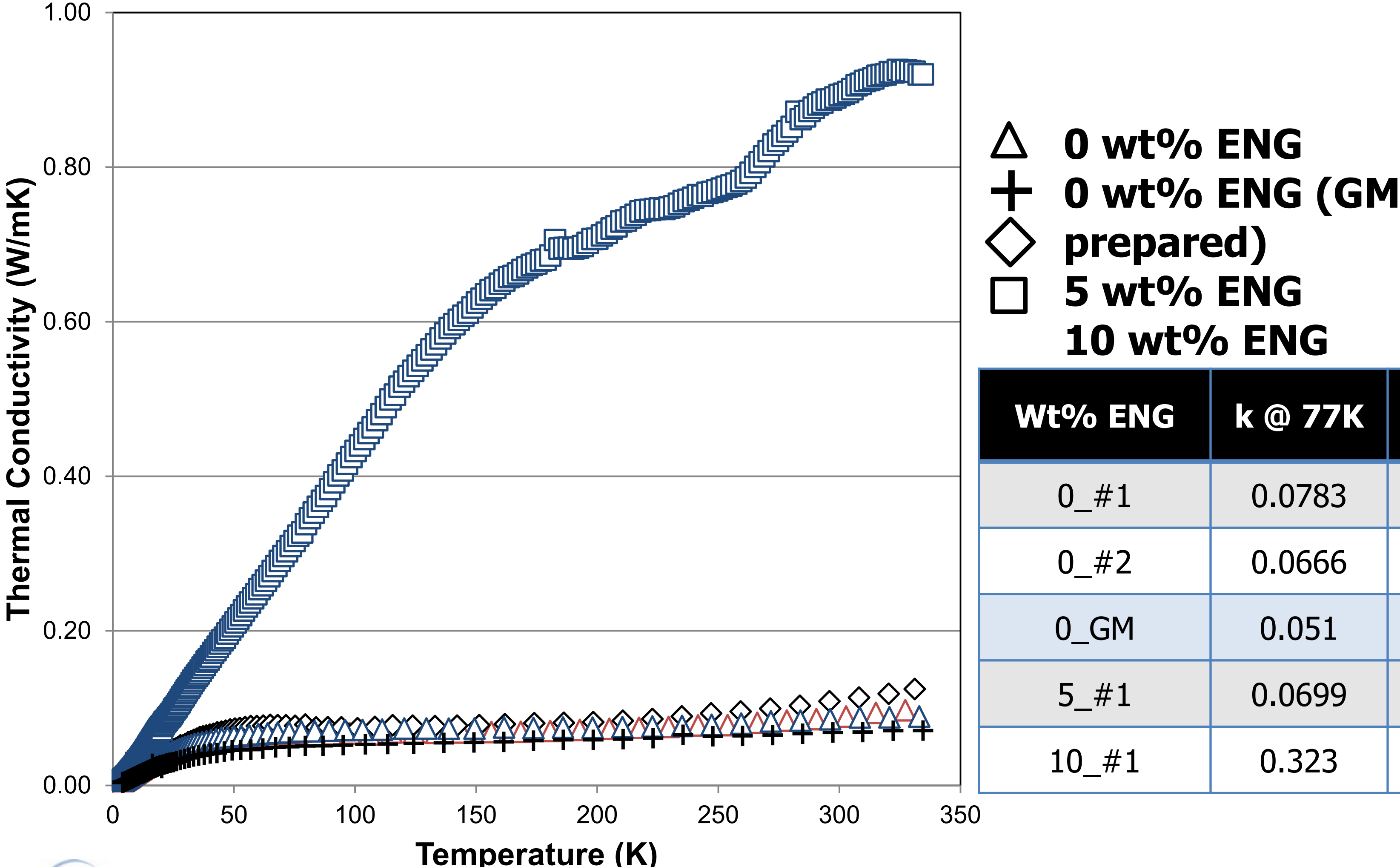
Low Temperature Measurements:

- Perform using a Quantum Design Thermal Transport System (right).
- Temperature profile 3 to 350 K.
- Thermal conductivity directly calculated from applied heat power, Δ T and sample geometry



HSECoE

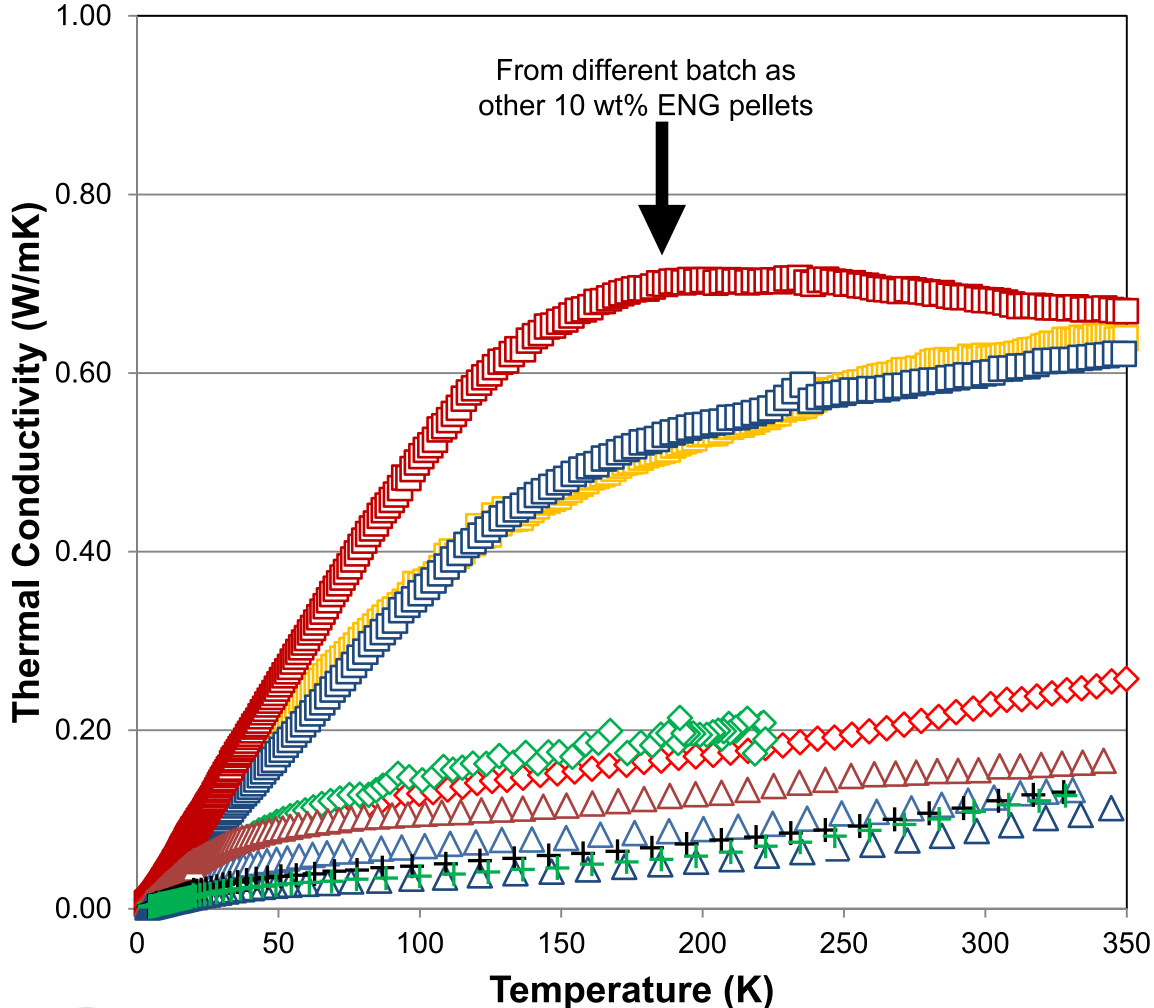
0.3 g/cm^3 MOF-5 Pellets



Wt% ENG	k @ 77K	k @ 160 K
0_#1	0.0783	0.0792
0_#2	0.0666	0.0694
0_GM	0.051	0.0563
5_#1	0.0699	0.075
10_#1	0.323	0.6533

Beyond 200K system exhibits radiative heat loss, which may skew data high

0.5 g/cm³ MOF-5 Pellets



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

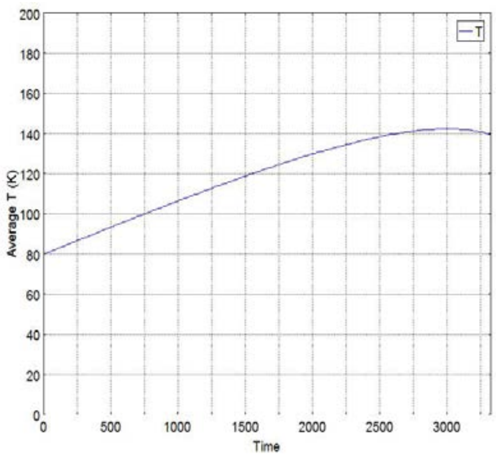
Wt% ENG	k @ 77K	k @ 160 K
0_#1	0.0309	0.044
0_#2	0.065	0.0829
0_#3	0.101	0.1178
0_GM#1	0.0432	0.0618
0_GM#2	0.033	0.0499
5_#1	0.114	0.1566
5_#2	0.1273	0.1841
10_#1	0.2729	0.4954
10_#2	0.2947	0.483

HSECoE Beyond 200K system exhibits radiative heat loss, which may skew data high

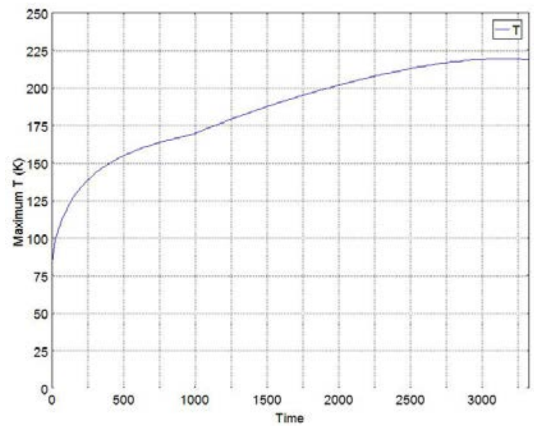
Temperature (K) distribution for the two cases

Case 1: Initial Pressure: 60 Bar

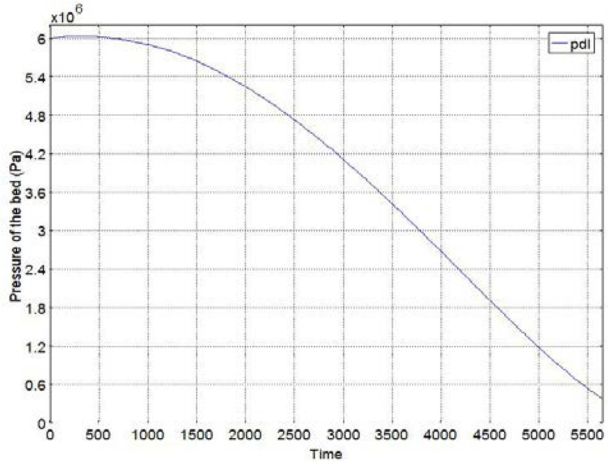
Avg T



Max T

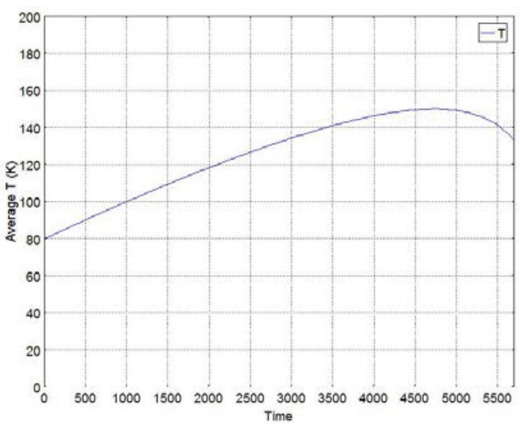


Pressure

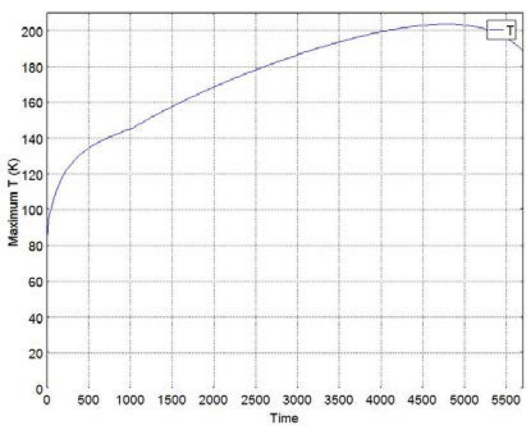


Case 2: Initial Pressure: 200 Bar

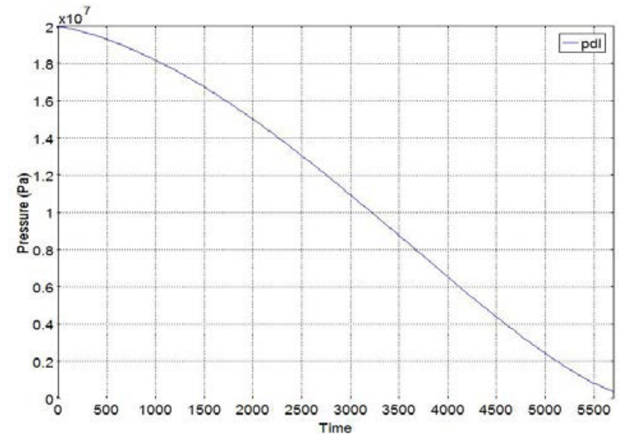
Avg T



Max T



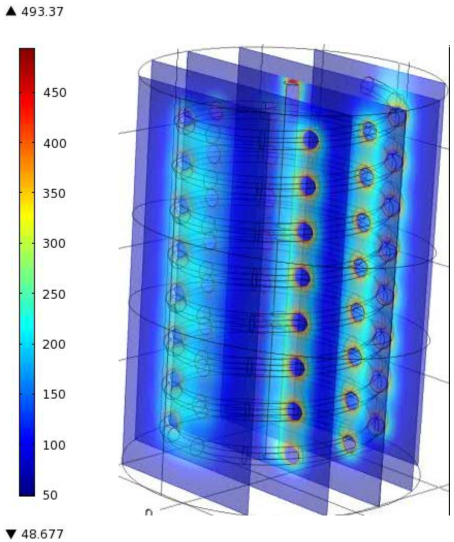
Pressure

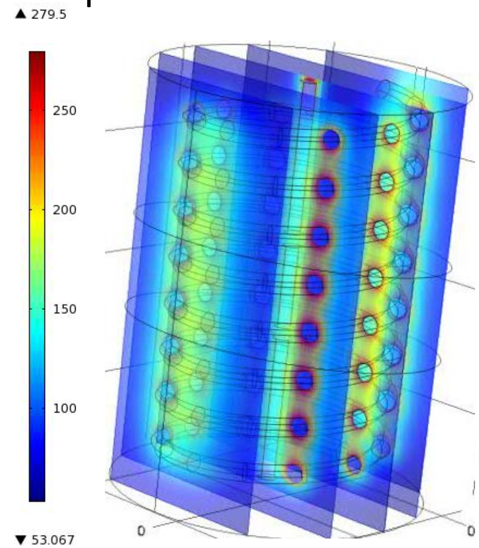


Final bed temperature for different thermal conductivities (W/m.K)

Initial bed pressure of 200 bars and initial bed temperature of 80 K

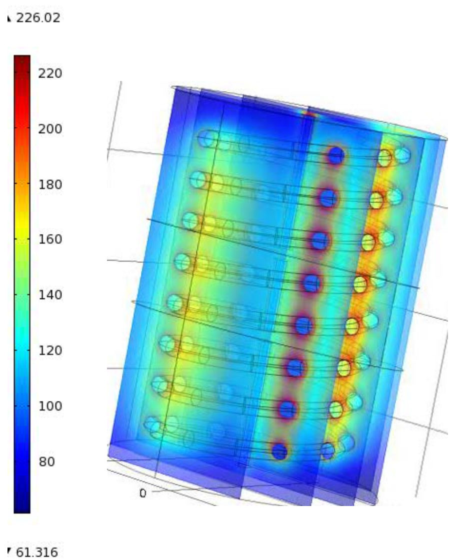
k = 0.1

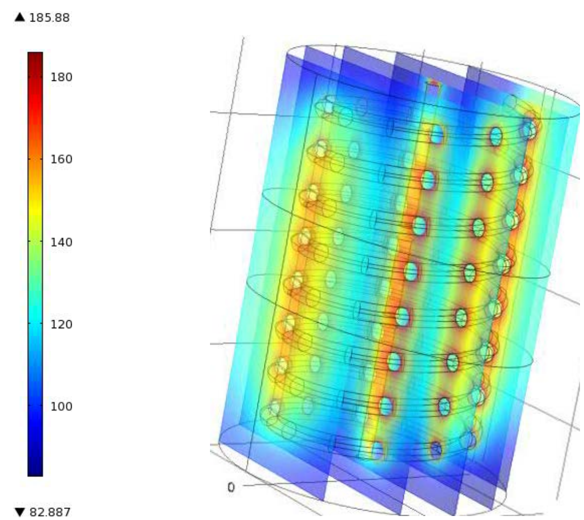




k = 0.2

k = 0.3

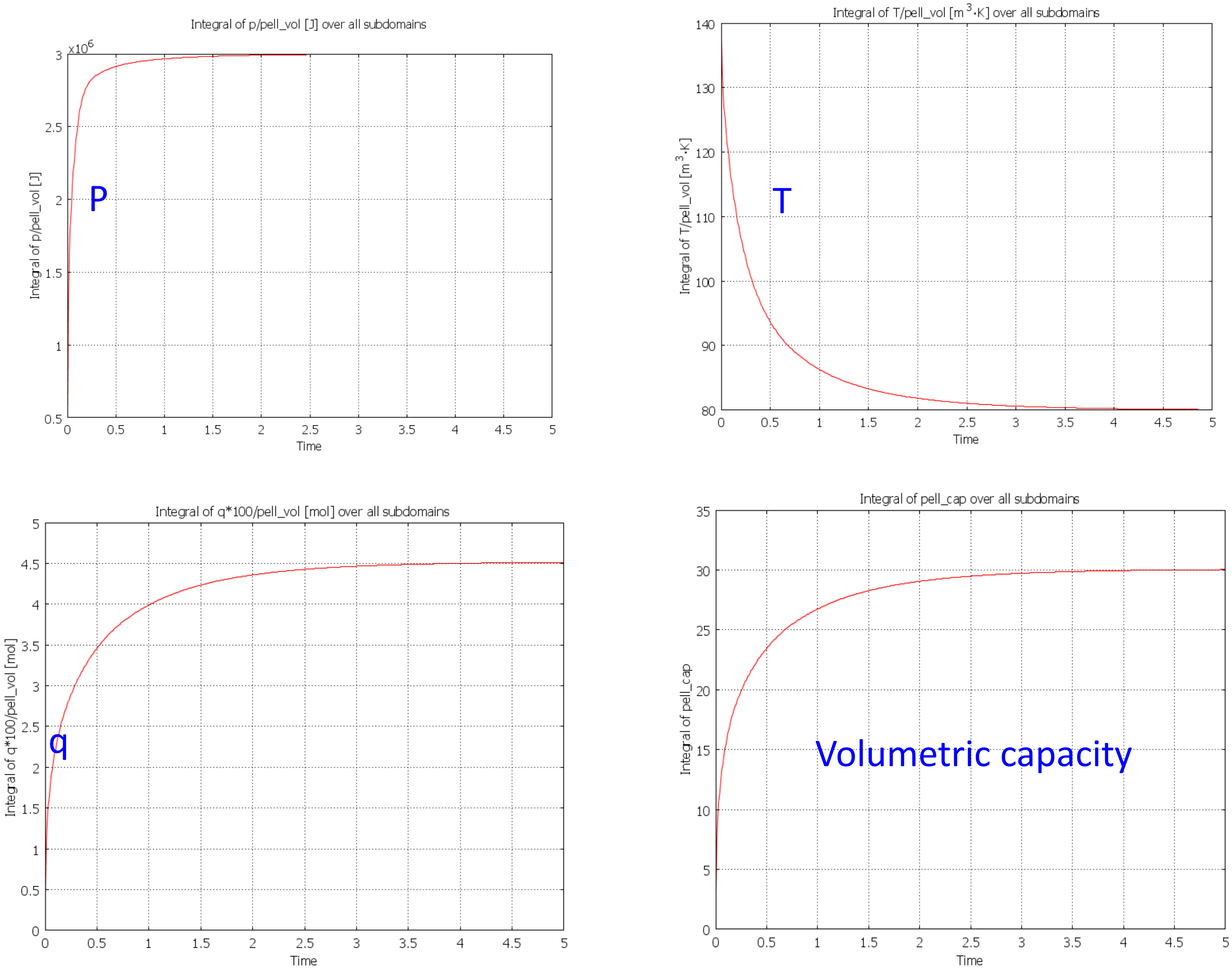




k = 0.5

HSECoE

Volume averaged evolutions - 3 mm pellet results



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