



Hydrogen Storage Engineering
CENTER OF EXCELLENCE

Chemical Hydrogen Rate Modeling, Validation, and System Demonstration

LANL Team

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LANL Project Overview

Timeline

- Project Start Date: Feb FY09
- Project End Date: FY15
- Percent Complete: 95%

Budget

- Total Funding: \$3.927k
 - 2014: \$150K
 - 2015: \$150K

Barriers

• Barriers Addressed

- System Weight and Volume*
- System Cost*
- Efficiency*
- Durability/Operability*
- Charging/Discharging Rates*
- Codes and Standards*
- Materials of Construction*
- Balance of Plant Components*
- Thermal Management*
- System Life-Cycle Assessments*
- By-Product/Spent Material Removal*

❖ Project Partners



Relevance

Develop novel high-pressure, low temperature thermal conductivity cell to measure thermal conductivities of engineered MOF-5 compacts under anticipated operating conditions

Measured material properties will feed directly into system level model

LANL Tasks and Results

(06/14 – 06/15)

- Task 1: Design and build high-pressure, low-temperature thermal conductivity cell for engineered MOF-5 Compacts
- Task 2: Measure thermal conductivities of engineered MOF-5 compacts at elevated hydrogen pressure and LN2 temperature
- Task 3: Interrogate MOF-5 compacts using x-ray tomography for gross structural defects and density distributions

❖ TASK 1: Design and Build High-Pressure, Low-Temperature Thermal Conductivity/Diffusivity Cell for Engineered MOF-5 Compacts

➤ Design Requirements

- Sample size: diameter < 5.00 cm, thickness < 2.7 cm
- Minimum Temperature = -196 °C
- Maximum Pressure = 100 bar

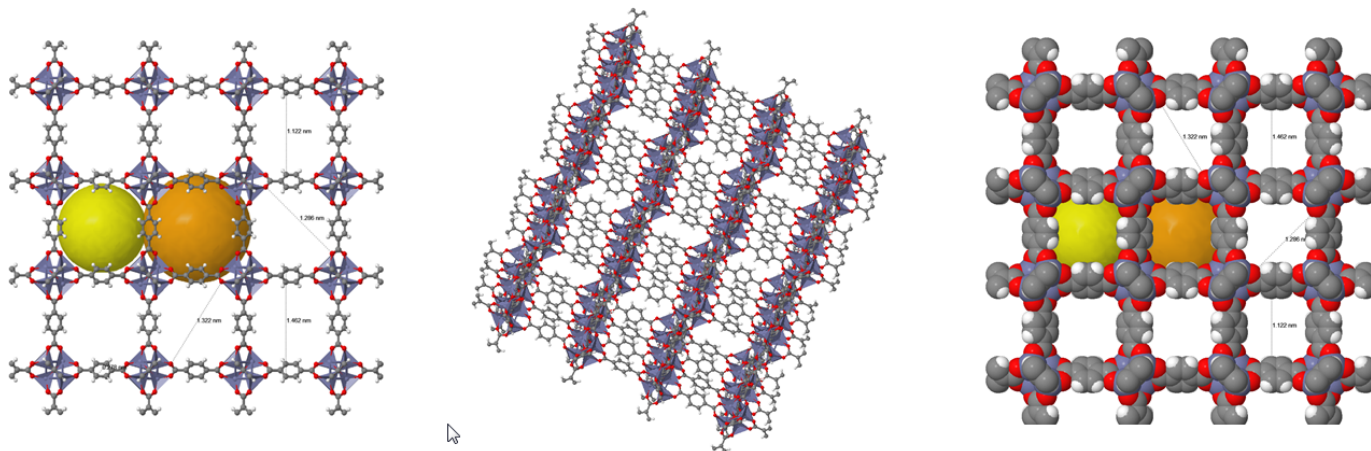
➔ Designed and built high-pressure ($P_{\max} = 100$ bar), Low-Temperature (-196 °C) sample holder for thermal conductivity measurements on engineered MOF-5 compacts



❖ TASK 2: Thermal Conductivity Measurements

Objective: Measure thermal conductivities of engineered MOF-5 compacts under anticipated operating conditions (i.e., high pressure, low temperature)—*data will directly feed into modeling framework*

MOF-5 (IRMOF-1)



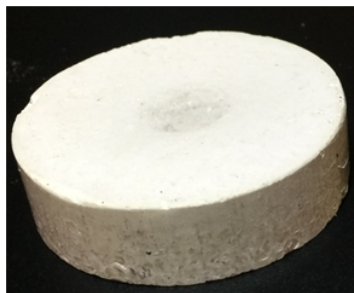
Images courtesy of University of Liverpool (www.chemtube3d/solidatate/MOF-MOF5.html)

MOF-5 (*aka* IRMOF-1) is a metal organic framework (MOF) formed from Zn_4O nodes with 1,4-benzodicyclohexane dicarboxylic acid struts between the nodes. The spheres represent the pore size that can be used for gas storage.

MOF-5 Synthesized by BASF Company



Engineered MOF-5 Compacts



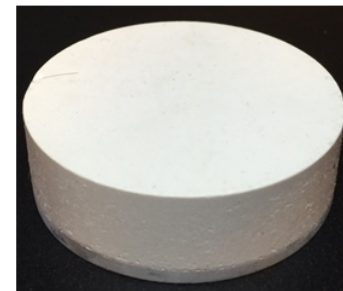
Neat MOF-5

Diameter = 5.00 cm
Height = 1.3–1.5 cm
Density = 0.350–0.575 g/cm³



MOF-5 with 10 wt. %ENG

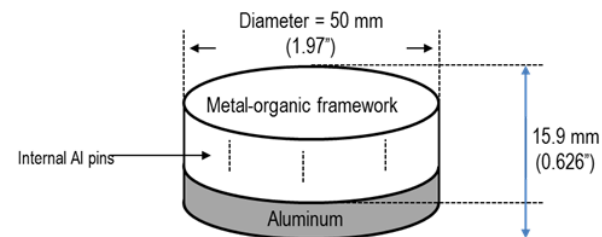
Diameter = 5.00 cm
Height = 1.3–1.5 cm
Density = 0.350–0.575 g/cm³



Neat MOF-5 with Al Pins

Diameter = 5.00 cm
Height = 1.59 cm
Density = 0.400 g/cm³

All Samples provided by Ford Motor Company



Ford: Engineered MOF-5 Compacts with Aluminum plate and Al pins
(received 24 April 2015, Microsoft Access Batch #: 13)

Thermal Conductivity Measurements

➤ Isotropic Measurements

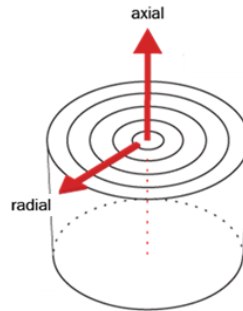
- Non-directional, bulk thermal conductivity/diffusivity measurements
- no *a priori* knowledge of density or volumetric heat capacity required for conductivity/diffusivity quantification

➤ Anisotropic Measurements

- Directional (axial, radial) thermal conductivity/diffusivity measurements
- *A priori* knowledge of density and volumetric heat capacity required for accurate conductivity/diffusivity quantification

$$\alpha_a = B$$

$$k_a = (\rho C_p) \cdot B$$



$$k_r = \frac{A^2}{(\rho C_p) \cdot B}$$

$$\alpha_r = \frac{A^2}{(\rho C_p)^2 \cdot B}$$



Accurate quantification of anisotropic thermal conductivities and diffusivities require known values of density and heat capacity at the measurement temperature

Ambient Isotropic Measurements (Room Temperature, Air)

MOF-5: Sample #1

- No ENG
- $\rho = 0.35 \text{ g/mL}$
- $h = 1.312 \text{ cm}$
- $D = 5.00 \text{ cm}$

MOF-5: Sample #2

- 10 wt. % ENG
- $\rho = 0.35 \text{ g/mL}$
- $h = 1.312 \text{ cm}$
- $D = 5.00 \text{ cm}$

MOF-5: Sample #3

- No ENG
- $\rho = 0.575 \text{ g/mL}$
- $h = 1.312 \text{ cm}$
- $D = 5.00 \text{ cm}$

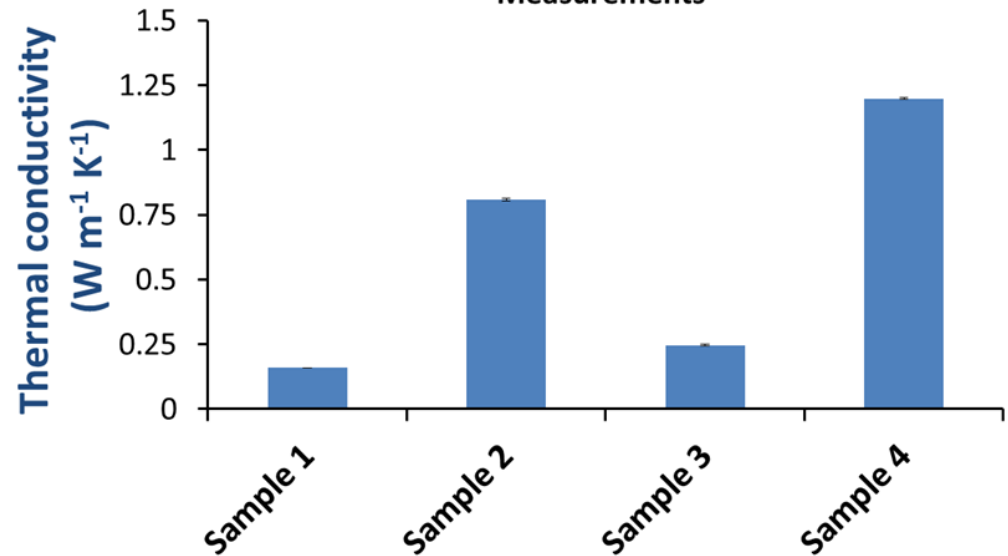
MOF-5: Sample #4

- 10 wt. % ENG
- $\rho = 0.529 \text{ g/mL}$
- $h = 1.370 \text{ cm}$
- $D = 5.00 \text{ cm}$

$$\bar{k}_{iso} \uparrow \quad \bar{w} \quad \rho_{MOF-5} \uparrow$$

$$\bar{k}_{iso} \uparrow \quad \bar{w} \quad wt.\% \text{ ENG} \uparrow$$

Thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$), Room Temperature Measurements



High-Pressure Hydrogen, Isotropic Measurements (Room Temperature)

MOF-5: Sample #3:

- No ENG
- $\rho = 0.575 \text{ g/mL}$
- $h = 1.312 \text{ cm}$
- $D = 5.00 \text{ cm}$

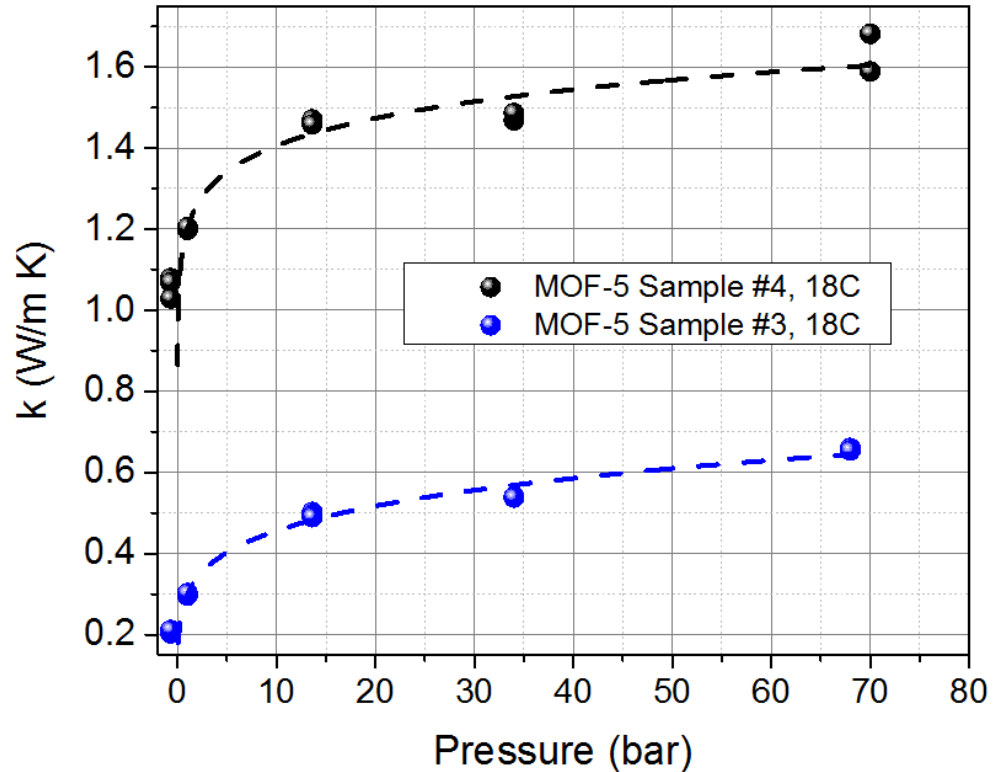
MOF-5: Sample #4

- 10 wt. % ENG
- $\rho = 0.529 \text{ g/mL}$
- $h = 1.370 \text{ cm}$
- $D = 5.00 \text{ cm}$

SUMMARY

$$\text{Sample 4 : } \bar{k}_{iso} \rightarrow 1.6 \frac{W}{m K} \Bigg|_{P \rightarrow 80 \text{ bar}}^{H_2}$$

$$\text{Sample 3 : } \bar{k}_{iso} \rightarrow 0.7 \frac{W}{m K} \Bigg|_{P \rightarrow 80 \text{ bar}}^{H_2}$$

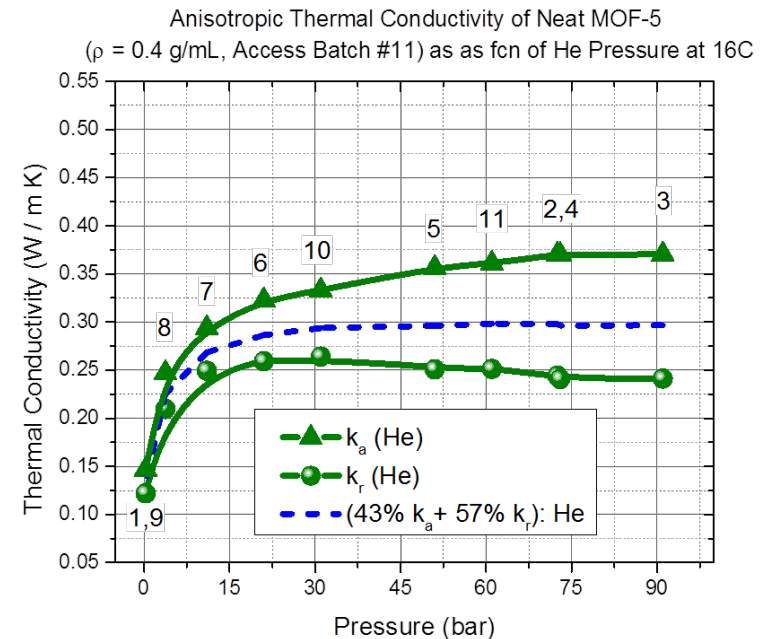
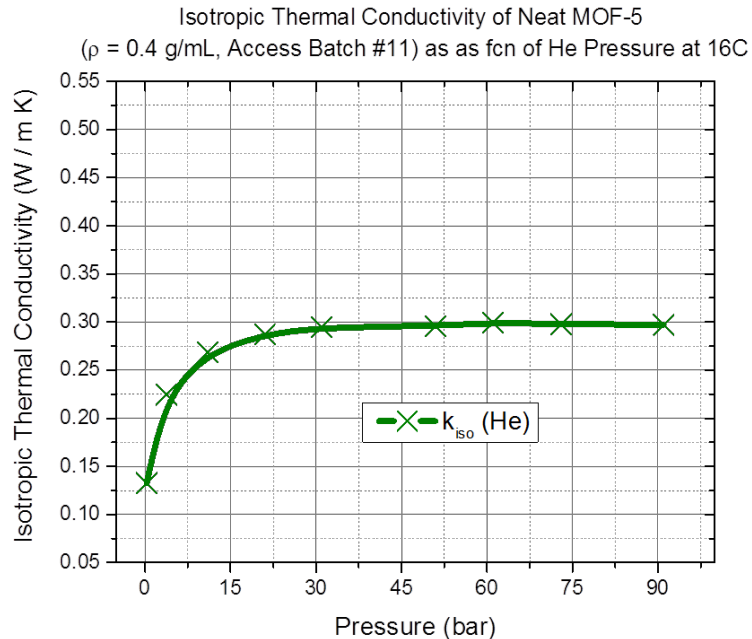


All samples were thermally treated in a UHP N_2 purged oven at $160 \text{ }^\circ\text{C}$ for a minimum of two days, followed by vacuum treatment for 12 hrs.

High Pressure Helium Measurements

MOF-5: Sample #11:

- No ENG
- $\rho = 0.4 \text{ g/mL}$
- $h = 1.312 \text{ cm}$
- $D = 5.00 \text{ cm}$



SUMMARY

- Bulk isotropic thermal conductivity increases from 0.12 W/m K (vacuum) to around 0.3 W/m K (30 bar He)
.....very little increase in thermal conductivity observed for pressures greater than 30 bar He
- Radial thermal conductivity was observed to be non-monotonic exhibiting a maximum in the pressure range of 15-30 bar He
- Axial thermal conductivity increased with increasing pressure throughout the pressure range investigated
- Bulk isotropic thermal conductivity dominated by radial component (57%)

k_a = axial thermal conductivity
 k_r = radial thermal conductivity

$$\bar{k}_{bulk, He} \approx 0.57 \bar{k}_{radial, He} + 0.43 \bar{k}_{axial, He}$$

High Pressure Hydrogen Measurements

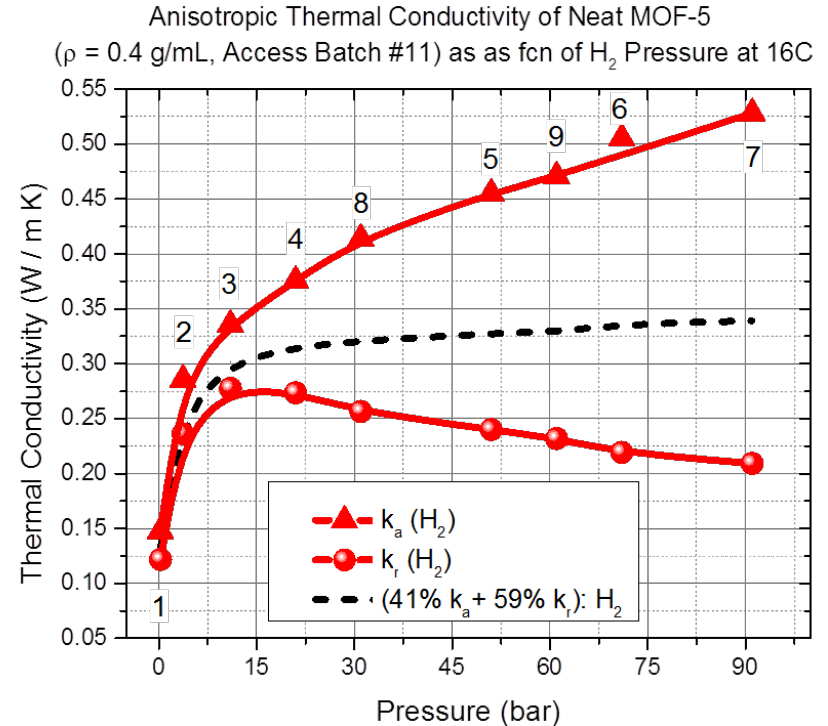
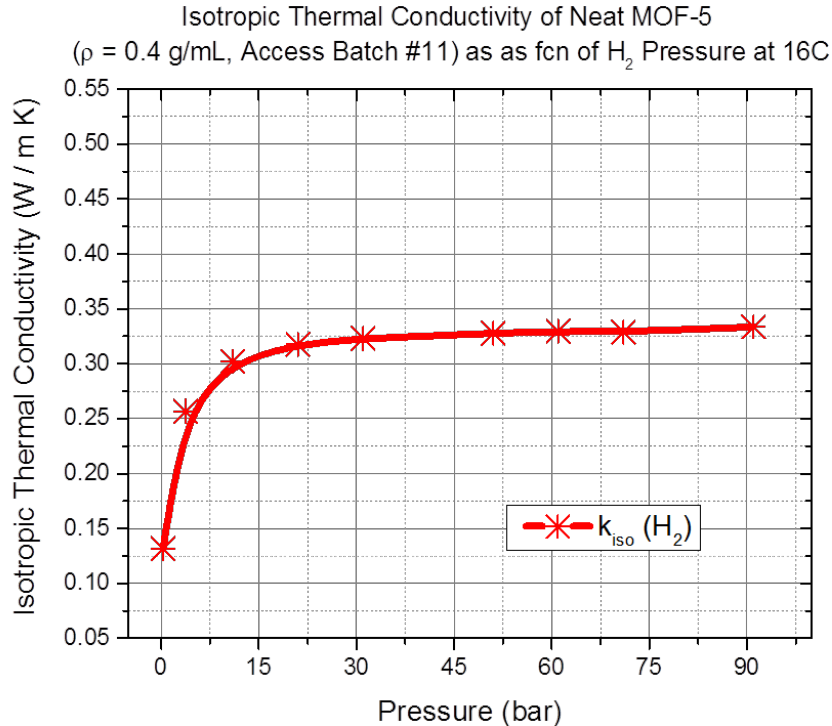
MOF-5: Sample #11

• No ENG

• $\rho = 0.4 \text{ g/mL}$

• $h = 1.312 \text{ cm}$

• $D = 5.00 \text{ cm}$



- All samples were thermally treated in a UHP N_2 purged oven at $160 \text{ }^\circ\text{C}$ for a minimum of two days, followed by a vacuum treatment of 12 hrs
- Average standard deviation for isotropic and anisotropic measurements with helium was Avg Stdev.s = $\pm 0.0135 \text{ W/m K}$ [Data set includes 137 measurements(average values plotted)]

k_a = axial thermal conductivity

k_r = radial thermal conductivity

High Pressure Hydrogen Measurements

SUMMARY

- Isotropic thermal conductivity increases from 0.12 W/m K (vacuum) to around 0.33 W/m K (30 bar H₂)
.....*very little increase in thermal conductivity observed for pressures greater than 30 bar H₂*
- Radial thermal conductivity was observed to be non-monotonic, exhibiting a maximum in the pressure range of 10-20 bar H₂
- Axial thermal conductivity increases with increasing pressure throughout the pressure range investigated
- Bulk isotropic thermal conductivity dominated by radial component (59%)

Neat MOF-5 (P = 0-100 bar H₂, 16 °C)

$$\bar{k}_{bulk, H_2} \approx 0.59 \bar{k}_{radial, H_2} + 0.41 \bar{k}_{axial, H_2}$$

Hydrogen-Helium Comparison

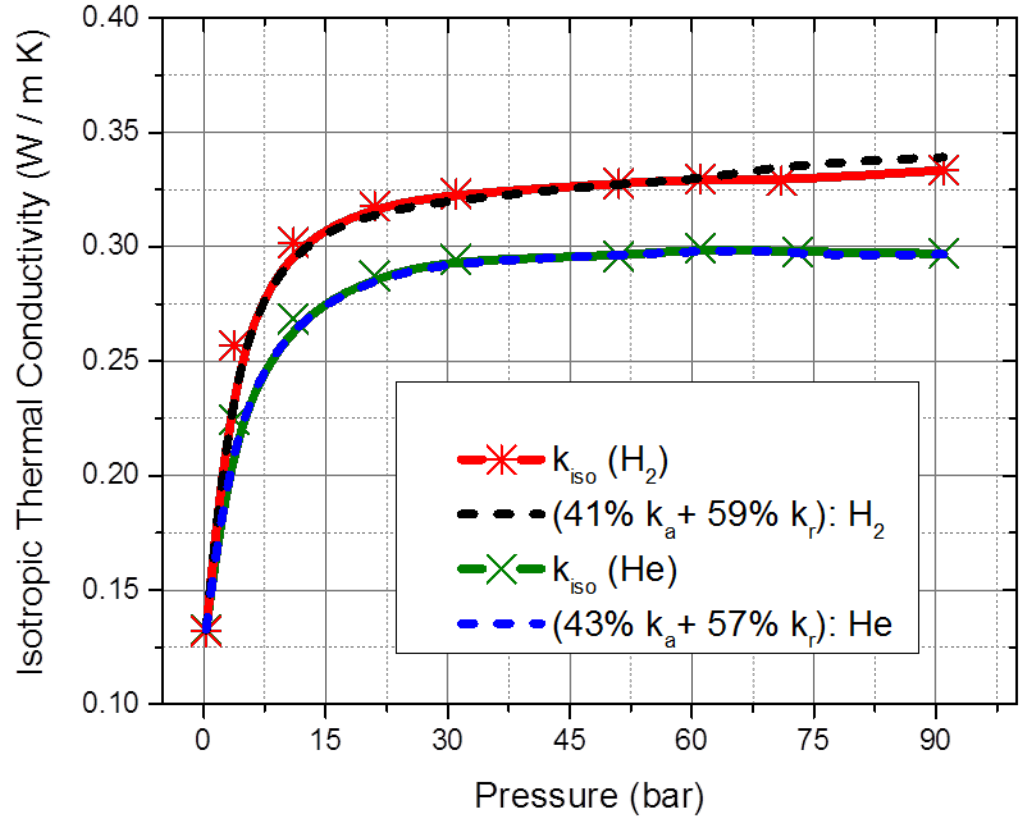
MOF-5: Sample #11

- No ENG
- $\rho = 0.4 \text{ g/mL}$
- $h = 1.312 \text{ cm}$
- $D = 5.00 \text{ cm}$

$$\bar{k}_{bulk, H_2} \rightarrow 0.33 \frac{W}{m K} \Big|_{P \rightarrow 100 \text{ bar}}^{H_2}$$

$$\bar{k}_{bulk, He} \rightarrow 0.30 \frac{W}{m K} \Big|_{P \rightarrow 100 \text{ bar}}^{He}$$

Isotropic Thermal Conductivity of Neat MOF-5 ($\rho = 0.4 \text{ g/mL}$, Access Batch #11) as a function of He and H₂ Pressure at 16 °C



- All samples were thermally treated in a UHP N₂ purged oven at 160 °C for a minimum of two days, followed by a vacuum treatment of 12 hrs
- Average standard deviation for isotropic and anisotropic measurements with helium was $Avg \text{ Stdev.s} = \pm 0.0135 \text{ W/m K}$ [Data set includes 137 measurements (average values plotted)]

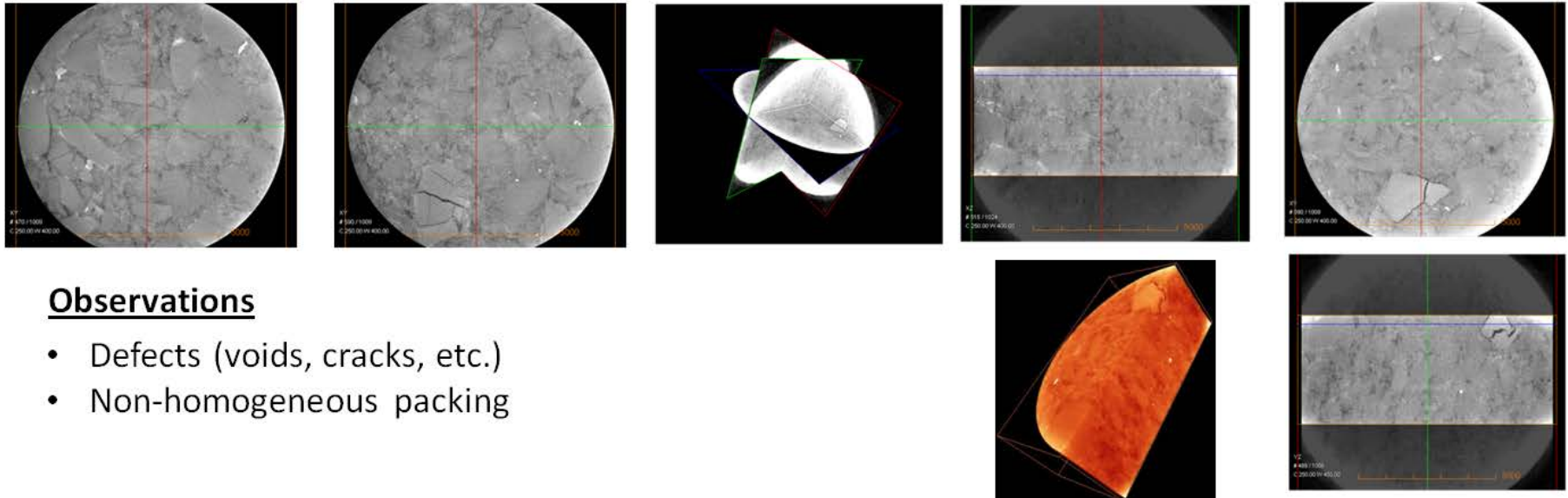
TASK 2 SUMMARY: Thermal Conductivity

- Thermal conductivity increases with increasing pressure and gas type
- Thermal conductivities measured with hydrogen demonstrated higher thermal conductivities than those measured with helium
- The ratio of thermal conductivities ($k_{\text{H}_2}/k_{\text{He}} = 1.10 @ 16^\circ\text{C}$) agrees well with the thermal conductivity ratio of reported values for gas phase hydrogen and helium ($k_{\text{H}_2}/k_{\text{He}} = 1.18 @ 25^\circ\text{C}$)
- Radial component dominates bulk isotropic thermal conductivity
- Bulk isotropic thermal conductivities are insensitive to pressures greater than 30 bar

❖ TASK 3: X-ray Tomography on MOF-5 Compacts

Objective: Probe density distribution of engineered MOF-5 compacts using x-ray tomography


MOF-5 (Sample #1): no ENG, $\rho = 0.35 \text{ g/mL}$, $h = 1.312 \text{ cm}$, $D = 5.00 \text{ cm}$

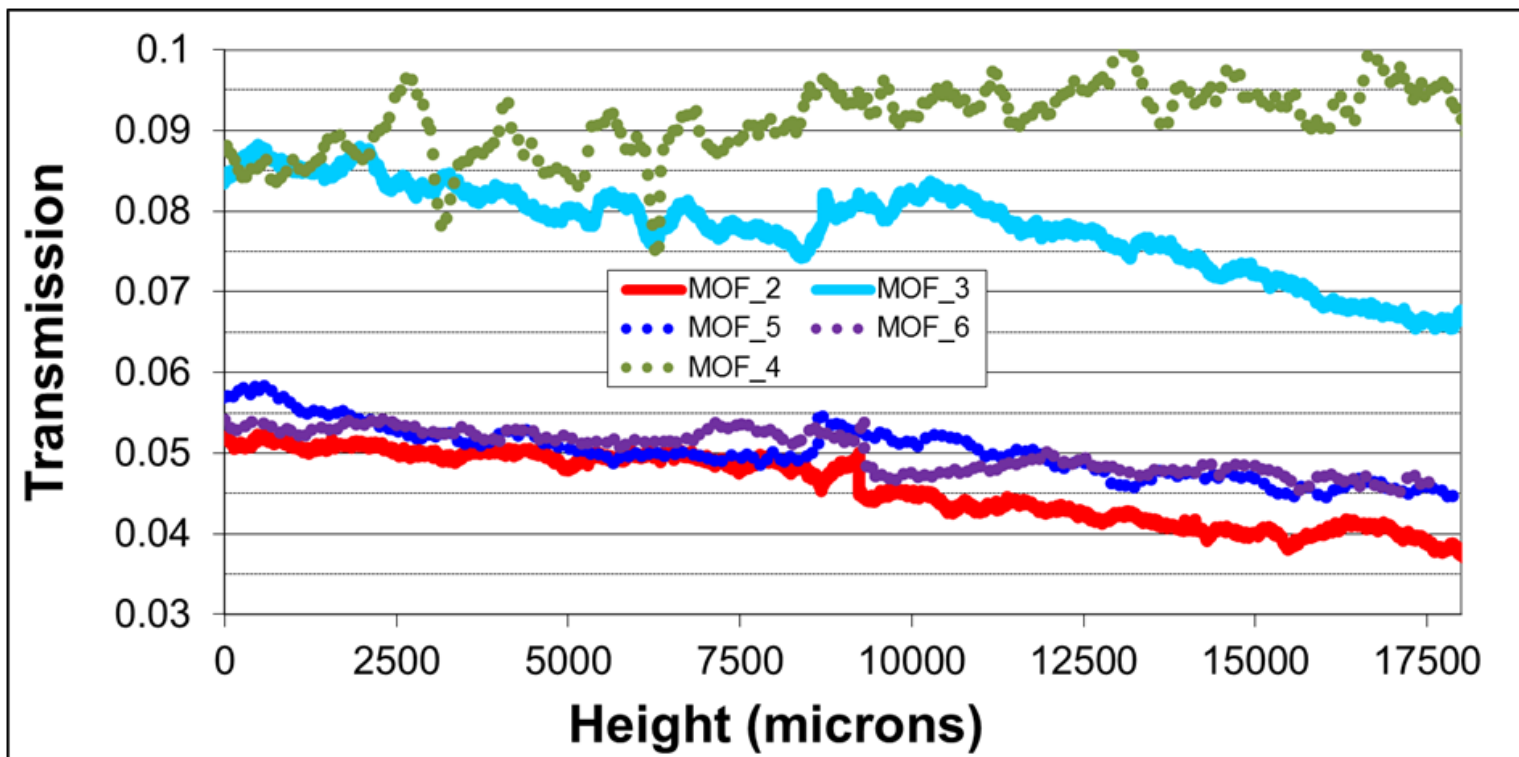


Observations

- Defects (voids, cracks, etc.)
- Non-homogeneous packing

MOF-5 Density Distribution

Less Dense

 More Dense



Sample #		Radius (cm)	Height (cm)	Mass (g)	Density (g/cc)
1	MOF5	0.635	2.338	1.133	0.3825
2	MOF5	0.635	2.228	1.402	0.4967
3	MOF5	0.635	2.262	1.059	0.3696
4	MOF5+10%ENG	0.635	2.232	1.462	0.5171
5	MOF5+10%ENG	0.635	1.970	1.311	0.5253
6	MOF5+10%ENG	0.635	2.384	1.065	0.3526

TASK 3 SUMMARY: X-Ray Tomography

- Axial density differences observed in MOF-5 compacts with x-ray tomography
- At identical densities, more carbon (ENG) leads to less attenuated signal
- All samples show non-homogeneous density distributions
.....i.e., non-uniform compaction along cylinder height
- Samples with decreased diameter would provide sharper images which would lead to greater discernment between samples

LANL Close-Out Work

- Collect heat capacity data for engineered MOF-5 compacts from $T = -196\text{ }^{\circ}\text{C} - +40\text{ }^{\circ}\text{C}$
- Recalculate anisotropic data at LN_2 temperature with temperature corrected heat capacity data
- Fit data to equations and publish results

Acknowledgements



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and Renewable Energy**

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is clean, abundant, reliable, and affordable

Ned Stetson and Jesse Adams