Hydrogen Storage Engineering
CENTER OF EXCELLENCE

Chemical Hydrogen Rate Modeling, Validation, and System Demonstration

LANL Team

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Project ID: st007_semelsberger_2015_P

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**
  - *A. System Weight and Volume*
  - *B. System Cost*
  - *C. Efficiency*
  - *D. Durability/Operability*
  - *E. Charging/Discharging Rates*
  - *F. Codes and Standards*
  - *G. Materials of Construction*
  - *H. Balance of Plant Components*
  - *J. Thermal Management*
  - *K. System Life-Cycle Assessments*
  - *S. 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

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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

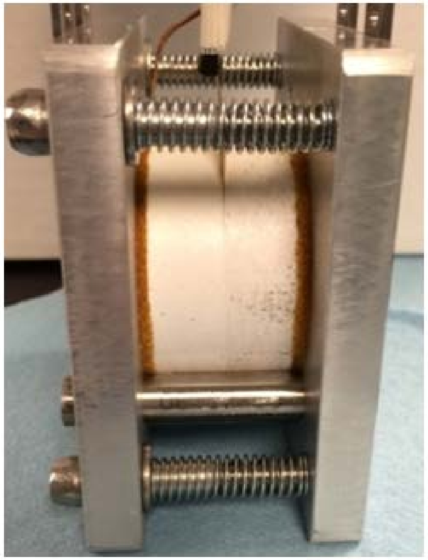
Task 3: Interrogate MOF-5 compacts using x-ray tomography for gross structural defects and density distributions

❖ 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



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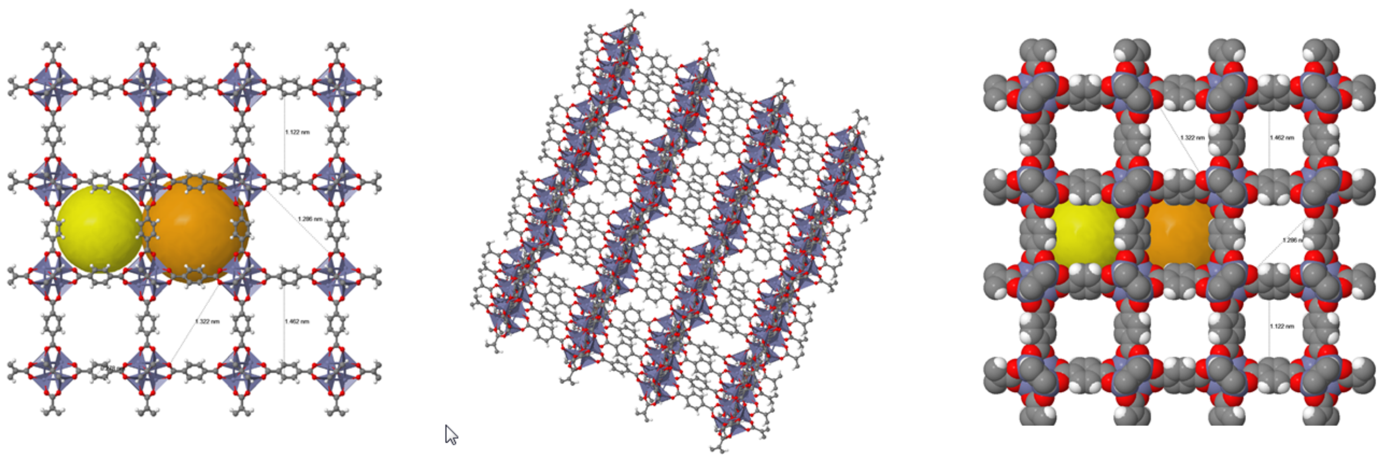
❖ TASK 2: Thermal Conductivity Measurements

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)

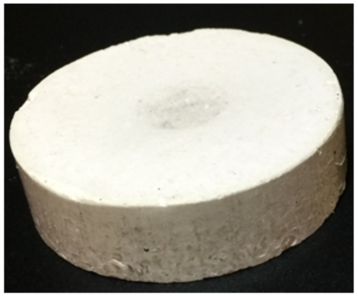


Images courtesy of University of Liverpool (www.chemtube3d/solidatate/MOF-MOF5.html)

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

MOF-5 Synthesized by BASF Company BASF The Chemical Company

Engineered MOF-5 Compacts



Neat MOF-5

Diameter = 5.00 cm
Height = 1.3–1.5 cm
Density = 0.350–0.575 g/cm^3

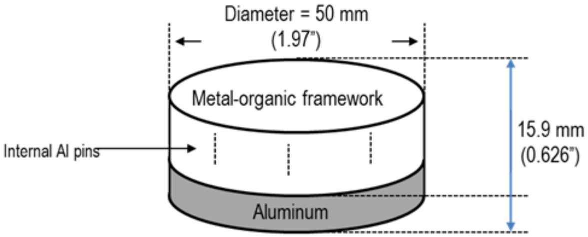
MOF-5 with 10 wt. %ENG

Diameter = 5.00 cm
Height = 1.3–1.5 cm
Density = 0.350–0.575 g/cm^3

Neat MOF-5 with Al Pins

Diameter = 5.00 cm
Height = 1.59 cm
Density = 0.400 g/cm^3

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)

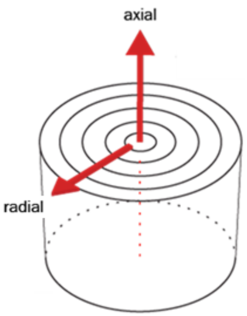
Thermal Conductivity Measurements

- 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

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Ambient Isotropic Measurements (Room Temperature, Air)

MOF-5: Sample #1
- No ENG
- ρ = 0.35 g/mL
- h = 1.312 cm
- D = 5.00 cm

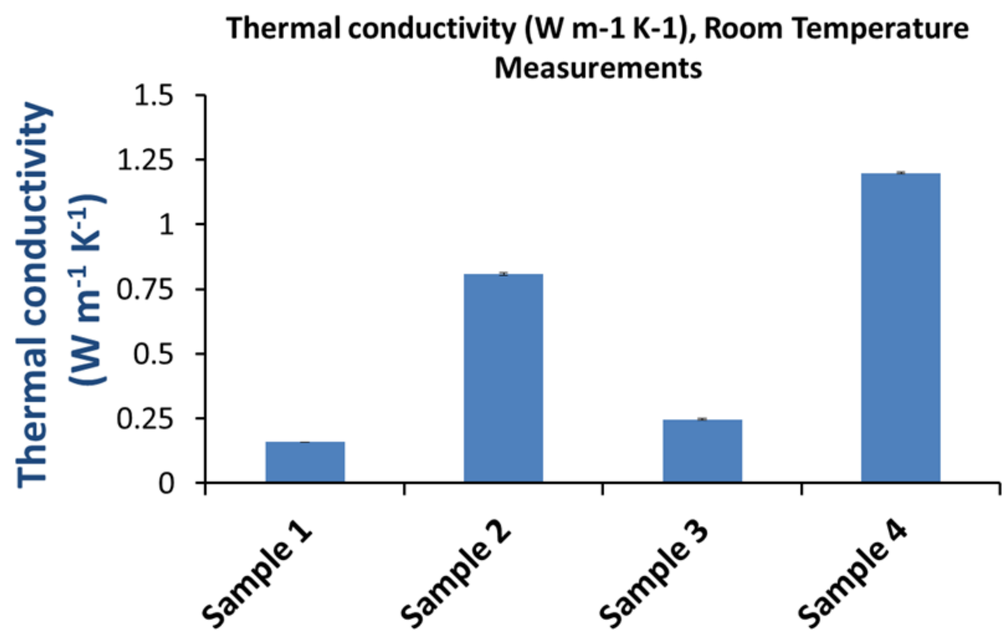
MOF-5: Sample #2
- 10 wt. % ENG
- ρ = 0.35 g/mL
- h = 1.312 cm
- D = 5.00 cm

MOF-5: Sample #3
- No ENG
- ρ = 0.575 g/mL
- h = 1.312 cm
- D = 5.00 cm

MOF-5: Sample #4
- 10 wt. % ENG
- ρ = 0.529 g/mL
- h = 1.370 cm
- D = 5.00 cm

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

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



High-Pressure Hydrogen, Isotropic Measurements (Room Temperature)

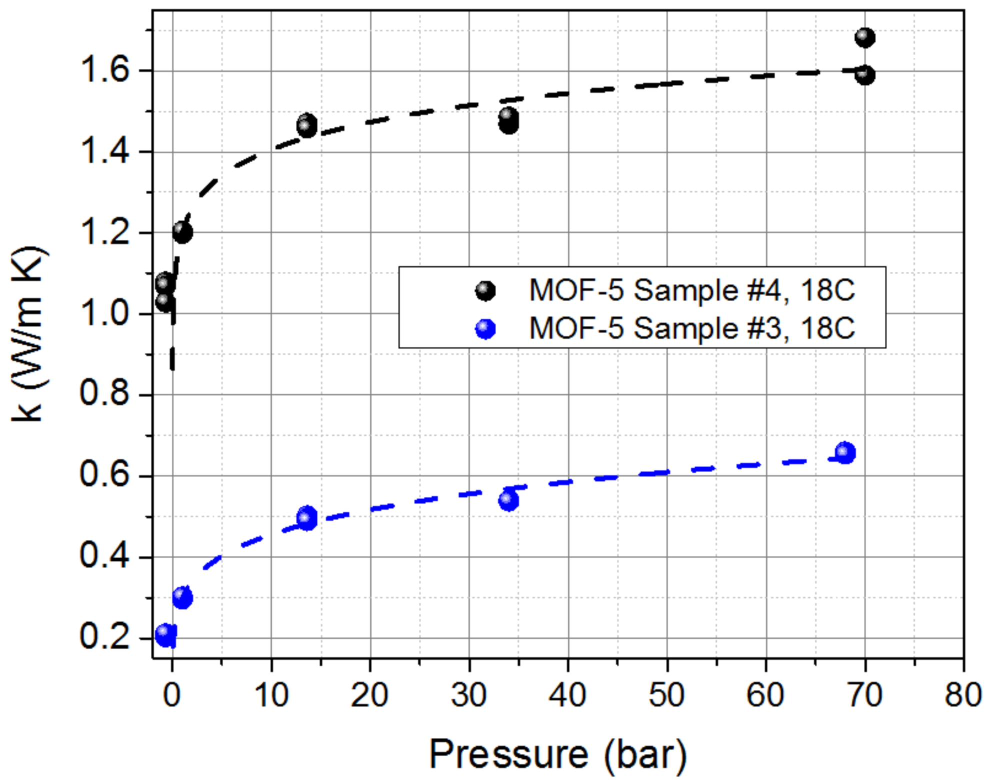
MOF-5: Sample #3:
- No ENG
- ρ = 0.575 g/mL
- h = 1.312 cm
- D = 5.00 cm

MOF-5: Sample #4
- 10 wt. % ENG
- ρ = 0.529 g/mL
- h = 1.370 cm
- D = 5.00 cm

SUMMARY

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

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

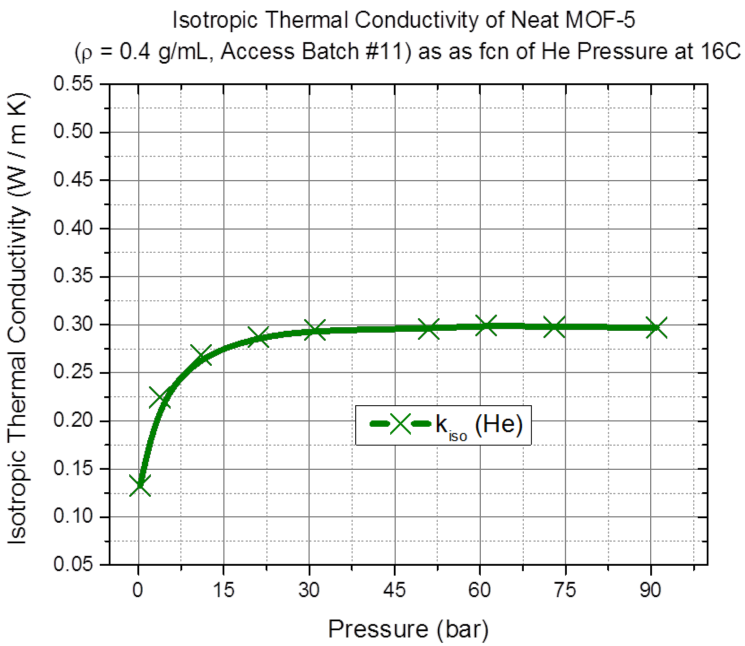


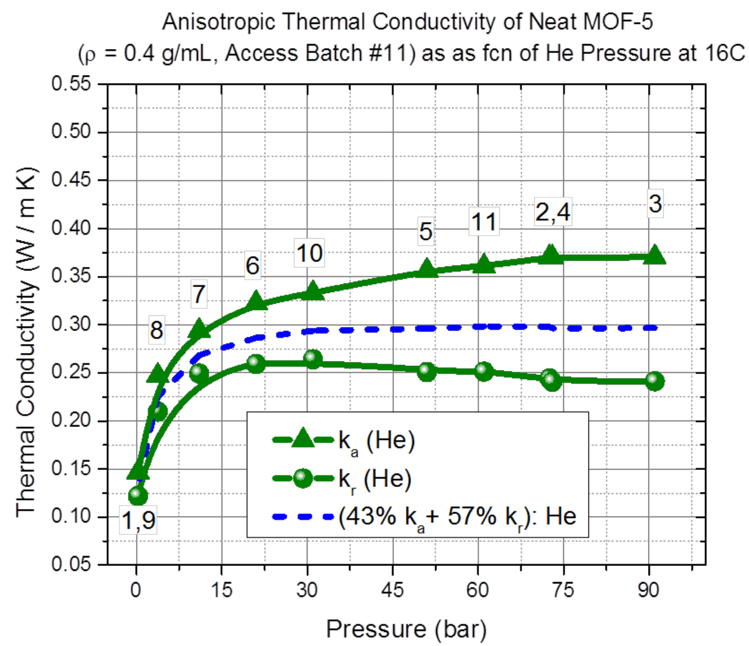
All samples were thermally treated in a UHP N_2 purged oven at 160 °C for a minimum of two days, followed by vacuum treatment for 12 hrs

High Pressure Helium Measurements

MOF-5: Sample #11:

- No ENG
- ρ = 0.4 g/mL
- h = 1.312 cm
- D = 5.00 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*

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

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- *All samples were thermally treated in a UHP N_2 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 Stdev.s = ±0.0135 W/m K [Data set includes 137 measurements(average values plotted)]*

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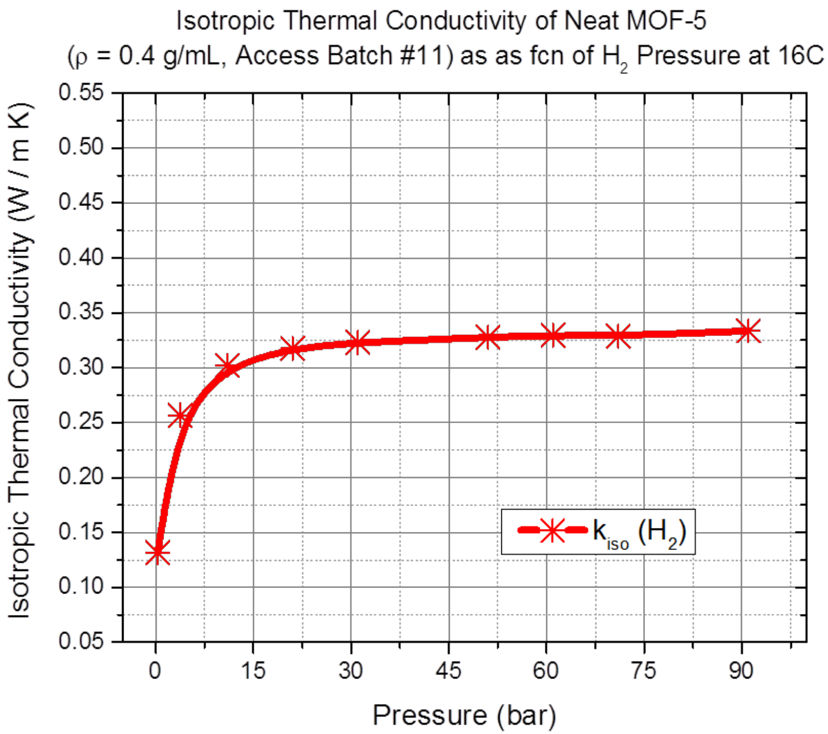
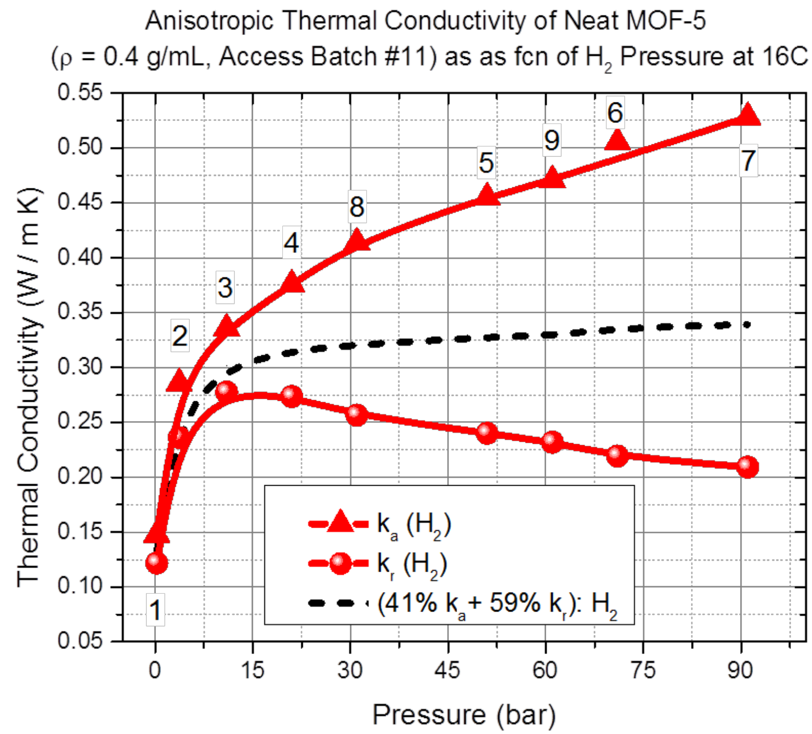
High Pressure Hydrogen Measurements

MOF-5: Sample #11

- No ENG
- ρ = 0.4 g/mL
- h = 1.312 cm
- D = 5.00 cm





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k_a = *axial thermal conductivity*

k_r = *radial thermal conductivity*

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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 H_2)
  .....very little increase in thermal conductivity observed for pressures greater than 30 bar H_2
- Radial thermal conductivity was observed to be non-monotonic, exhibiting a maximum in the pressure range of 10-20 bar H_2
- 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 H_2, 16 °C)

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

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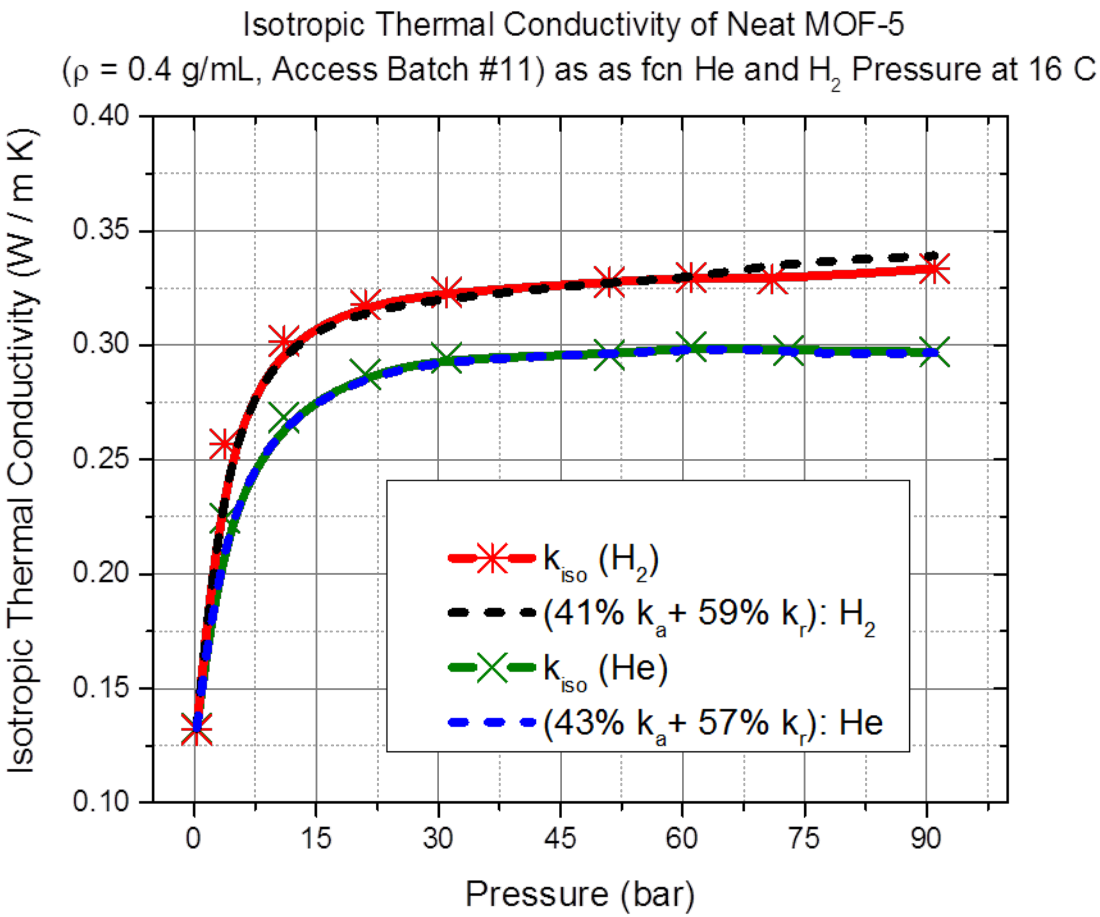
Hydrogen-Helium Comparison

MOF-5: Sample #11

- No ENG
- h = 1.312 cm
- ρ = 0.4 g/mL
- D = 5.00 cm

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

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



- *All samples were thermally treated in a UHP N_2 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 Stdev.s = ±0.0135 W/m K [Data set includes 137 measurements(average values plotted)]*

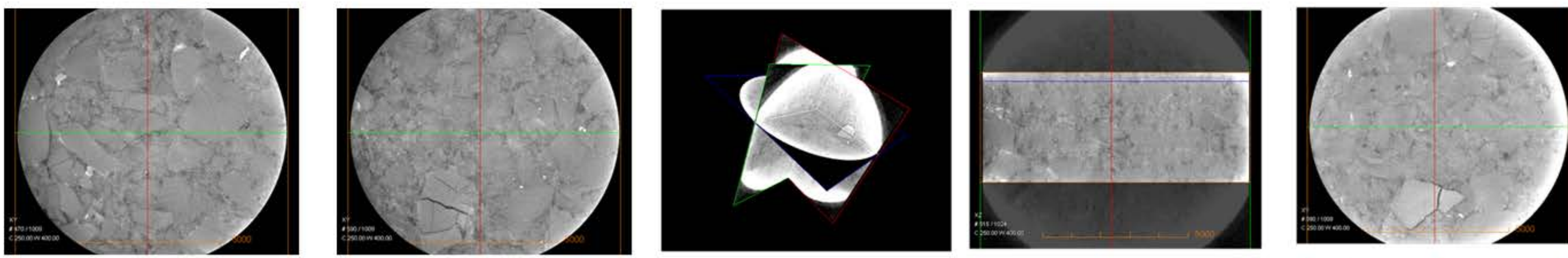
TASK 2 SUMMARY: Thermal Conductivity

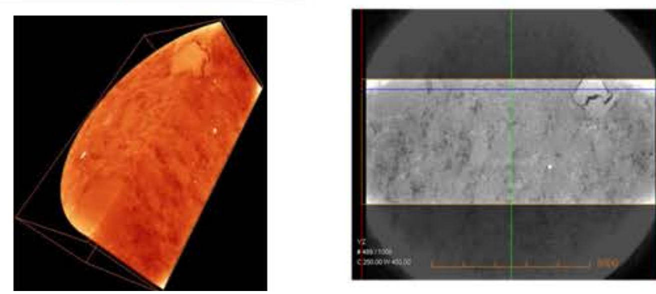
- Thermal conductivity increases with increasing pressure and gas type
- Thermal conductivities measured with hydrogen demonstrated higher thermal conductivities than those measured with helium
- The ratio of thermal conductivities (k_{H2}/k_{He} = 1.10 @ 16°C) agrees well with the thermal conductivity ratio of reported values for gas phase hydrogen and helium (k_{H2}/k_{He} = 1.18 @ 25°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, $\rho = 0.35$ g/mL, h = 1.312 cm, D = 5.00 cm





<u>Observations</u>

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

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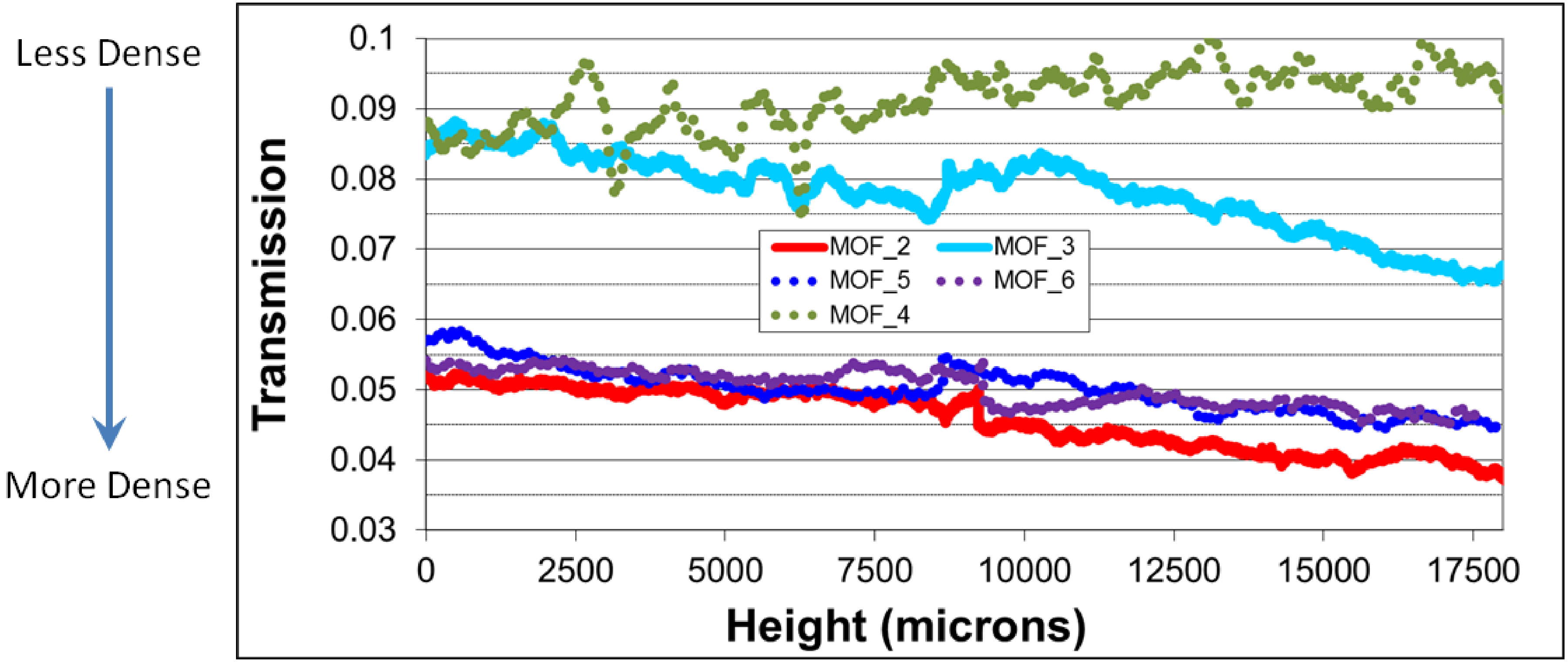
MOF-5 Density Distribution



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 °C – +40 °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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Bringing you a prosperous future where energy is clean, abundant, reliable, and affordable

Ned Stetson and Jesse Adams