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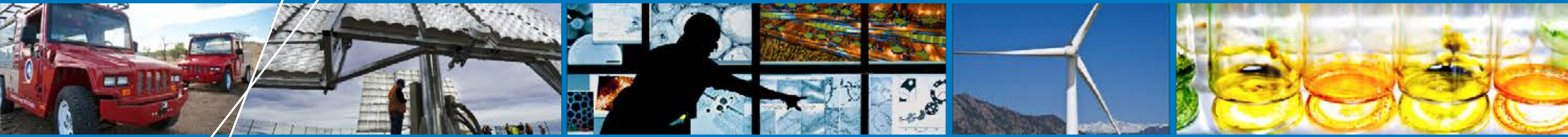
Hydrogen Sorbent Measurement Qualification and Characterization



Philip Parilla
National Renewable Energy Laboratory

June 8, 2017

ST014

This presentation does not contain any proprietary, confidential, or otherwise restricted information.

Overview

HySCORE

Timeline*

Project Start: 10/1/2015
End: Project continuation determined by DOE. Currently scheduled through 9/30/18
(*previously a component of NREL's materials development program and supported annually since 2006)

Budget

Total Team Budget: (HySCORE): $8.2M
Federal Share:
NREL: $2.6M
LBNL: $2.4M
PNNL: $2.4M
NIST: $0.8M
NREL Funds Spent: ~$1.2M
(Estimated as of 3/31/17)

Barriers addressed

General:
- A. Cost, B. Weight and Volume, C. Efficiency,
- E. Refueling Time

Reversible Solid-State Material:
- M. Hydrogen Capacity and Reversibility
- N. Understanding of Hydrogen Physi- and Chemisorption
- O. Test Protocols and Evaluation Facilities

Partners/Collaborators

NIST – Craig Brown, Terry Udovic
PNNL – Tom Autrey, Mark Bowden
LBNL – Jeff Long, Martin Head-Gordon
HyMARC – SNL, LLNL, LBNL
LANL, USA – Troy Semelsberger
H2Technology Consulting, USA – Karl Gross
H_2ST^2, USA – Hydrogen Storage Tech Team
IEA-HIA Task 32 Participants
Thesis Corporation, Justin Lee
Univ. Wyoming, Bruce Parkinson

Relevance: Project Objectives

HySCORE

An NREL-led National Laboratory collaboration and synergistic research effort between:

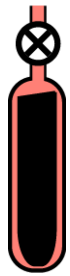
NREL, LBNL, PNNL, NIST

- To *Develop* and *Enhance* Hydrogen Storage Core Capabilities, i.e. Characterization Techniques
- To *Validate* claims, concepts, and theories of hydrogen storage materials
- To *Double* hydrogen storage energy density (increase from 25g/L to 50 g/L)

Relevance/Approach: Volumetric Capacity Measurements

Relevance:

- **Volumetric capacity metrics are critical**
  - Must be uniform, consistent, and unambiguous
  - Established protocol for determining and reporting
- **Goal: double the capacity over 700-bar tanks**
  - Move towards ~50 g-H_2/L.



Approach:

Lead: Katie Hurst

- **Compare volumetric capacity (VC) measurements with "round robin"**
  - Organize and manage an inter-laboratory comparison (ILC) on the hydrogen capacity measurements of 2 standard samples.
  - Analyze the data to discern sources leading to variations of the results, common errors, and misunderstandings.
  - Report on these findings to the scientific community.
  - Based on previously established protocols.(Parilla, et al, Appl. Phys. A, 2016).

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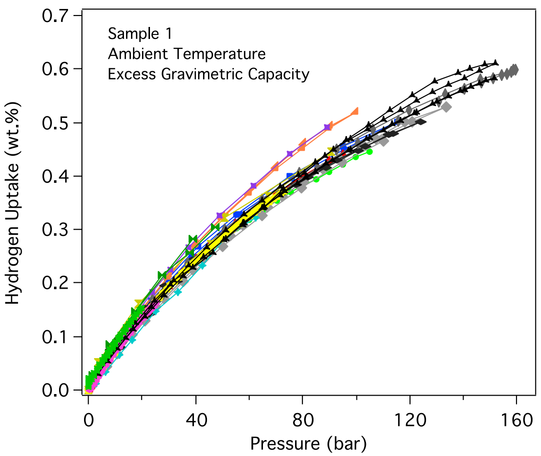
Accomplishment: ILC Data Gathering Finished

- **Milestone Completed**
  - Submit full report to DOE on results of volumetric capacity of at least 5-laboratory inter-lab comparison.

- **Goal: Study and Understand Variability in Volumetric Capacity Determinations**
  - Two sample types: pellets and powder
  - Two targeted temperatures: "Ambient" and liquid nitrogen
  - Includes determinations of 3 capacities
  - Builds on smaller previous study focused on excess gravimetric capacity

    (K.E. Hurst, P.A. Parilla, K.J. O'Neill, T. Gennett Appl. Phys. A 122; 42, 2016.)
  - 5 grams of each material sent to participants in February 2016
  - Detailed instructions were provided to each participant including:
    - degas conditions for each sample
    - measurement methods for the volume of the sample
    - recommended calculations for the capacities
  - 15 confirmed participants (including NREL)
  - USA, International (Europe, Asia), IEA-HIA
  - academia, national laboratory, industry



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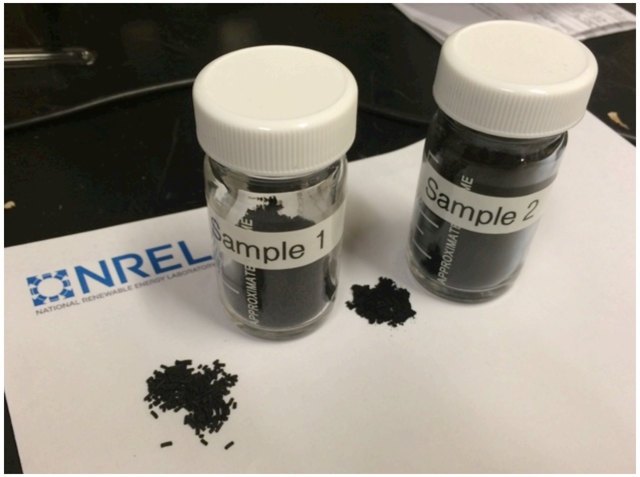
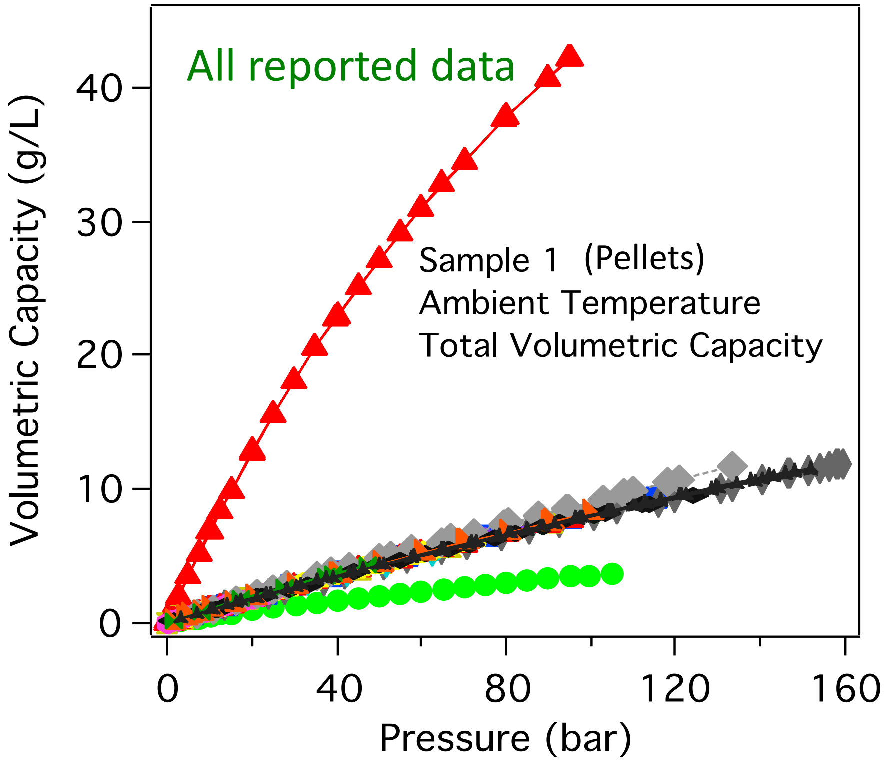
Accomplishment: ILC Data Analysis

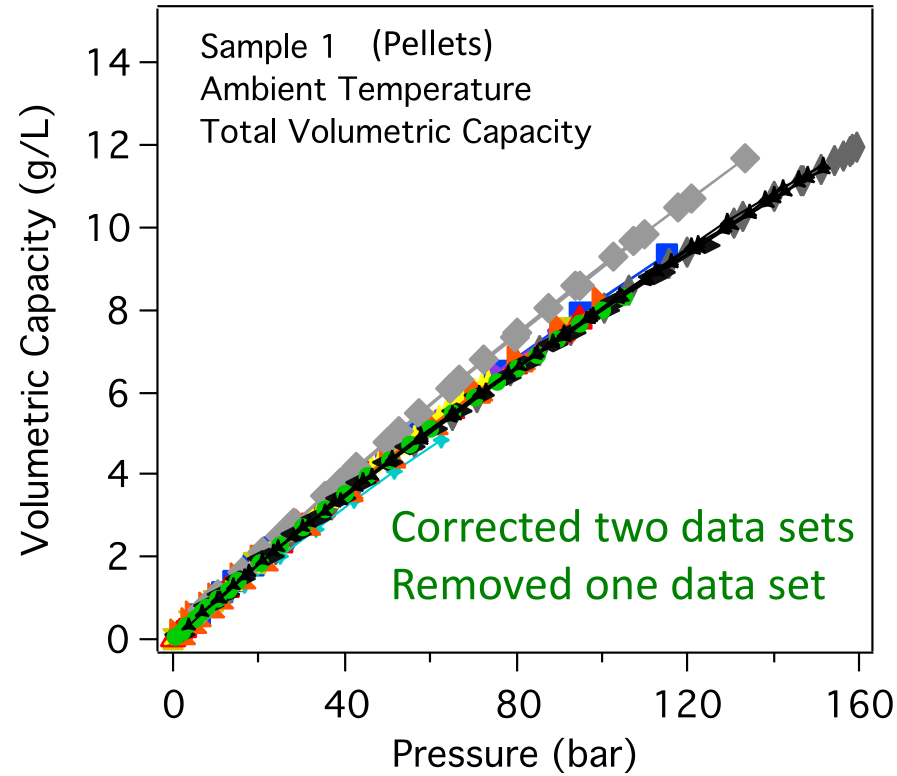


- **Data Received:**
  - 14 data sets at ambient conditions Sample 1
  - 13 data sets at ambient conditions Sample 2
  - 10 data sets at liquid N_2 data Sample 1
  - 9 data sets at liquid N_2 data Sample 2
  - Data from 13 participation laboratories including:
    - 1 industry, 8 government, 4 academic labs.
    - 9 US, 4 international institutions
    - 12 manometric instruments, 1 gravimetric instrument
    - Participants will be notified of their results
- **Data Analysis:**
  - Data received was inspected and investigated for gross errors
  - Gross errors from misunderstandings, experimental failures, or miscalculations were revisited and corrected by participants
  - Isotherms were interpolated to a common set of pressures to allow statistical analysis
  - Detailed analyses are in the initial stages; correlations will be investigated, conclusions drawn and results will be published

Accomplishment: Finding Gross Errors

Example: Sample 1 (Pellets) Total Volumetric Capacity





- One participant corrected free-gas density to fix data.
- One participant fixed incorrect normalization of packing volume.
- One participant had outlier packing density and was removed.

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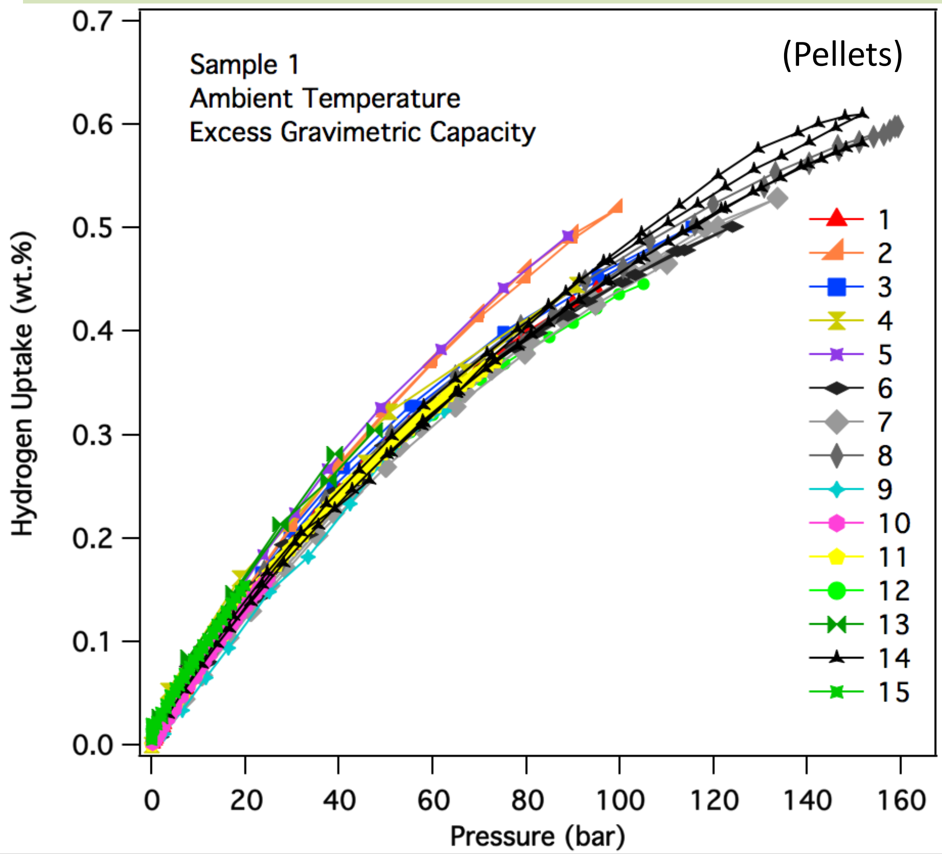
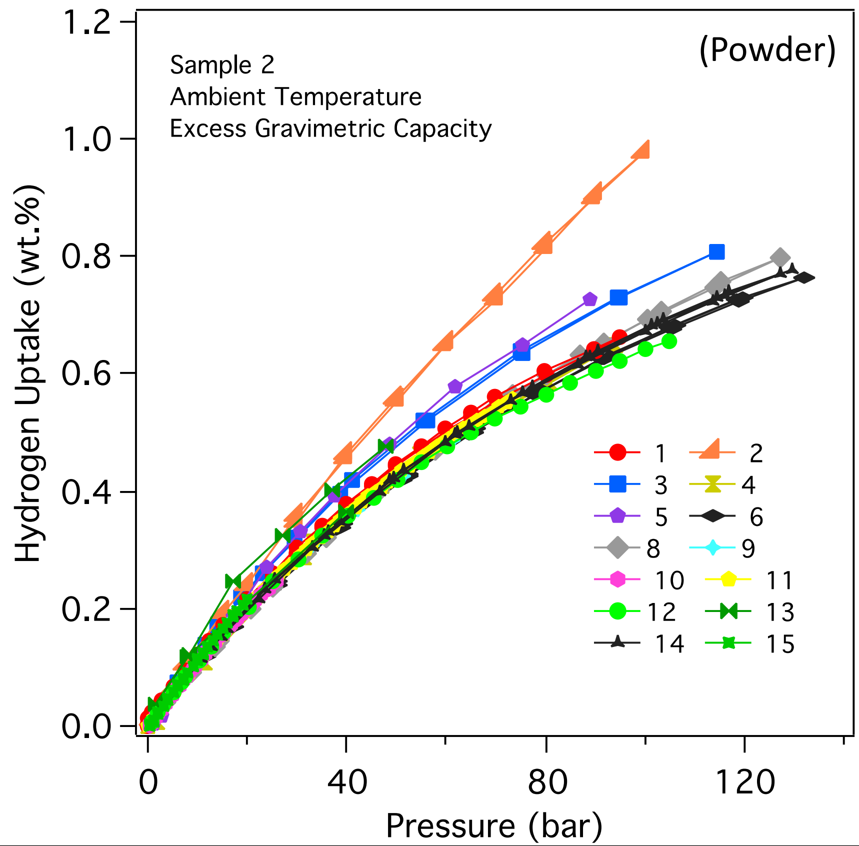
Accomplishment: Data! (Lots of data)

- **Approach for study with regard to capacities**
  - Excess Gravimetric – Simplest data acquisition and analysis
  - Excess Volumetric – Adds complexity of packing volume
  - Total Volumetric – Has complexities of both packing volume and free-gas contribution





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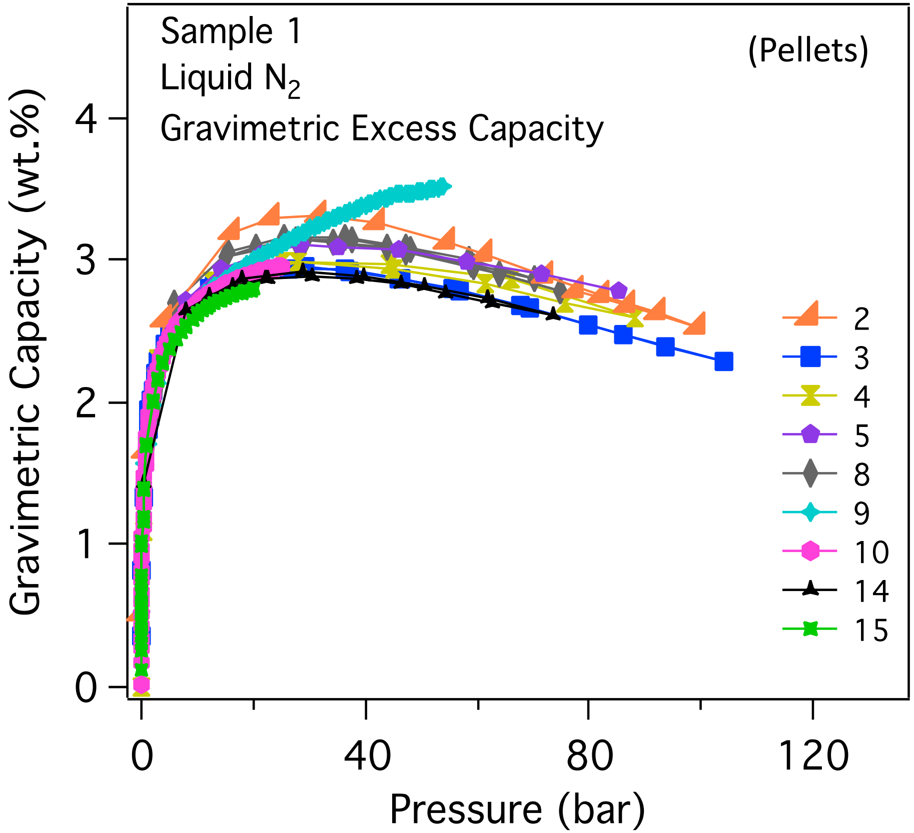
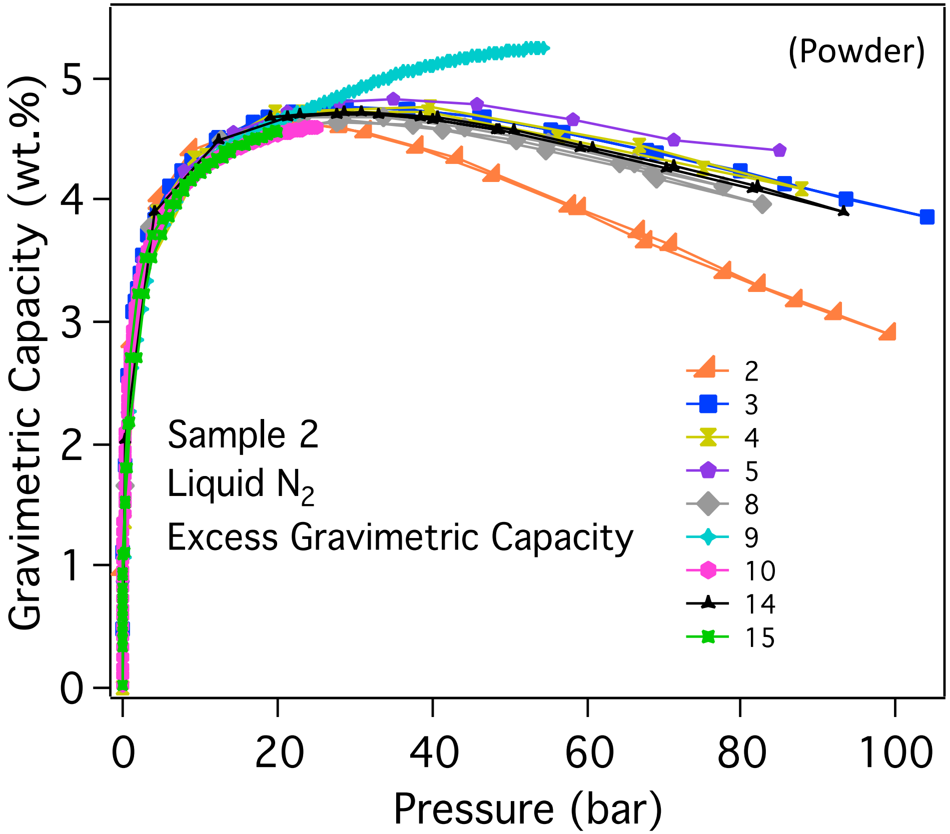
Accomplishment: More Data

- **Approach for study with regard to temperatures**
  - Ambient – Manometric: simplest mole-balance; Gravimetric: simplest buoyancy
  - Liquid Nitrogen – Manometric: more complicated mole balance
  - Liquid Nitrogen – Gravimetric: more complicated temperature control & buoyancy





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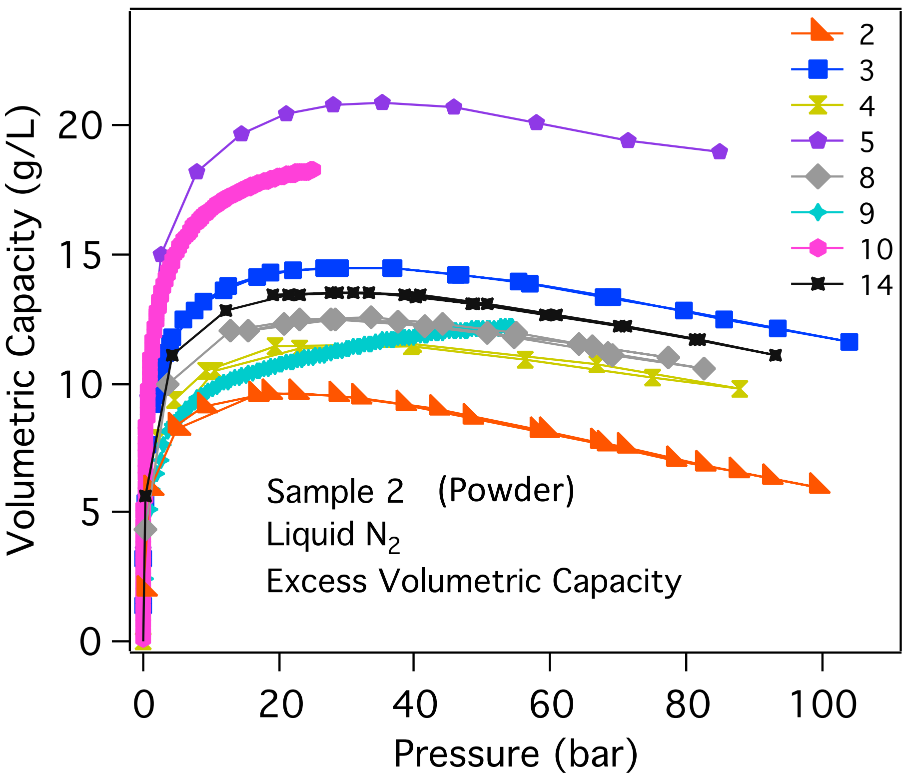
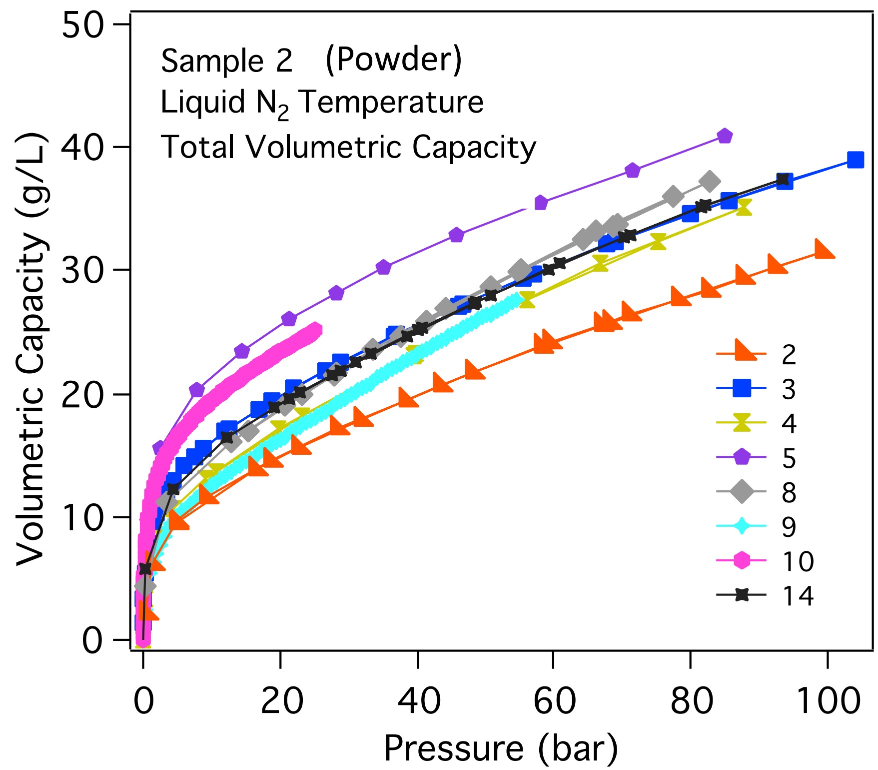
Example: Sample 2, Liquid N_2, Variations Do Exist

Excess Volumetric Capacity



Total Volumetric Capacity



- All data is currently included in analysis of the both volumetric capacities.
- No obvious errors were identified for data discrepancies.
- Some expected variation in data due to different packing volumes.

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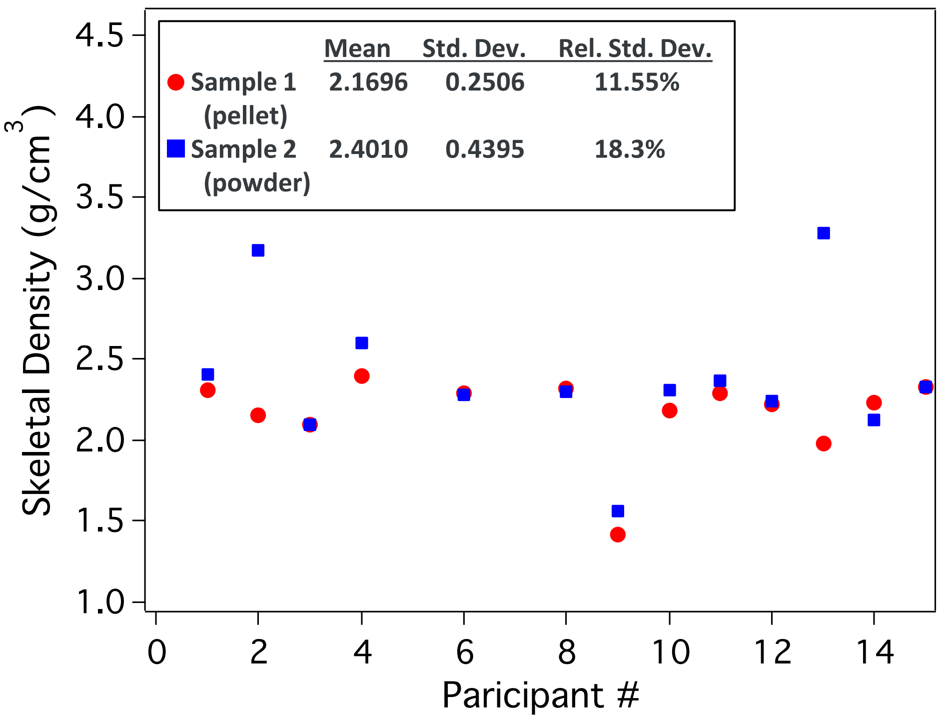
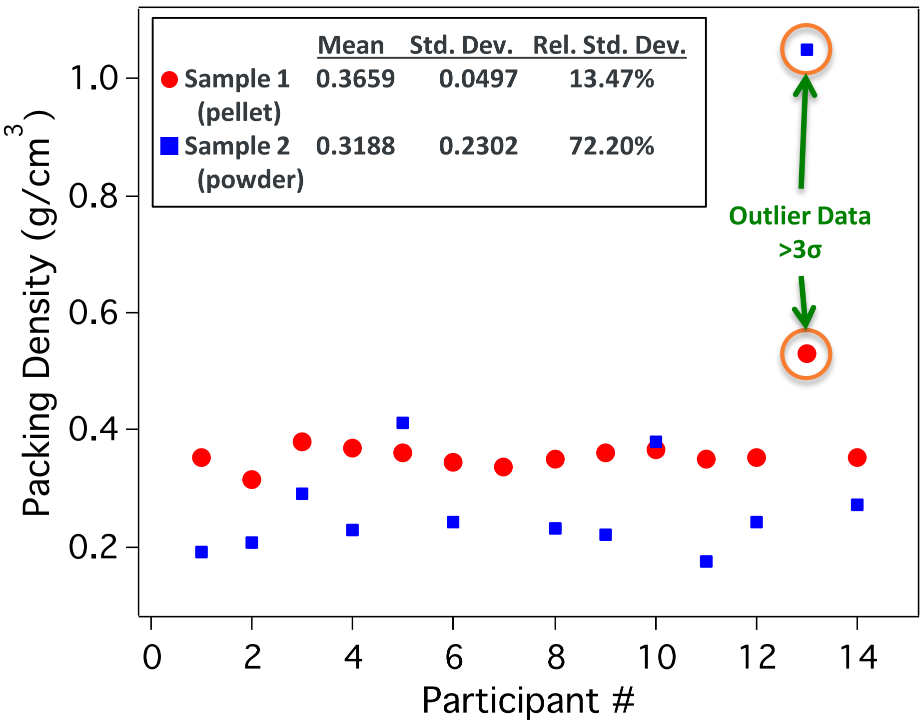
Accomplishment: Skeletal and Packing Densities

Including All Data (Except Self-Reported Errors)





- There was significant variation in determining the skeletal and packing volumes.
  - These variations will influence the isotherm data
- Variations in the packing density strongly depends on the sample preparation and therefore does not necessarily represent a measurement error.

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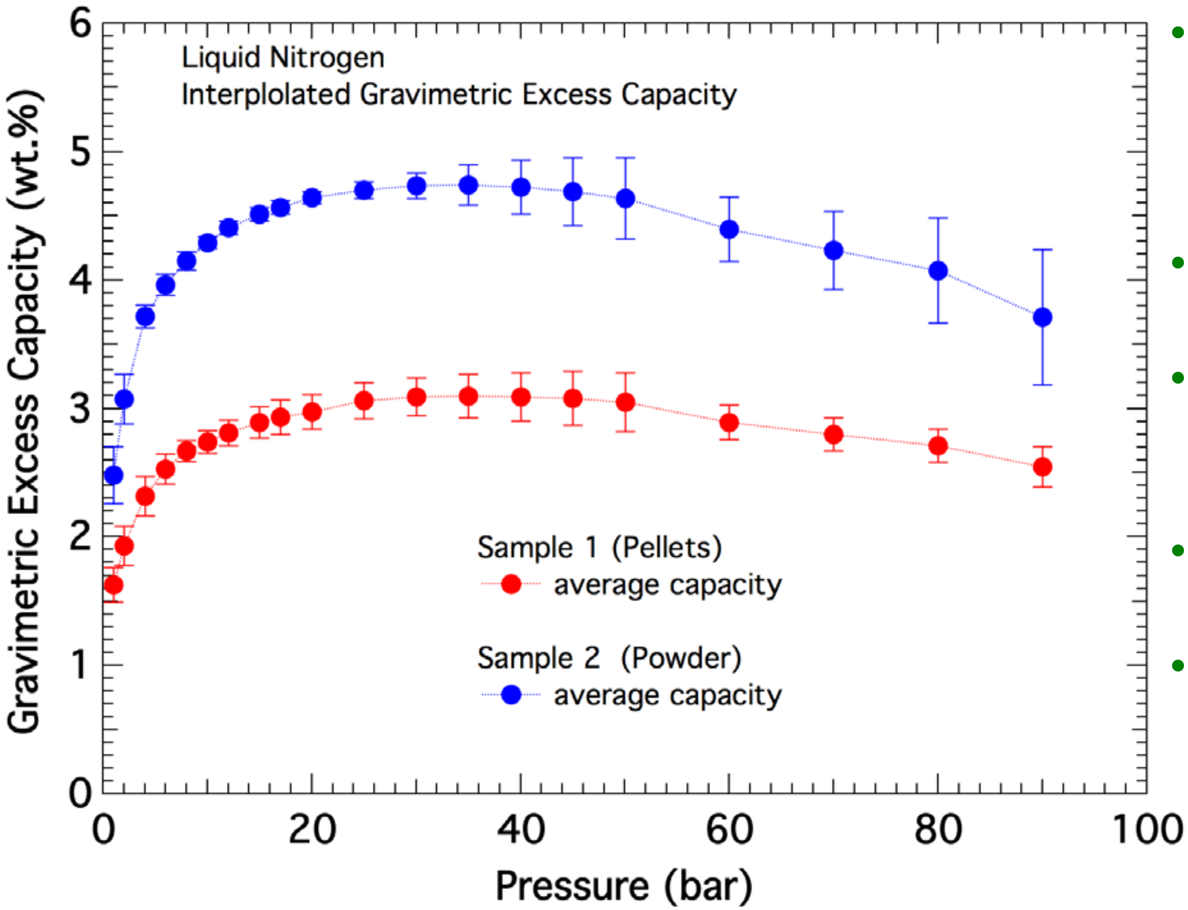
Accomplishment: Analysis of Interpolated Data

Average and standard deviation of interpolated data to common pressures: gravimetric excess capacity at liquid-nitrogen temperature.



- Each raw data set was interpolated to a common set of pressures to allow statistical comparisons.
- Here, the average of the data at those pressures is graphed.
- The error bars represent the standard deviations (SDs) at those same pressures.
- SDs are expected to increase with pressure.
- Sudden decreases in the SDs are caused by data sets no longer contributing to statistics at those pressures.

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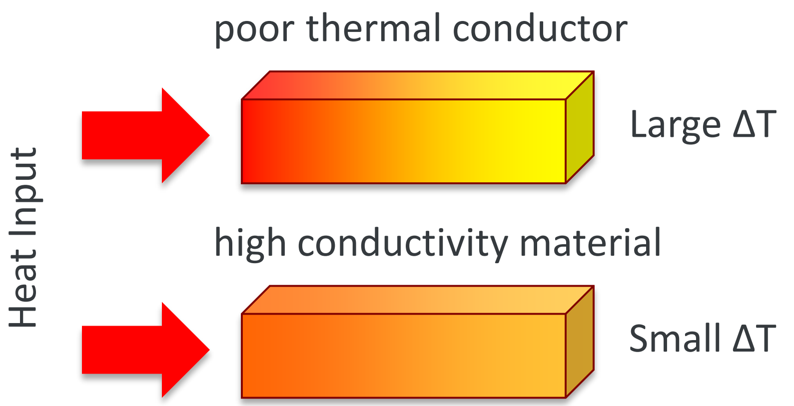
Relevance/Approach: Thermal Conductivity Characterization

Relevance:

- Thermal conductivity properties of H_2-storage materials is a critical engineering issue for developing H_2-storage systems.
- Thermal conductivity measurements for H_2-storage materials must accurately be determined under relevant operating conditions.
- Centralize this capability so it is available for the DOE H_2-storage program both as a resource and as a verification facility.



Approach:

Lead: Michele Olsen

- **Develop thermal conductivity measurement apparatus for hydrogen storage materials from 40K to 400K, and at pressures up to 100 bar.**
  - Establish methodology for characterizing materials with different form factors.
  - Validate measurement technique over entire temperature and pressure range.
- **Assist materials-research groups to characterize and validate their thermal conductivity measurements.**
  - Measure external samples at NREL to supplement the source group's measurement capabilities.
  - Validate extraordinary properties claims for novel hydrogen storage materials.

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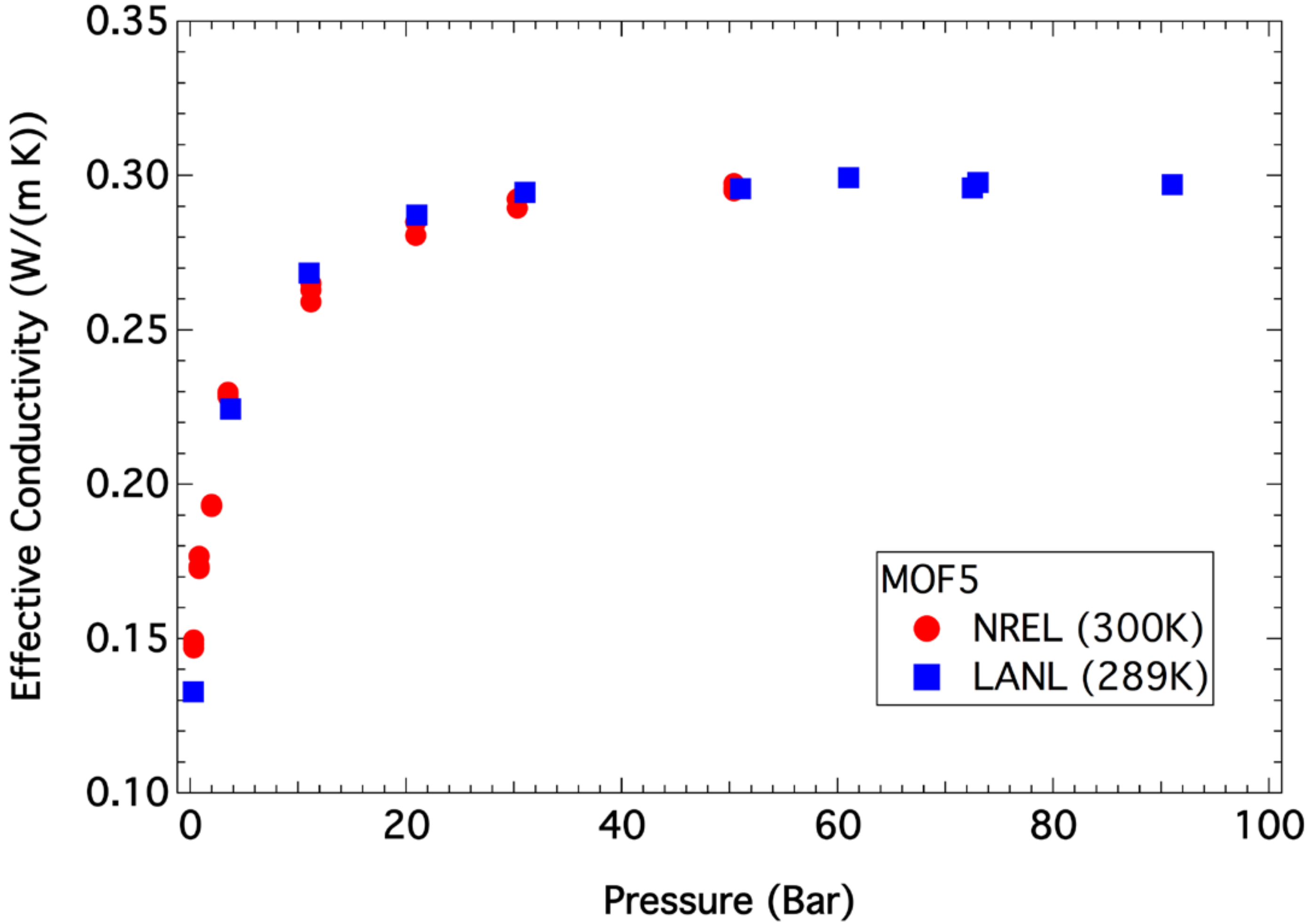
Accomplishment/Status: Thermal Conductivity Apparatus

- **Gas manifold completed with H_2 and He gases**
  - Operational & safety checks passed
- **Verification of apparatus continues**
  - More extensive testing of MOF5 pucks
- **Data acquisition software development on-going**
  - Basics are done; more automation is needed
- **Replacement for Michele Olsen near completion**
  - Four post doc candidates being interviewed
- **Milestone: Instrumentation report proceeding**

Accomplishment: Thermal Conductivity Validation Measurements

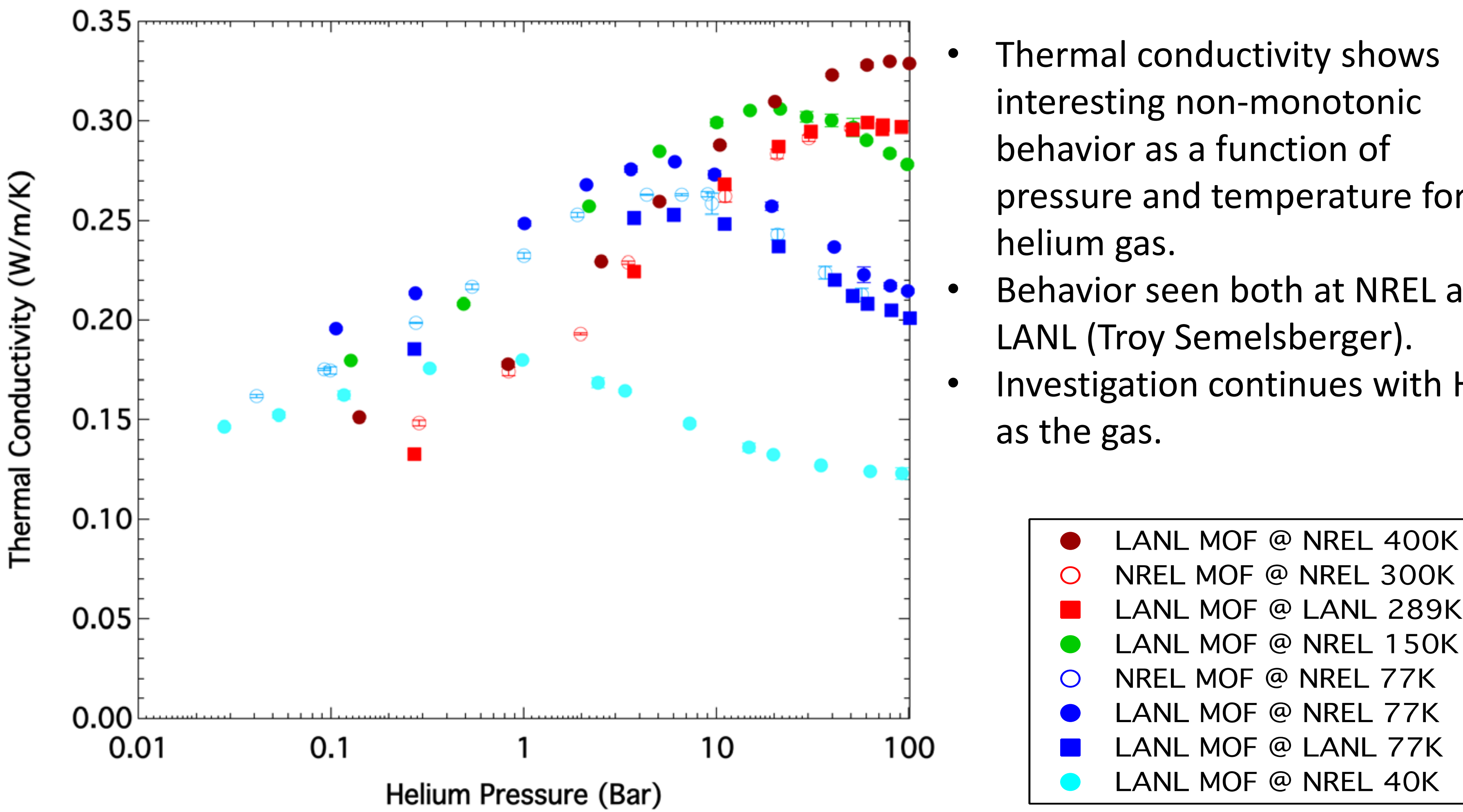
MOF-5 Room temperature and isotropic measurement



Results Agree!

Accomplishment: Thermal Conductivity Validation Measurements

Thermal conductivity of MOF-5 in helium as a function of pressure at different temperatures.



- Thermal conductivity shows interesting non-monotonic behavior as a function of pressure and temperature for helium gas.
- Behavior seen both at NREL and LANL (Troy Semelsberger).
- Investigation continues with H_2 as the gas.

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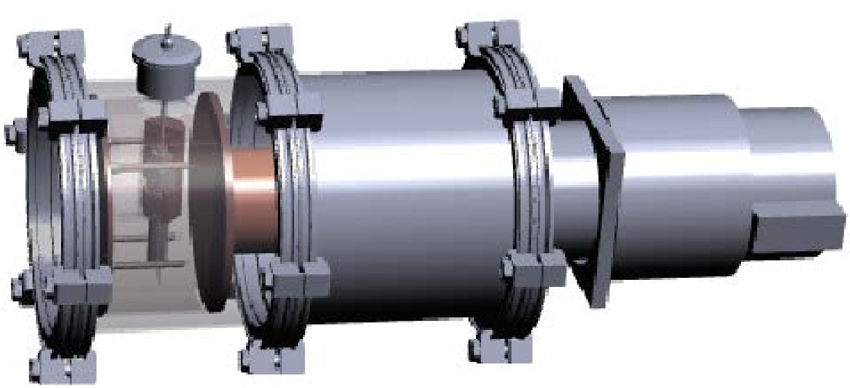
Relevance/Approach: Continuously Variable Temperature PCT

Relevance:

DOE Objective: To compete with 700-bar tanks, storage materials need to operate at reasonable temperatures approaching ambient and much lower pressures. Materials need to be tested at the expected operating temperatures and pressures.

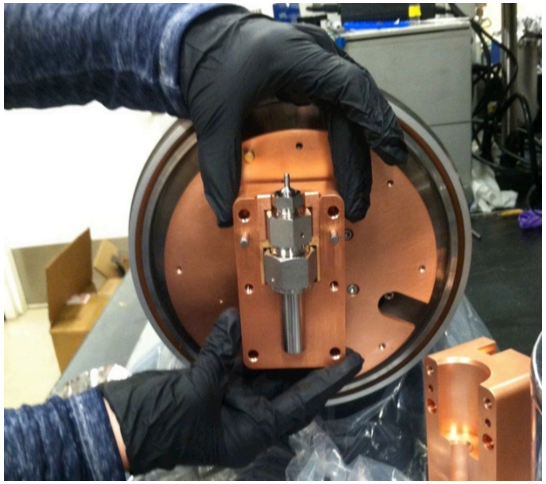


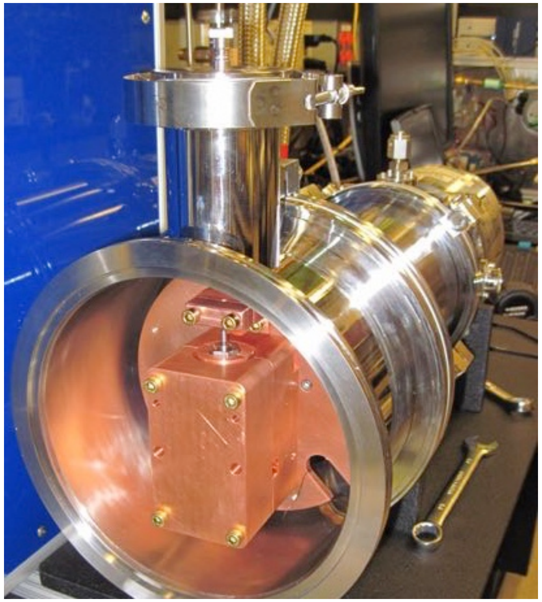
Approach:

Lead: Katie Hurst

- **Develop a continuously variable temperature PCT**
  - Will allow obtaining applicable Temperatures & Pressures
  - Must maintain exceptional accuracy
  - Commercial units suffer from non-uniform & unstable temperatures
  - Use high-capacity cryo-cooler with custom sample holder and thermal engineering
- **Steps**
  - Determine cryostat specifications & sample holder design ✓
  - Have cryostat & sample holder built ✓
  - Integrate hardware ←
  - Perform initial tests & measurements ←
  - Integrate software enhancements
- **Publish paper on design & performance**

Accomplishment: Continuously Variable Temperature PCT

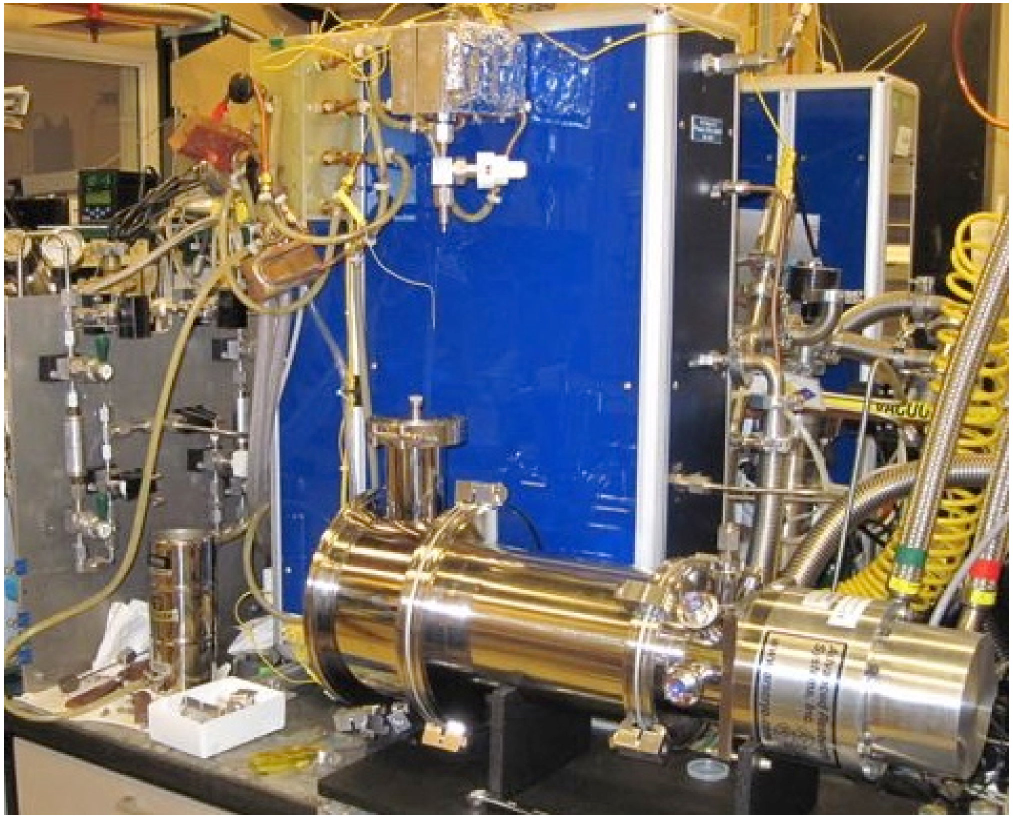




- **Modified PCTPro 2000 instrument**
  - Pressures up to ~200 bar
- **Added cryocooler/cryostat**
  - Temperature: ~50K to 350K
- **Custom-made sample holder**
  - Copper temperature stabilizer
  - Stainless sample holder
  - Thermally designed to minimize temperature gradients at sample

Next Steps: Continuously Variable Temperature PCT

- **Testing**
  - Verify operation of cryostat with existing PCT instrument to produce accurate and reliable measurements
    - Null measurements must show acceptable results at all temperatures and pressures
    - Initial null measurements do show good results consistent with those obtained in liquid baths
  - Integrate new LabVIEW software into instrument
  - Validate isosteric heat of adsorption measurement

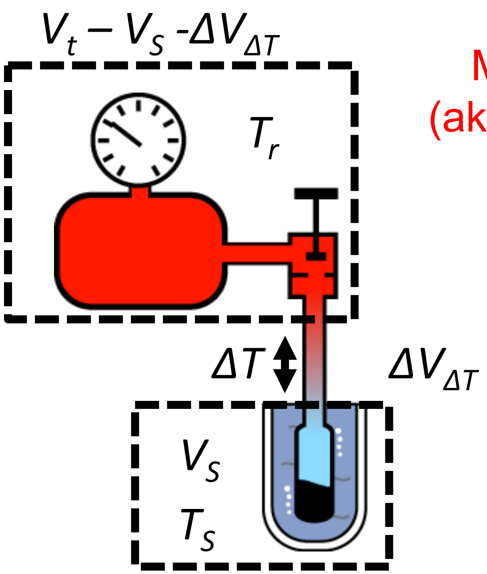


Cryostat will integrate with existing PCTPro 2000 that has been modified to improve thermal stability and uniformity.

Relevance/Approach: Measurement Validation & Error Analysis

Relevance:

DOE Objective: Capacity measurements for hydrogen-storage materials must be based on valid and accurate results to ensure proper identification of promising materials for DOE support.



Manometric (aka Volumetric) System

Approach:

Leads: Katie Hurst & Phil Parilla

- **Assist materials-research groups**
  - Validate external samples at NREL
  - Discover sources of discrepancies
  - Advise on corrective actions
- **Investigate sources of measurement error**
  - Analyze realistic models
  - Identify major error sources
  - Recommend improvements
    - Instrumentation
    - Experimental procedures
    - Data analysis
- **Disseminate Findings**

Accomplishments: Measurement Validation 2017

- **Milestone: Worked with groups funded by DOE to validate measurements and analyze results.**
  - 1 Validated sample capacity. Results reported to DOE.
    (Data is considered proprietary and cannot be shared.)
    (Measurements include TPD, PCT, BET etc.)
    9 measurements
  - Multi-laboratory measurement study - 18 measurements
  - Trained DOE personnel to perform PCT measurements – 12 measurements

- **Collaborated with groups for discussion of error analysis and advisement on protocols to enhance accurate measurements.**
  - 3 groups (H2M, Berkeley, Sandia (HyMARC))
  - Collaborated with HYMARC – measured 2 samples - 27 measurements
  - Investigated commercial instrument for systematic error

FY17 Characterization Milestones

Description	Due	Status
Submit full report to DOE on results of volumetric capacity of at least 5-laboratory inter-lab comparison.	12/31/16	100% complete
Submit DOE report and/or a manuscript to peer-reviewed journal on Variable-Temperature Thermal Conductivity apparatus, methodology and results.	03/31/17	In progress, delayed due to staff departure.
Completed construction of variable-temperature cyro-cooling add-on to the PCT Apparatus. Perform validated gravimetric capacity, volumetric capacity and isosteric heats of adsorption determination on an agreed upon sorbent standard to within 15% of the accepted value.	06/30/17	In progress and on schedule.
Measure and validate the gravimetric capacity, volumetric capacity and/or thermal conductivity of 2 samples as assigned by DOE. Submit full report to DOE within 30 days of completion of analysis.	09/30/17	In progress and on schedule. 1st sample already measured and reported on. 2nd sample awaiting DOE request.

Future Work & Challenges

- **Volumetric Capacity: Inter-Laboratory Comparison**
  - Analyze data and publish results from the inter-laboratory hydrogen capacity study. Inform participants of their results in the study.
  - Massive amount of data, many variables and complex interplay will make this a challenge.
- **Thermal Conductivity Measurement and Validation**
  - Finish validation work; hire post doc; improve software
  - Develop powder-handling & validate
- **Variable-Temperature PCT**
  - Verify operation of cryostat with existing PCT instrument to produce accurate and reliable measurements
  - Integrate new LabVIEW software into instrument
  - Validate isosteric heat of adsorption measurement
- **Measurement Validation & Error Analysis**
  - Need to validate 1 more sample (FY17)
  - Contacted company to fix issue with PCT instrument

Summary

- **Volumetric Capacity: Inter-Laboratory Comparison**
  - Inter-laboratory comparison is complete.
  - Data analysis is in progress and results will be published.
- **Thermal Conductivity Measurement and Validation**
  - Validation studies are almost complete.
  - Thermal conductivity measurement for others are starting.
  - Instrumentation publication planned for near future.
- **Variable-Temperature PCT**
  - Hardware integration is near completion.
  - Validation testing will be next, followed by sample measurements.
- **Measurement Validation & Error Analysis**
  - More samples are expected for validation.
  - Error analysis and assisting others is continuing.

Technical Back-Up Slides

Inter-laboratory Measurement Study - Samples

Two Carbon Samples:

- **Sample 1:**
  - Norit ROW
  - Pellets
  - BET SSA 740 m^2/g
- **Sample 2:**
  - MSC20
  - Powder
  - BET SSA 2400 m^2/g

Inter-laboratory Measurement Study - Run Sheet

Participants were asked to fill out a *Run Sheet* that included experimental information.

<u>This included:</u>

- **sample mass (before/after degas)**
- **skeletal density**
- **packing density**
- **methods for determining skeletal density**
- **hydrogen purity**
- **equation of state**
- **whether degas protocol was followed**
- base pressure for degas instrument
- base pressure for volumetric instrument
- equilibrium time for adsorption
- temperature stability
- pressure sensor accuracy

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INTER-LABORATORY COMPARISON RUN SHEET

INSTRUCTIONS

Please fill out a run sheet for each measurement. You may want to fill out the fields that will be common for all measurements and then save this file so you do not have to fill in those fields every time.

Please provide isotherm data calculated as excess gravimetric (wt%), excess volumetric (g H_2/L) and total volumetric (g H_2/L) in either tab-delimited format or an Excel spreadsheet. See the instruction sheet for additional details. If you correct for helium adsorption that occurs during the calibration, please supply both the corrected and uncorrected data if possible.

If you have any questions call or email Katherine Hurst (303-384-7673; katherine.hurst@nrel.gov)

LABORATORY INFORMATION

Laboratory Institution | **Person filling out run sheet**

Phone number for person | **E-mail for person**

Filename(s) for this data:

NOTE: The above information will be removed when the final results are reported. Laboratories will be identified anonymously using a randomly assigned number.

SAMPLE TYPE: ☐ Sample 1 or ☐ Sample 2

SAMPLE PREPARATION (skip if null measurement data)

SAMPLE MASS

Initial Mass: ± mg Date:

After degas (optional): ± mg Date:

Final Mass: ± mg Date:

SAMPLE DEGAS **Begin Date:** **End Date:**

Base Vacuum Pressure: Units:

Degas Protocol: ☐ **Degas protocol followed** ☐ **Degas protocol exception (explain)**

Degas Explanation:

Was sample exposed to air after degas and prior to measurement? ☐ **No** ☐ **Yes (explain)**

Air Exposure Explanation:

MEASUREMENT INFORMATION

Measurement Method: ☐ **Gravimetric** ☐ **Volumetric** ☐ **Other:** | ☐ **Static** ☐ **Dynamic**

Measurement Temperature: ☐ **Liquid Nitrogen** ☐ **Ambient:** **K** | **If dynamic, flow rate:**

Hydrogen Purity: **%** **Additional purifier used?** ☐**Yes** ☐**No**

Base Vacuum Pressure: Units:

Sequence order: ☐ **He calibration done first** ☐ **H_2 measurement done first**

Equilibrium time/step: (min.) | **Total time for measurement:** min.

Temperature stability: **Standard Deviation:** **K** | **Pressure Sensor Accuracy:** **%** ☐ **FS** ☐**Reading**

Equation of State: ☐ **Ideal** ☐**Real:** **Model:**

CALIBRATION

Helium adsorption correction: **Supplied data has** **Method:** no correction **if other, explain:**

Skeletal Density: ☐ **Not Measured** ☐ **Measured:** **g/cm^3** **Method used:**

Packing Density: **Measured:** **g/cm^3** **Method used:**

COMMENTS

2/15/16 **Page 1 of 1**

Definitions for Inter-Laboratory Metrics

- **Gravimetric Excess Capacity**

$$wt.\% = \frac{100\, m_{ex\,H}}{m_s + m_{ex\,H}}; \quad m_{ex\,H} = M_{H_2\,AMU}\, n_{ex\,H_2}$$

- **Volumetric Excess Capacity** (normalized by packing volume)

$$\Lambda_{ep} = \frac{m_{ex\,H}}{V_{pk}}$$

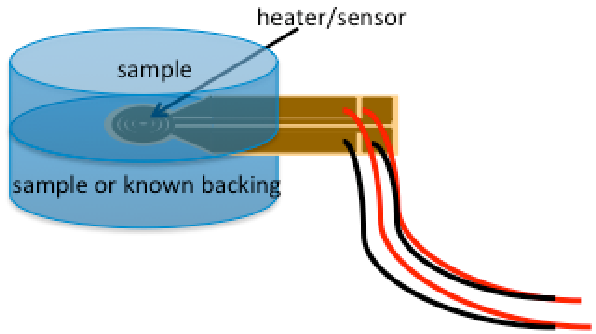
- **Volumetric Total Capacity** (normalized by packing volume)

$$\Lambda_{tp} = \frac{m_{tot\,H}}{V_{pk}} \qquad n_{tot\,H_2} = n_{ex\,H_2} + \rho_{fg}\left(V_{pk} - V_{sk}\right)$$

Thermal Conductivity Apparatus

Designed and built an apparatus capable of measuring the thermal conductivity of hydrogen storage materials under ***expected operating conditions***:

- ***Transient Plane Source Technique***
- 40 K to 400 K
- up to 100 bar
- capable of measuring pucks and powders (down to ~ 1 cm^3)



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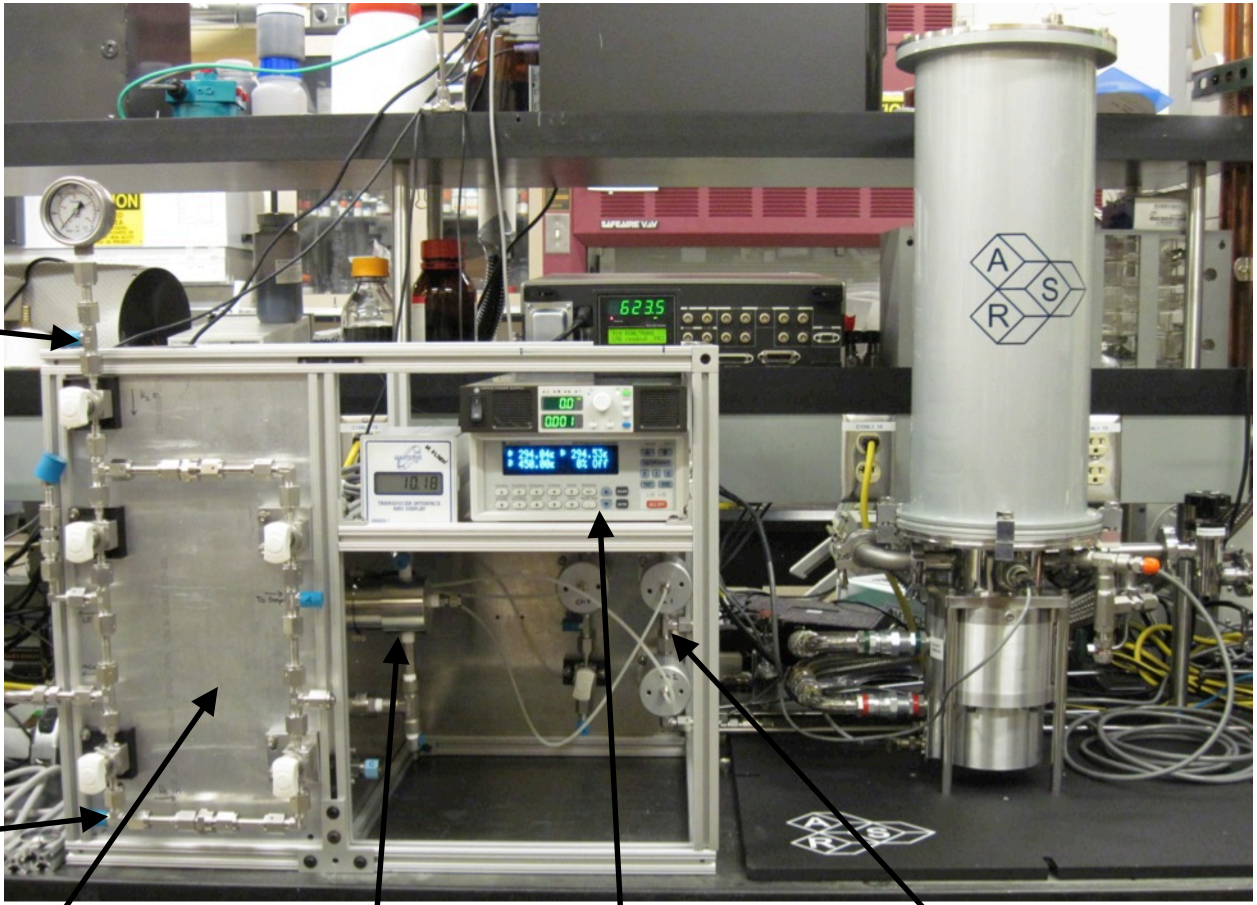
Thermal Conductivity: Cryostat and Pressure-Control System

System was built in FY16

Hydrogen inlet

(Control electronics behind manual valve panel)

Helium inlet



Manual valves

Pressure regulator

Cryostat temp. controls

Pneumatic valves