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Tritium Aging Studies of $LaNi_{4.15}Al_{0.85}$ (LANA.85)

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36th Tritium Focus Group – Fall 2015

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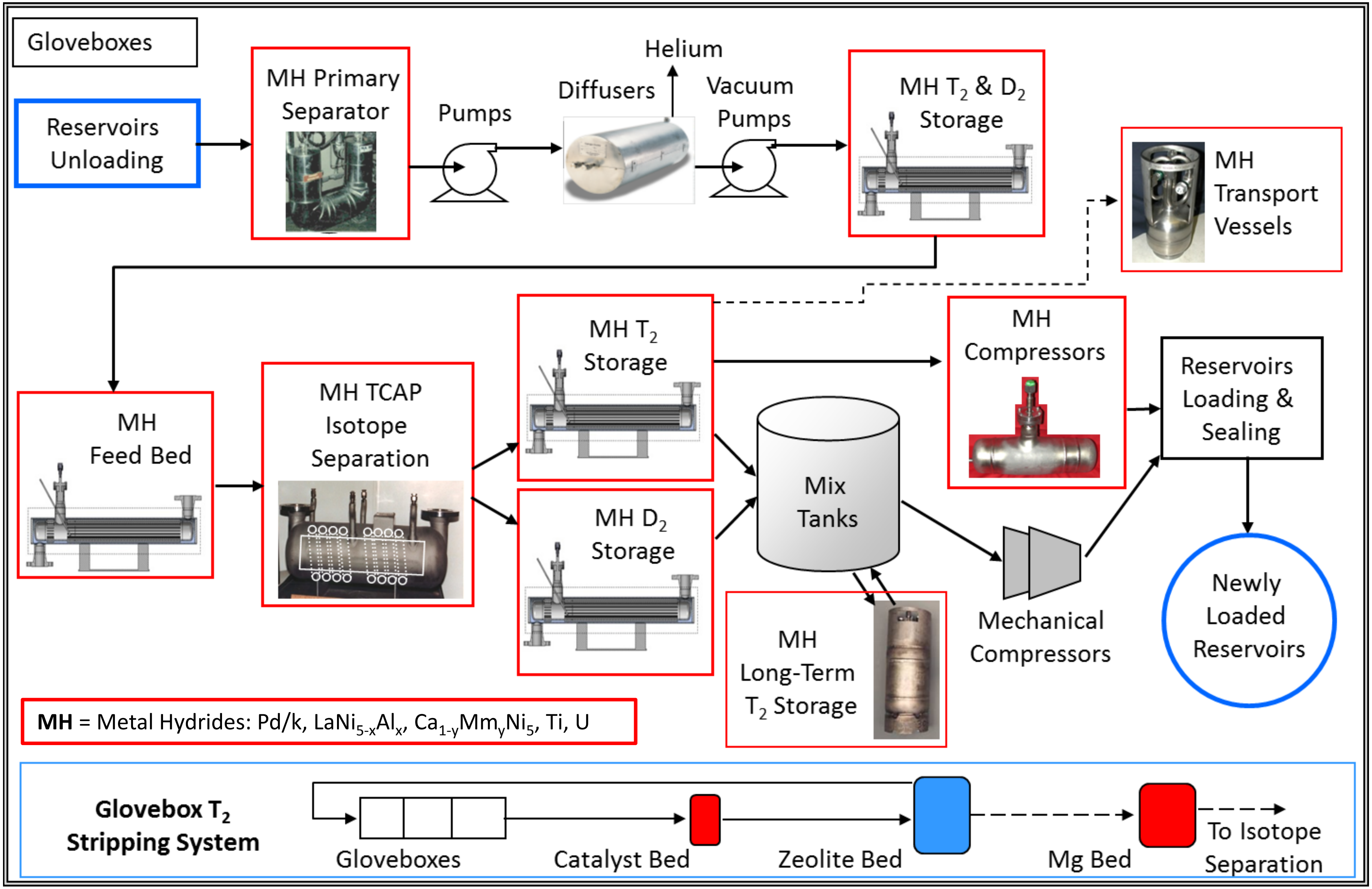
Introduction

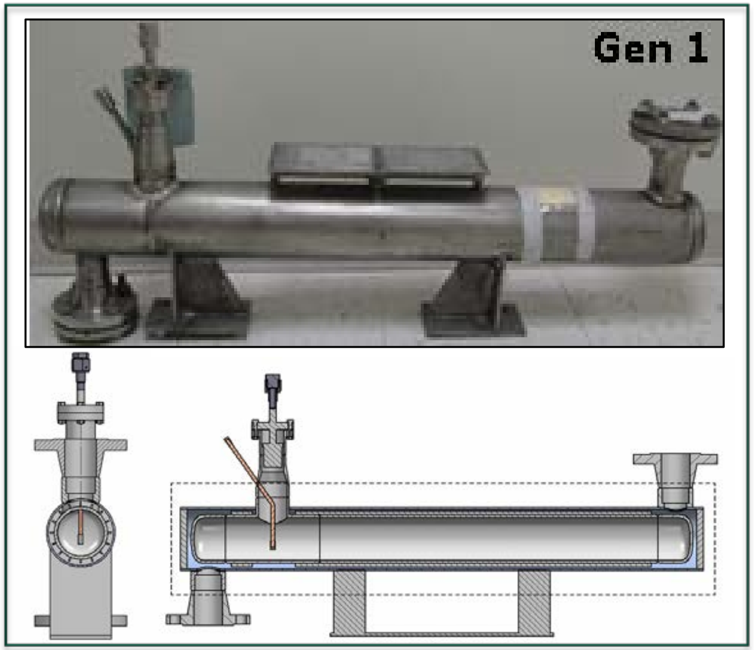
- LANA Hydride Relationship to SRS
- LANA aging with Tritium
- Isotherms in General
- Project Details
- LANA.85
  - van't Hoff Plots
  - Tritium Isotherms

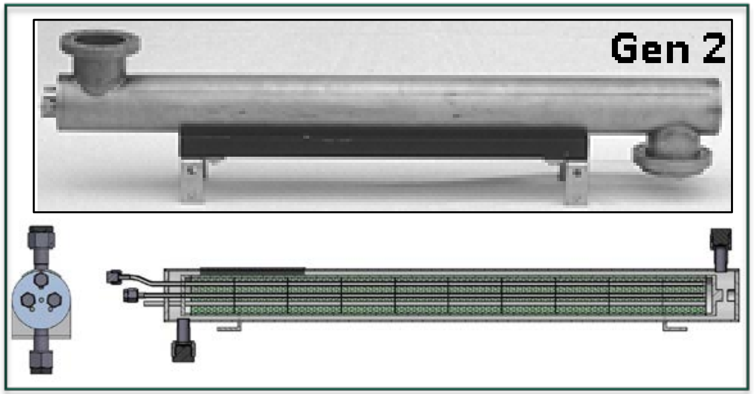
Tritium Processing at SRS – The Largest MH Based Facility in the World



Background Tritium Aging Studies

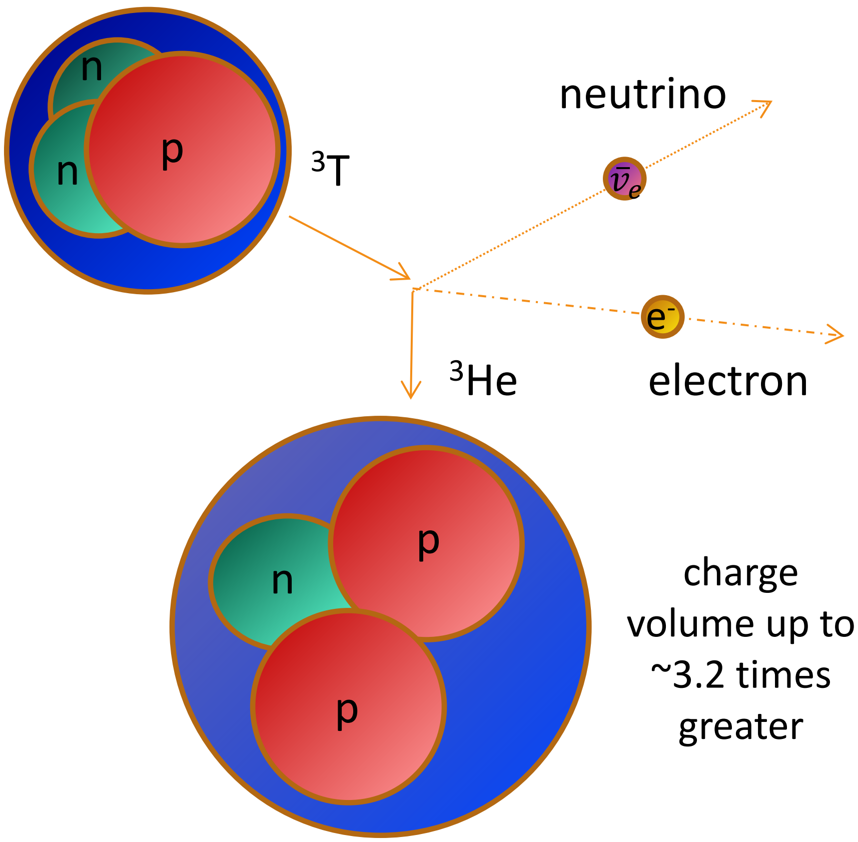
- SRTE uses hydride beds store and process hydrogen isotopes
- Gen 1 & Gen 2
  - Bed Material: $LaNi_{4.25}Al_{0.75}$ (LANA.75)
  - Bed Design
    - *Gen 1 - Hot and Cold Nitrogen System*
    - *Gen 2*
      - Electric Heaters
      - Forced Glovebox Nitrogen for Cooling
  - Desorption
    - *Endothermic*
    - *Beds heated to increase rate*
    - *At Constant Q/M Higher Temp = Higher Vapor Pressure*
  - Absorption
    - *Exothermic*
    - *Beds cooled to increase rate*
    - *At Constant Q/M Lower Temp = Lower Vapor Pressure*





Tritium Induced Hydride Behavior

- Tritium Compromises the Crystal Lattice of $LaNi_{5-x}Al_x$ alloys
  - Half life ~12.3 years, He-3 and β particle
  - He-3 born in Hydride causes radiogenic helium agglomerations (micro-bubbles)
    - *Causes swelling*
    - *Variations in tritide structure*
      - Increase in LANA hydride stability
      - Size of interstitial holes increases solubility
        - » *Variations of tritium equilibrium pressure*
        - » *Decrease in plateau pressure*

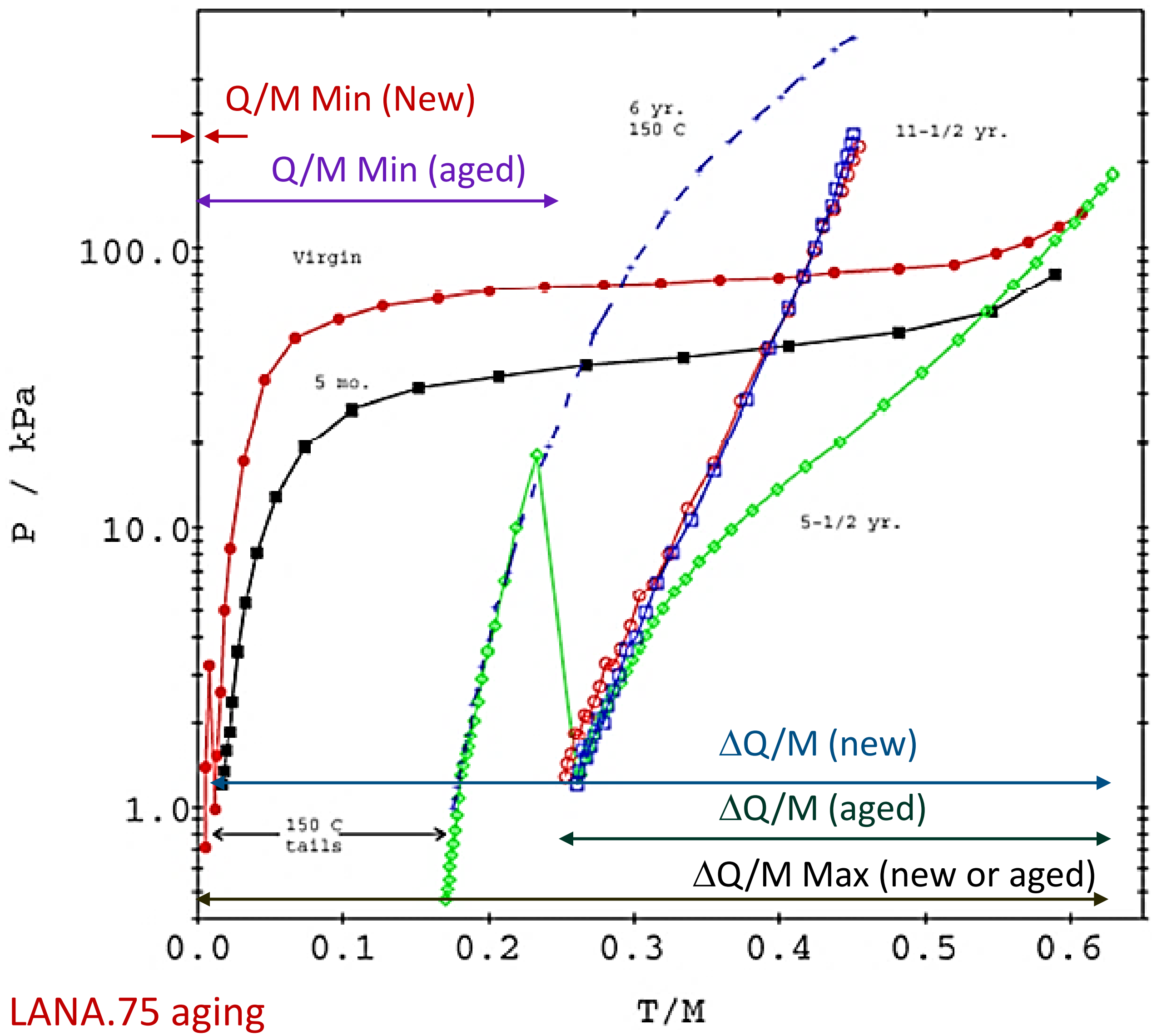


$$ {}_1^3T \xrightarrow{yields} {}_2^3He^{1+} + e^- + \bar{\nu}_e $$

Demina, S.V., et al., 2012

Tritium Aging

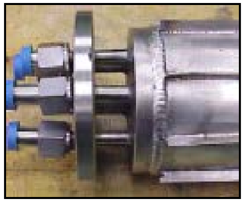
- LANA materials are limited lifetime components
- LANA properties change with tritium aging
  - Formation of "heel"
    - *Inventory Holdup*
    - *Reduced Capacity*
  - Decreased plateau pressure
  - Eventual loss of plateau
  - Eventual weeping of He-3



LANA.75 aging

Gen 3 FISH Beds

- $LaNi_{4.15}Al_{0.85}$ (LANA.85), was selected for use in the next generation of hydride beds
  - – Incorporation of LANA.85 in the Four Inch Short (FISH) beds is expected to meet the prescribed hydrogen absorption and desorption performance criteria without the assistance of a Hot and Cold Nitrogen (HCN) system.
    - *Electrically Heated*
    - *Forced Glovebox Cooled*



  - – LANA.85 Lower Plateau Pressure than LANA.75
    - *Less gas remaining in pipes = less reprocessing*
    - *Higher Aluminum Content*
      - – Helps provide lower vapor pressure
      - – Lower Capacity = more hydride material

Project Motivation

- The new beds, like previous beds, are expected to have a limited service life due to radiolytic decay of tritium to He-3 within the hydride metal matrix.

- <u>Goal of this multiyear project:</u>

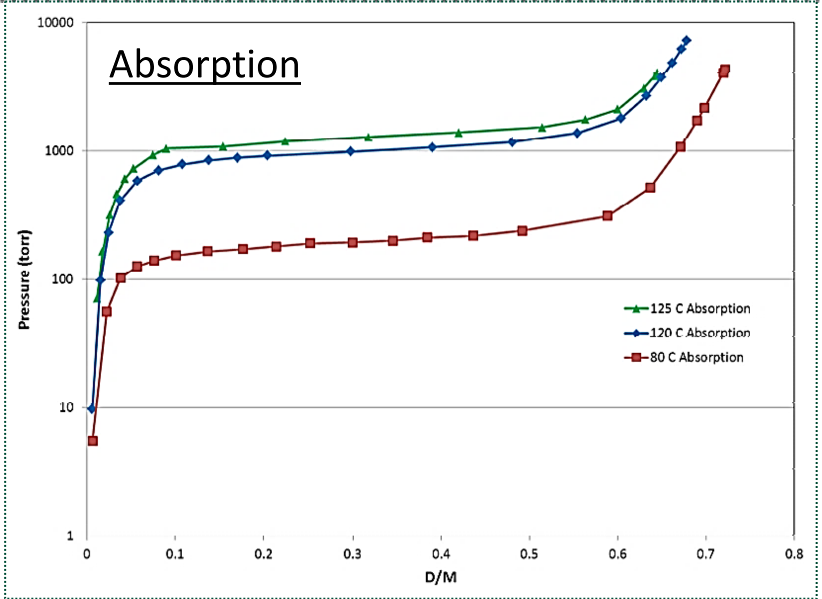
Examine how the properties of $LaNi_{4.15}Al_{0.85}$ *(LANA.85) are impacted by tritium exposure before it is placed in service in the Savannah River Tritium Enterprises (SRTE).*

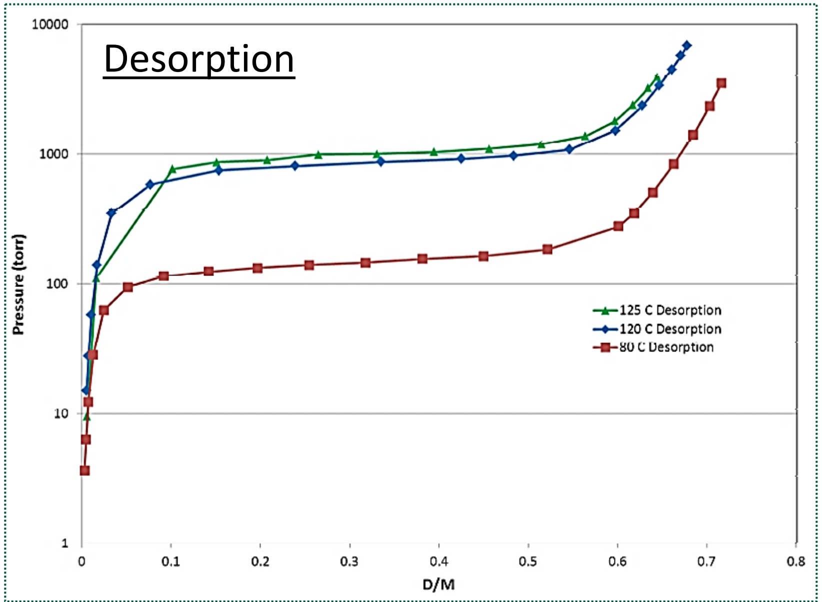
Experimental Design for Tritium Aging Studies LANA.85

- 2 Samples being tracked ~ 4 grams each
  - Overhead gas
    - *^{3}He Solubility @ ambient*
  - Isotherm Collection
    - *80°C, 100°C, 120°C & 160°C (Desorption)*
    - *120°C (Absorption)*
    - *Reversible capacity of bed*
    - *Heel formation*
    - *Plateau pressure decrease*
    - *Increase in plateau slope*

Experimental Design: “Cold” Testing

- <u>Deuterium Baseline</u>
  - Understand behavior before exposure to tritium
  - Cycle with deuterium / gather baseline isotherms
    - *80°C, 120°C, and 150°C*
    - *Evacuate sample between temperatures*
    - *Evacuate at 120°C for 2 hours to desorb residual deuterium*
  - See nothing abnormal in the isotherms





Experimental Design: "Hot" Testing

- <u>Tritium Facility Testing</u>

  – Load at ambient temperature into the beta phase with tritium

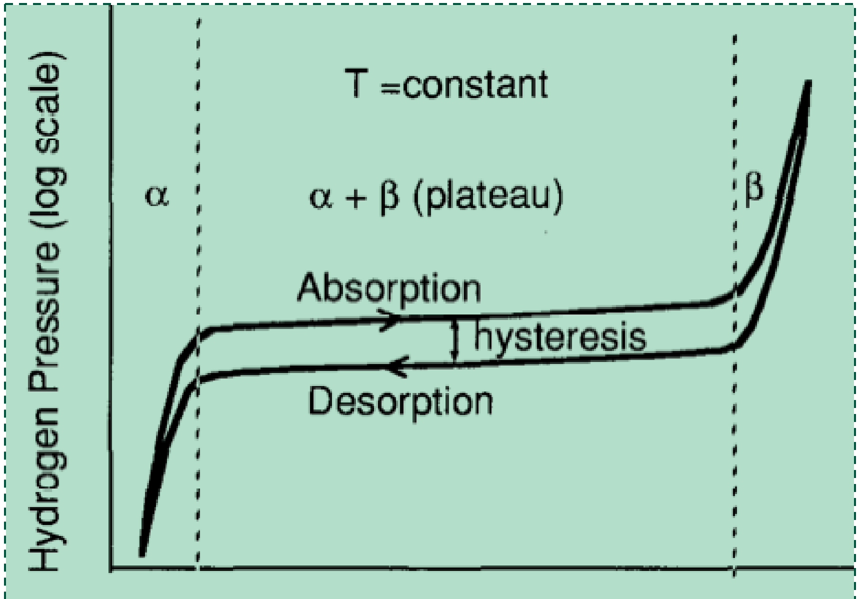
  <u>Sample Overhead Gas</u>

  – Replace tritium removed during ^3He sampling

  <u>Sample Isotherm Collection</u>

  – Gather baseline desorption isotherms
    - *80°C, 120°C, and 160°C*

  – Single baseline 120°C absorption isotherm



Heung, 1993

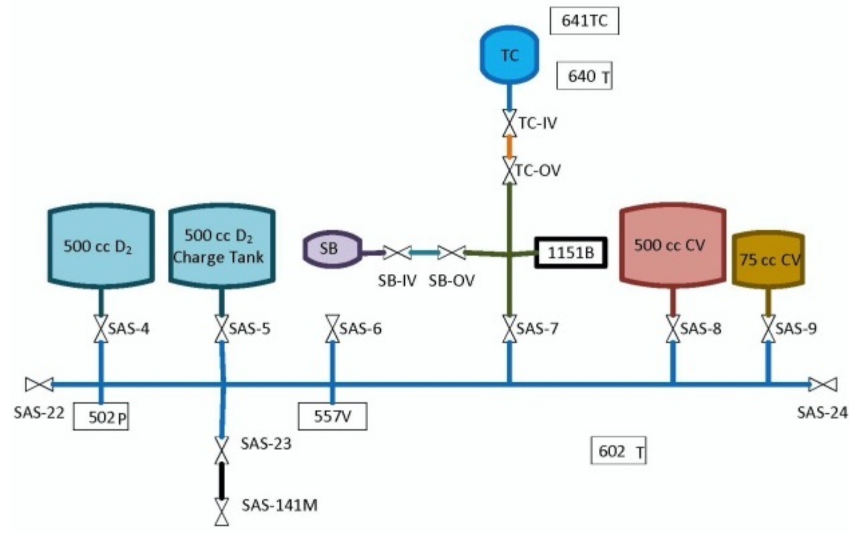
  – Perform yearly measurements
    - *80°C, 120°C, and 160°C Original Design*
    - *Plateau pressure at the α & β to α was lower than manifold capacity*
    - *100°C, 120°C, and 160°C Revised Design*

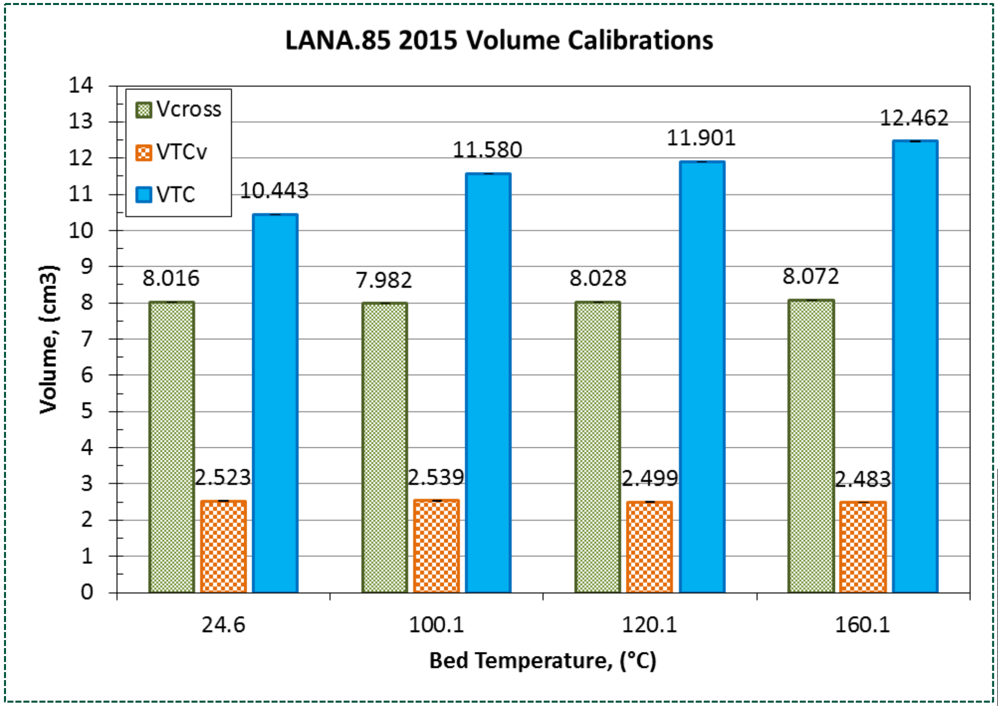
Experimental Apparatus: Sample Assay System (SAS) Manifold

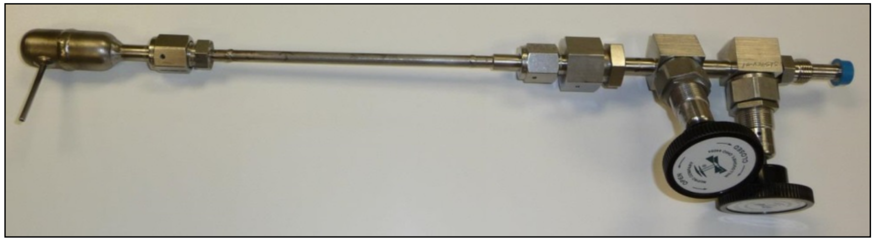
Volume of the low pressure manifold

- $81.883\ cm^3$
- Used to calibrate other volumes

$$PV = nRT$$

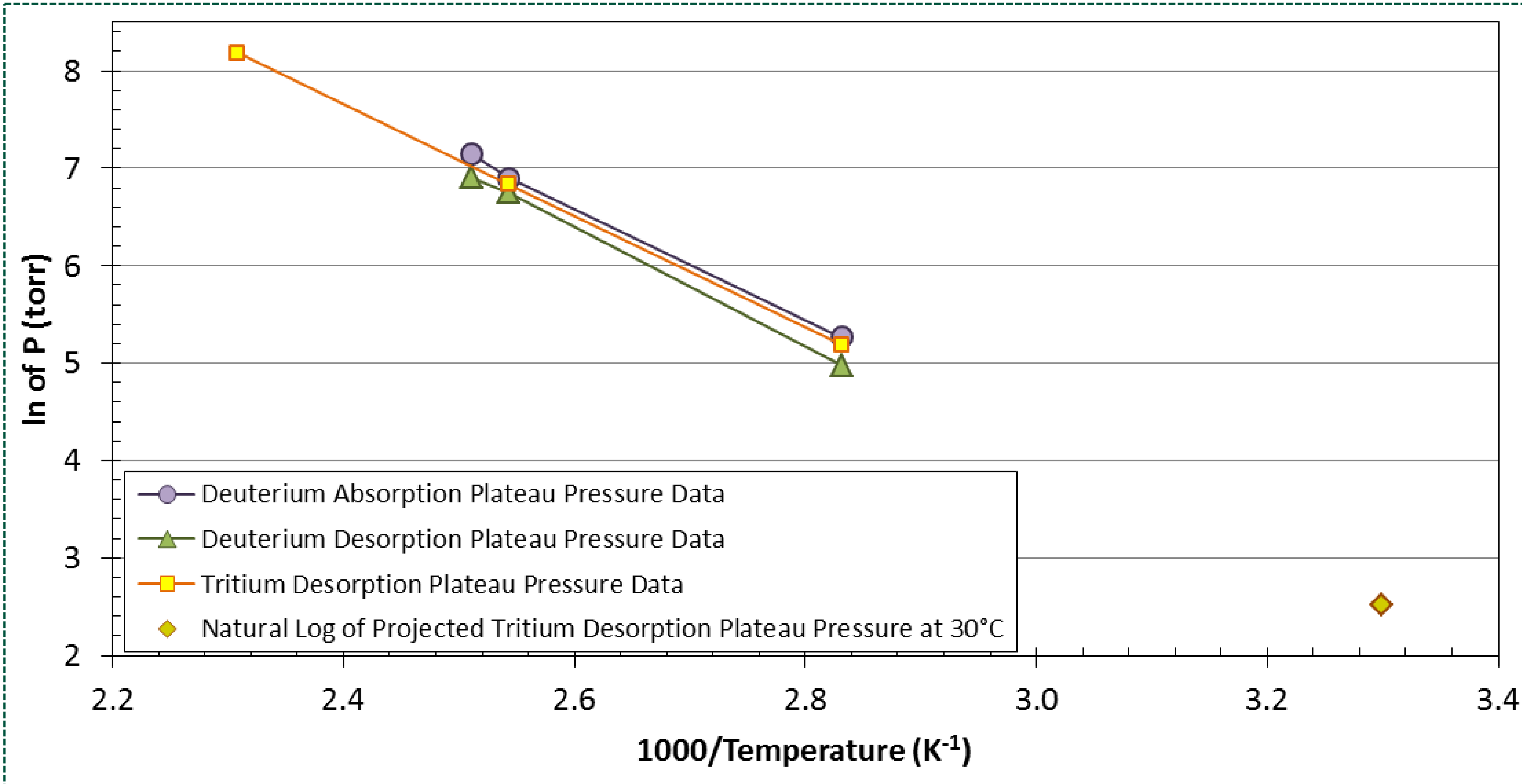






Heat transfer up the spool piece and to the glovebox environment will change the "apparent" volume of the test cell (VTC) by ~19% from ambient to 160°C

van't Hoff Plot



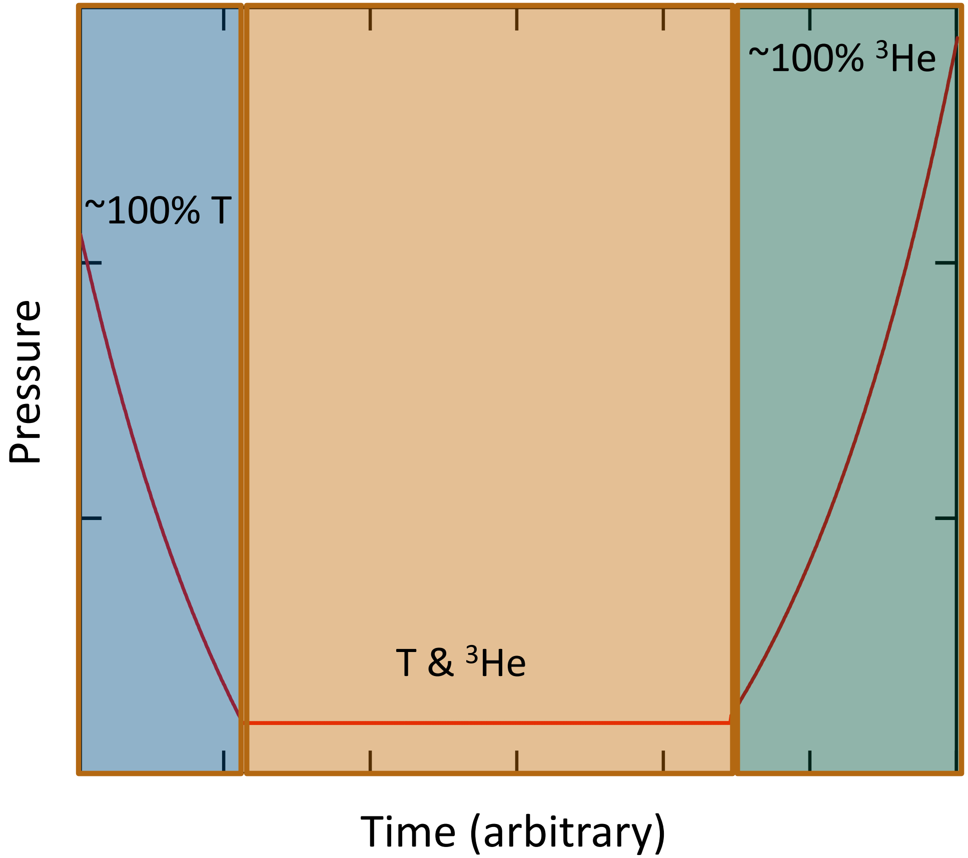
$$ln\,of\;P\;(torr) = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

$$R = 62.36\;\;(L * torr)/(mol * K)$$

	D_2 Absorption	D_2 Desorption	T_2 Desorption
DH (L*torr/mol)	352976	382810	356970
DS (L*torr/mol/K)	1328	1394	1334

Overhead Pressure

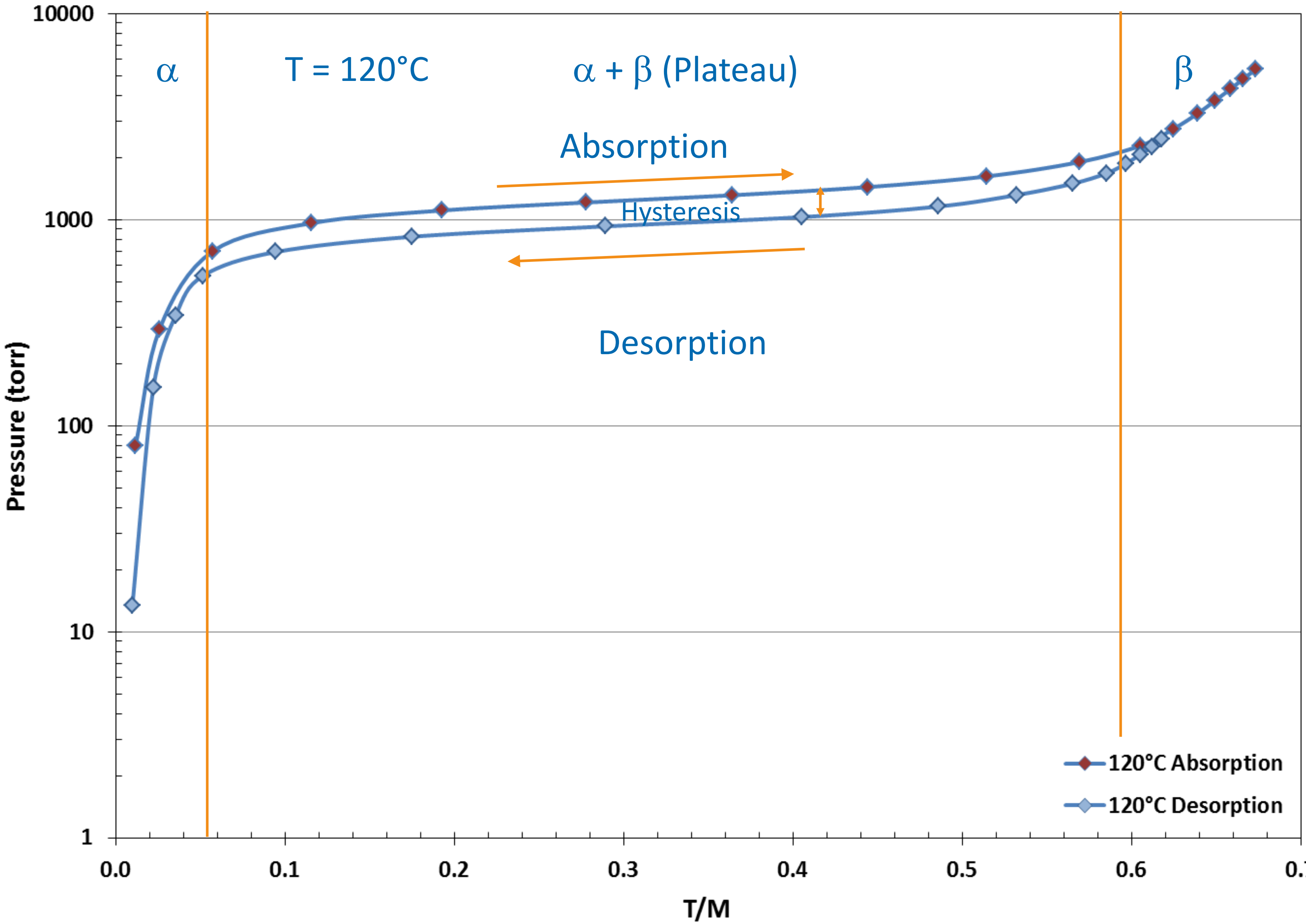
1. Steepness of curve related to loading of sample, & volume of headspace.
   - Δ in isotherm Pressure is a function tritium absorption in solid as equilibrium shifts due to beta decay in solid
2. Represents plateau pressure
3. Once solid nears saturation, pressure increases



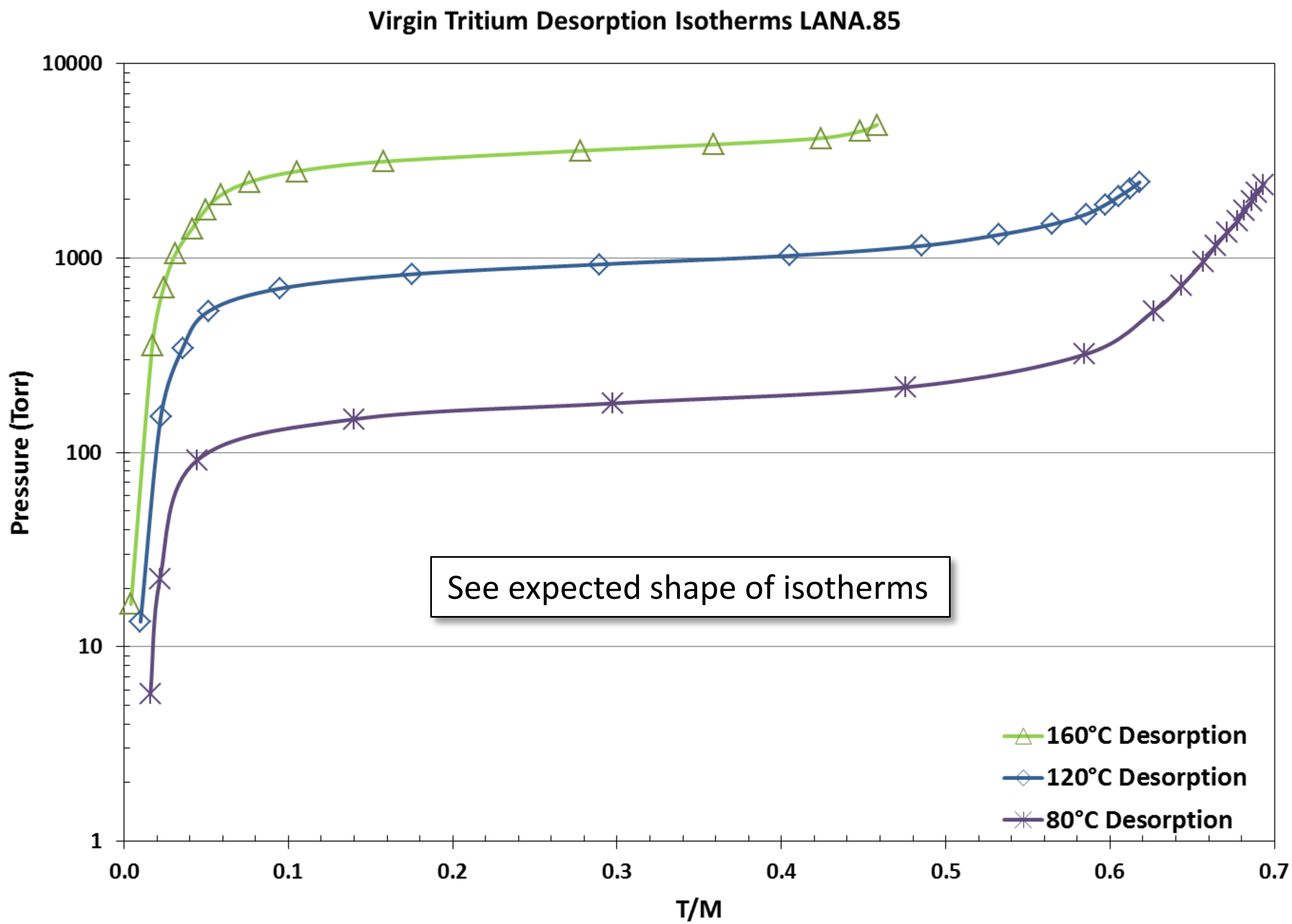
- ΔP_T is related to isotherm
  - If $T_{solid} >> T_{gas}$, P decreases as tritium is absorbed to maintain equilibrium
  - This effect is compounded by tritium aging changing isotherm

- ΔP_{He} is related to:
  - T in gas, P increases as Tritium in gas decays (2:1 ratio)
  - Helium in the solid,
    - *helium release is negligible for low $^3He/M$*
    - *increases when solid approaches saturation*

Results: LANA.85 T_2 Initial 120°C Absorption/Desorption Isotherm

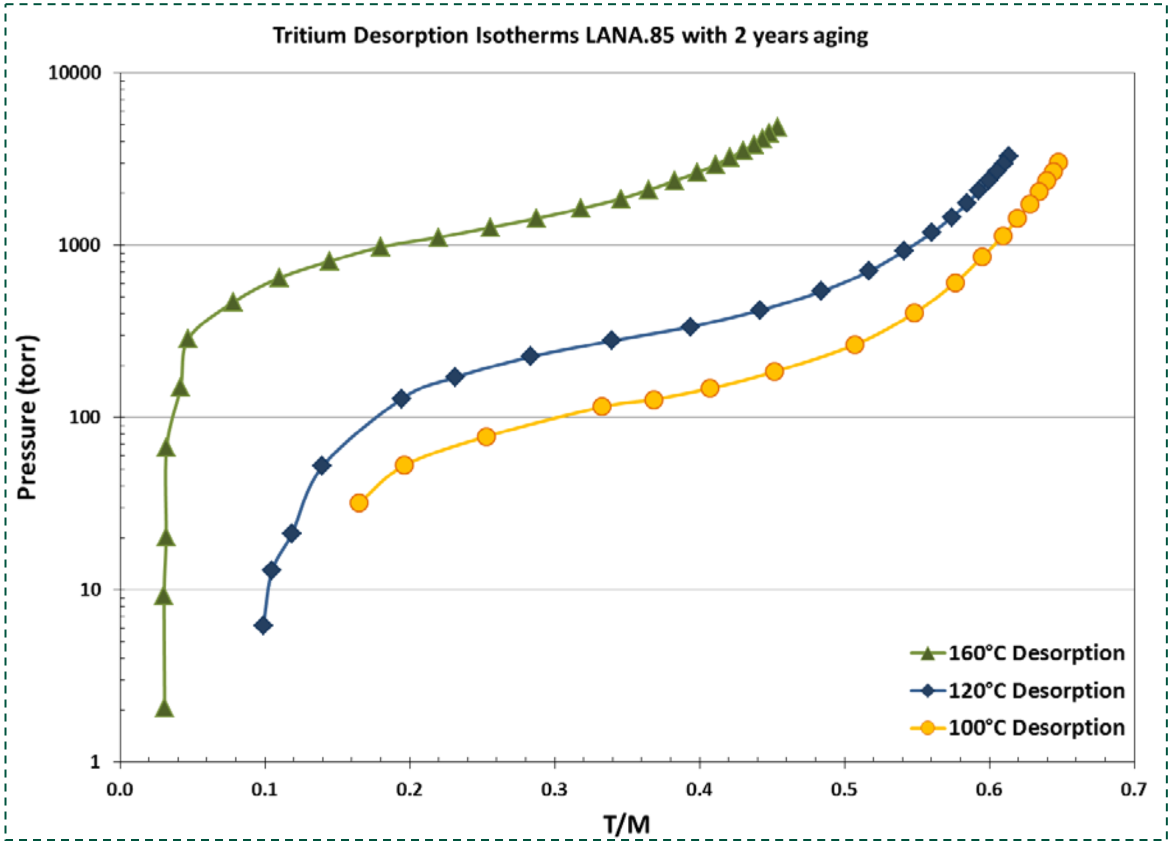


Results: Initial LANA.85 Desorption Isotherms

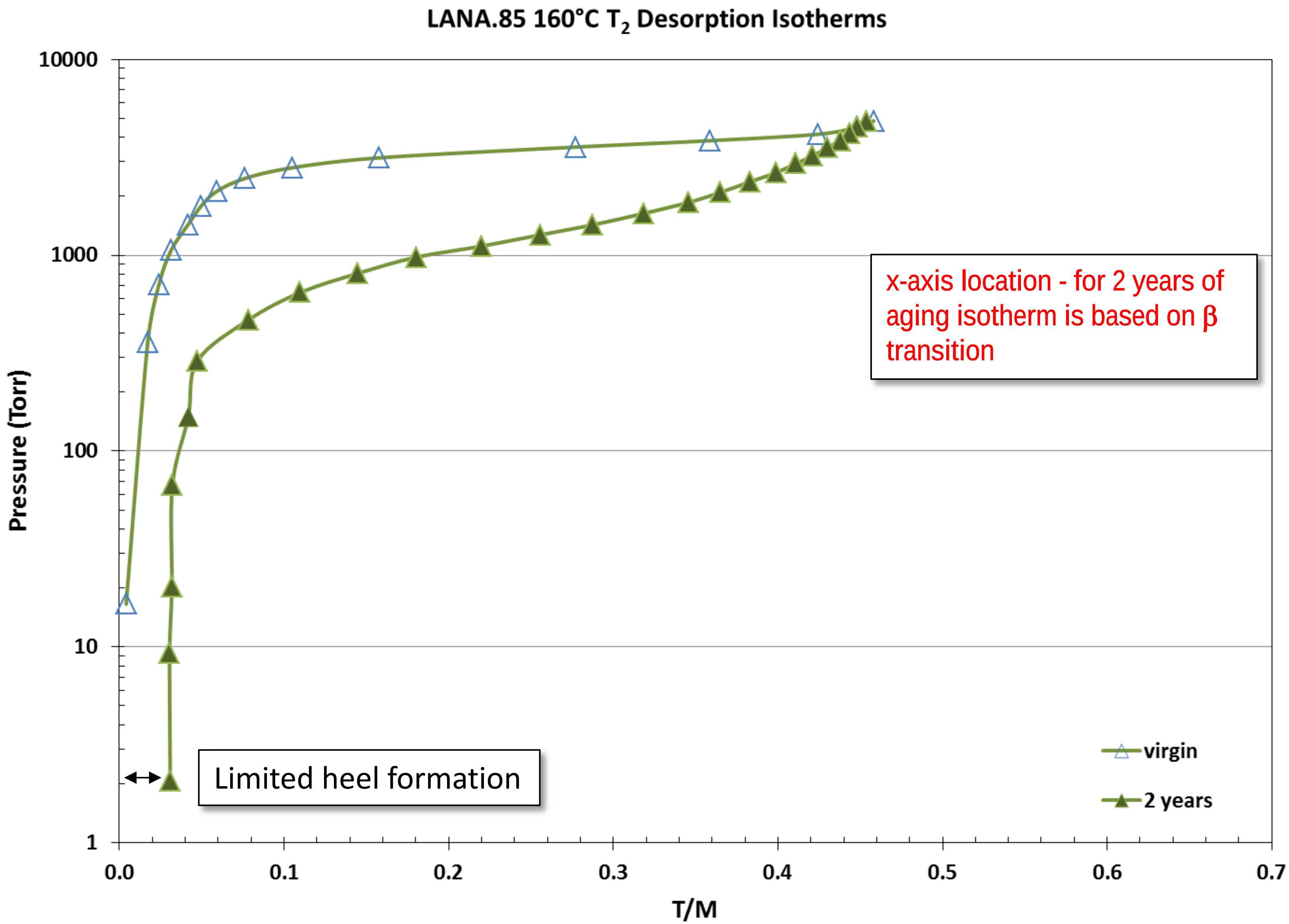


Results: Desorption Isotherms 2 years of Aging

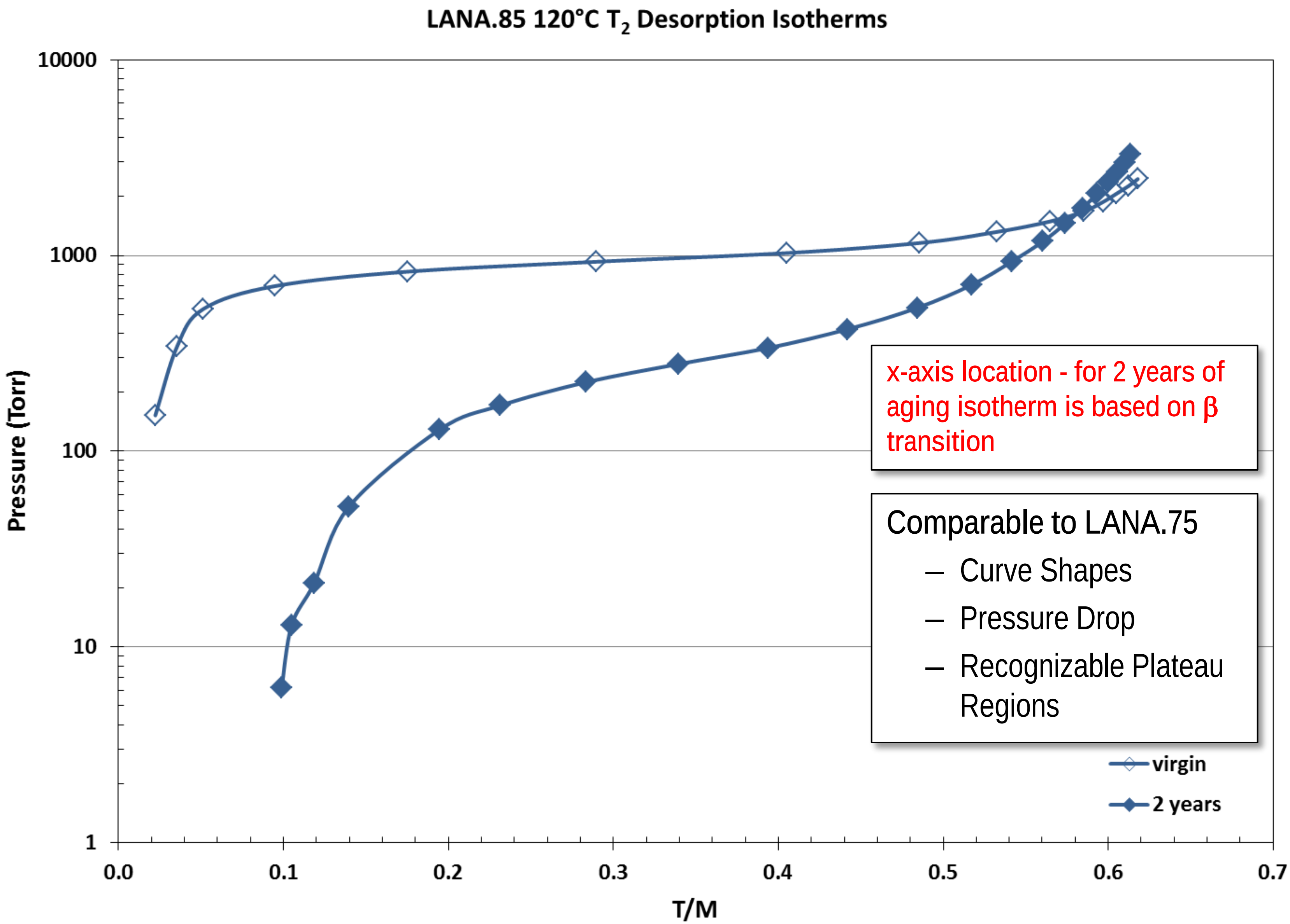
- T/M Location is approximate
  - Overhead gas sample identified N_2
  - Loss of material balance
  - Initial T/M based on β transition
- Intend to perform isotope exchange to re-establish material balance this upcoming year
- LANA.85 has expected isotherm shape



Results – 160°C Desorption Isotherms



Results – 120°C Desorption Isotherms



Tritium Aging Studies Summary / Path Forward

- Restoration of the material balance in both cells is expected next year through a partial isotope exchange followed by gas analysis.

- Two years of tritium aging data have been collected on LANA.85.

  – LANA.85 is comparable to LANA.75
    - *Limited Heel formation based on 160°C Isotherm*
    - *Pressure drop* ***not*** *unexpected*
    - *Isotherms show recognizable plateau regions*

- FISH bed service life is expected to be ~8+ years.

- Further evaluation is still recommended on an annual basis to track the effects of tritium exposure on both isotherm performance and ^{3}He evolution before this material is incorporated in full scale process beds.

SRNL - Acknowledgements

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- Contributions / Insights of / from:
  - Dante Pilgram (data Collection)
  - Kirk Shannahan (previous contributions to Deuterium data sets)

  - Gregg Morgan (technical review of PDRD report)

References/Related Documents

- Demina, S.V., et al., *Helium-3 Impact on the Equilibrium Pressures of La-Ni-Al Tritides*, in *Hydrogen Materials Science and Chemistry of Metal Hydrides*, M.D. Hampton, et al., Editors. 2012, Springer Science & Business Media. p. 237-241.

- Heung, L.K., "RTF Hydride Bed Technical Operating Guide", WSRC-TR-93-140 (1993).

- Staack, G.C., S.E. Murph, and D.W. James, Tritium Aging Studies on $LaNi_{4.15}Al_{0.85}$ (LANA.85) Metal Hydride - Year 3 SRNL-STI-2015-00505. 2015, Savannah River National Laboratory: Aiken, SC.

- Staack, G.C., and S.E. Murph, Virgin Material Characterization of $LaNi_{4.15}Al_{0.85}$ for FISH Bed Applications SRNL-STI-2013-00579. 2015, Savannah River National Laboratory: Aiken, SC.