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Neutron Diffraction and Imaging of a Full-Scale Sodium Alanate Hydrogen Storage System

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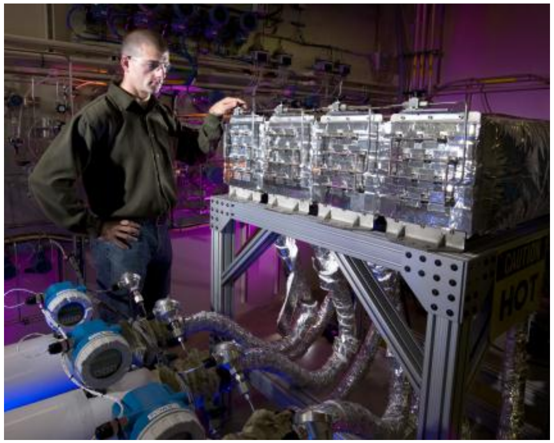
Presentation Outline

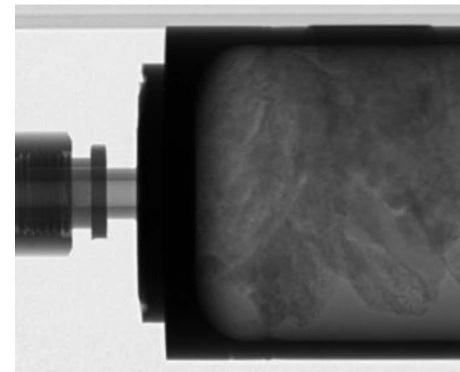
1) Overview of the Hydrogen Storage System



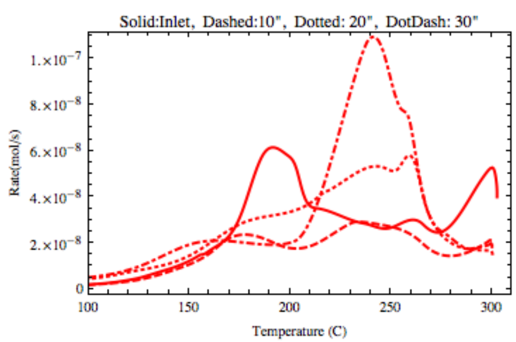
2) Motivation

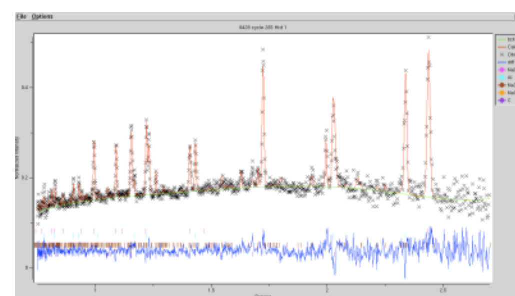
- Determine mechanism for capacity degradation
- Validate understanding of H_2 transport

3) Results: Physical Structure



4) Results: Chemical Structure





Overview of the GM/Sandia Hydrogen Storage System

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Sodium alanates were used as the hydrogen storage material for our engineering demonstration

Total Theoretical Capacity = 5.6 wt% hydrogen

$$NaAlH_4 \Rightarrow 1/3Na_3AlH_6 + 2/3Al + H_2 \Rightarrow NaH + Al + 3/2H_2$$

3.7 wt.% *1.9 wt.%*

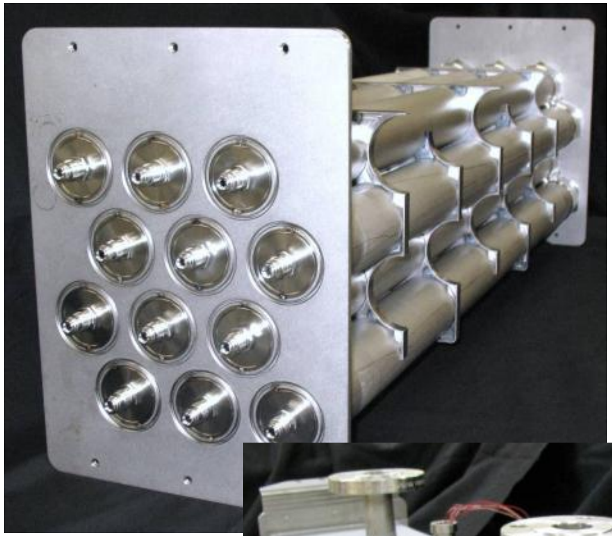
Our specific recipe:

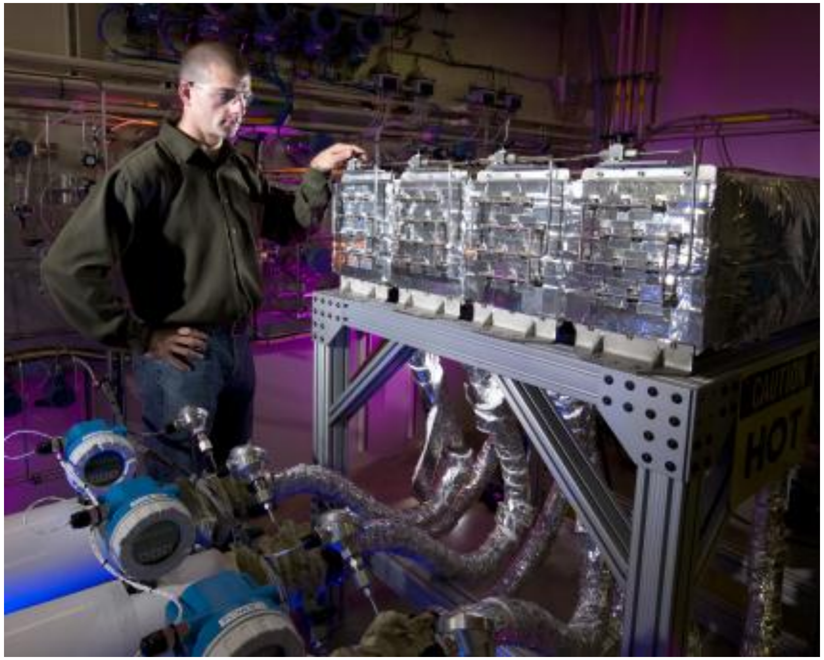
- NaH, Al, and $TiCl_3$ powders ball-milled
- 3 mol% $TiCl_3$
- Enhanced thermal conductivity
  - Extra Al, Graphite (ENG) mixed in
- 1 g/cc packing density
- Sintered porous solid upon cycling

Constituent Mass Fractions

Phase	Ti	Al	NaCl	NaH	Na_3AlH_6	$NaAlH_4$	Graphite
NaH	1.9%	49.9%	7.0%	32.0%	0.0%	0.0%	9.1%
Hex	1.9%	37.4%	6.9%	0.0%	44.8%	0.0%	9.0%
Tet	1.8%	13.3%	6.8%	0.0%	0.0%	69.3%	8.7%

3 kg H_2 system designed for mass and volume efficiency as well as simplicity and low cost



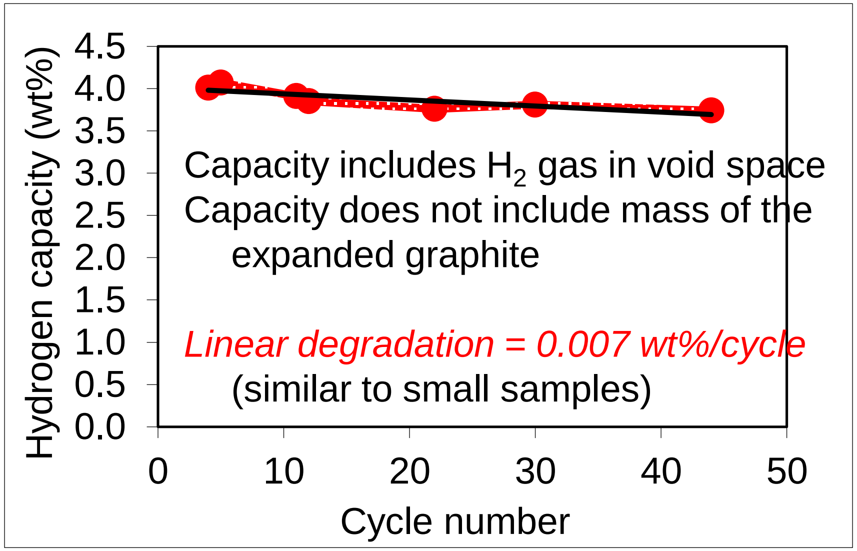


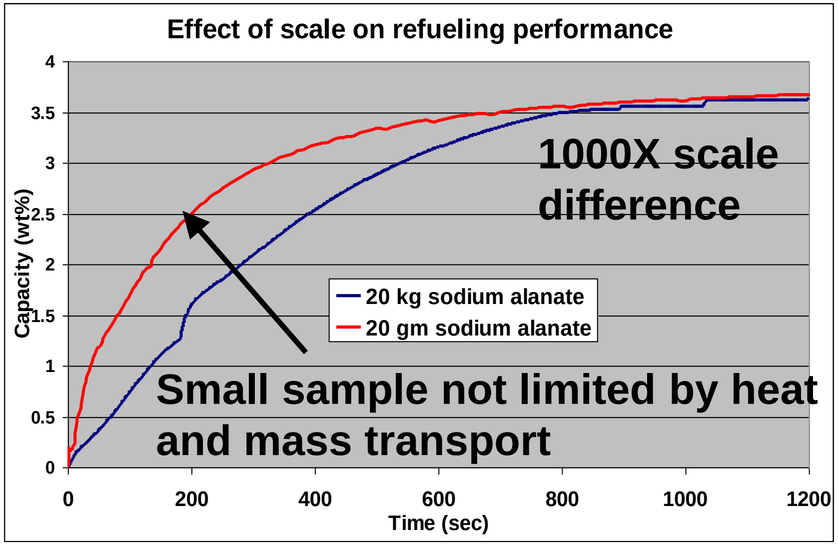
Extensive data collection:

- Pressure, mass flow
- 18 total external shell thermocouples
- 48 thermocouples installed into end caps
- 26 RTDs on tube surfaces

Motivation

Cycling showed capacity loss and effects of heat and mass transport limitations

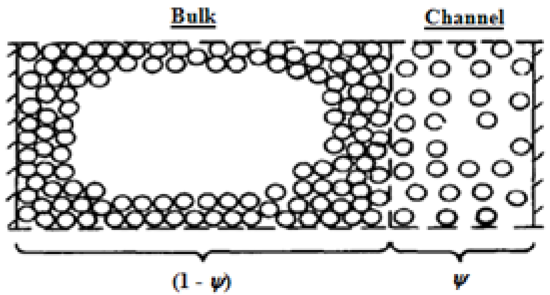




- Capacity loss similar to small samples
- Large-scale system heat and mass transport limited by design
- But, detailed explanation of capacity loss unknown and some transport mechanisms not well understood

Wall channeling added to hydrogen transport model required to explain experimental results

Wall channeling is a region of low density and high permeability near the vessel wall

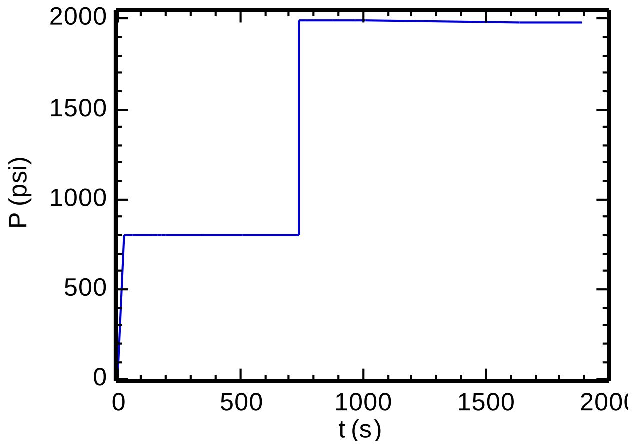


Mass transport ⇨ hydrogen pressure gradients

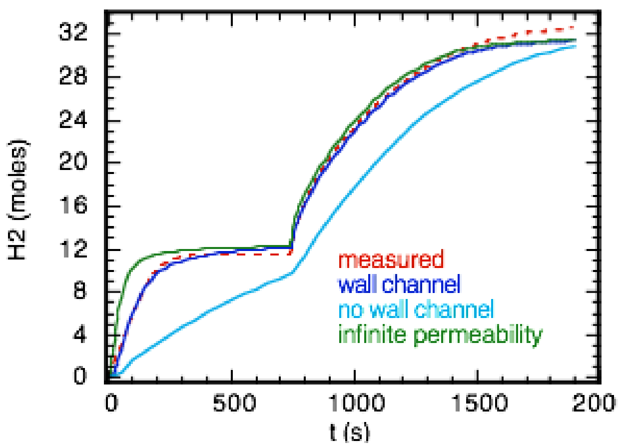
Heat transport ⇨ temperature gradients

Chemical kinetics f(P,T) ⇨ concentration gradients

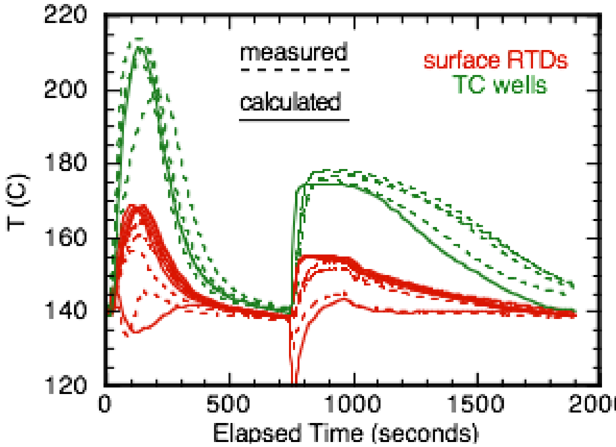
Measured pressure used for BC



Hydrogen Capacity



Temperature Response



Results: Physical Structure

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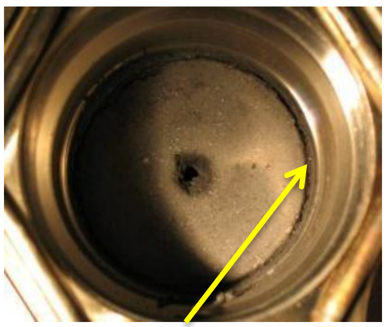
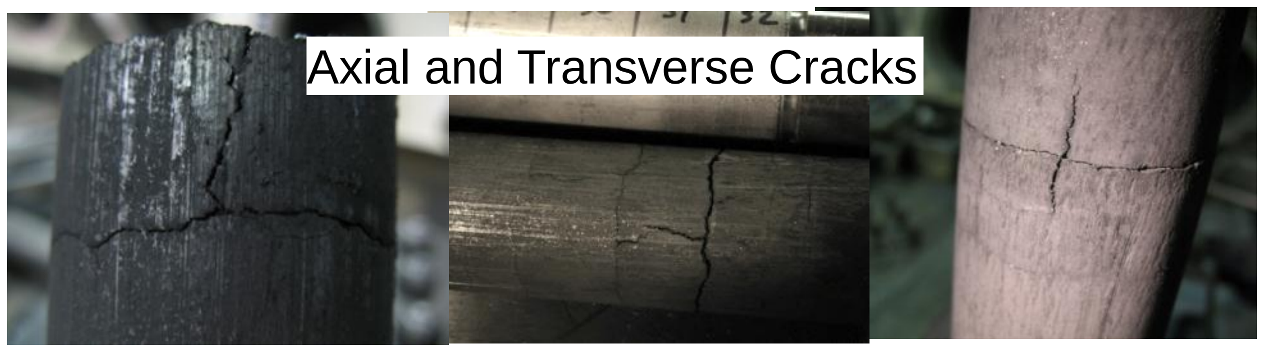
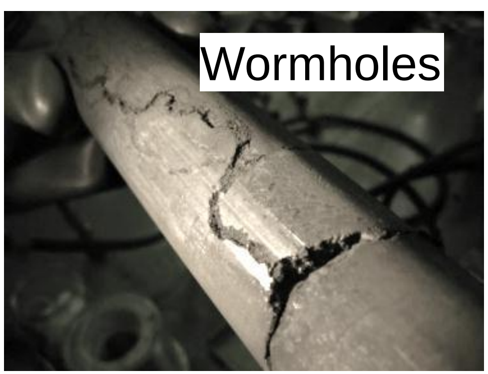
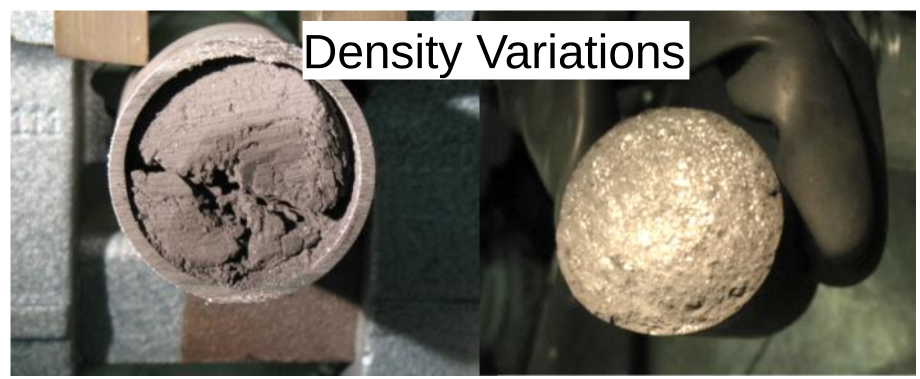
Tube sectioning confirms wall channel; reveals cracks, wormholes, and density differences



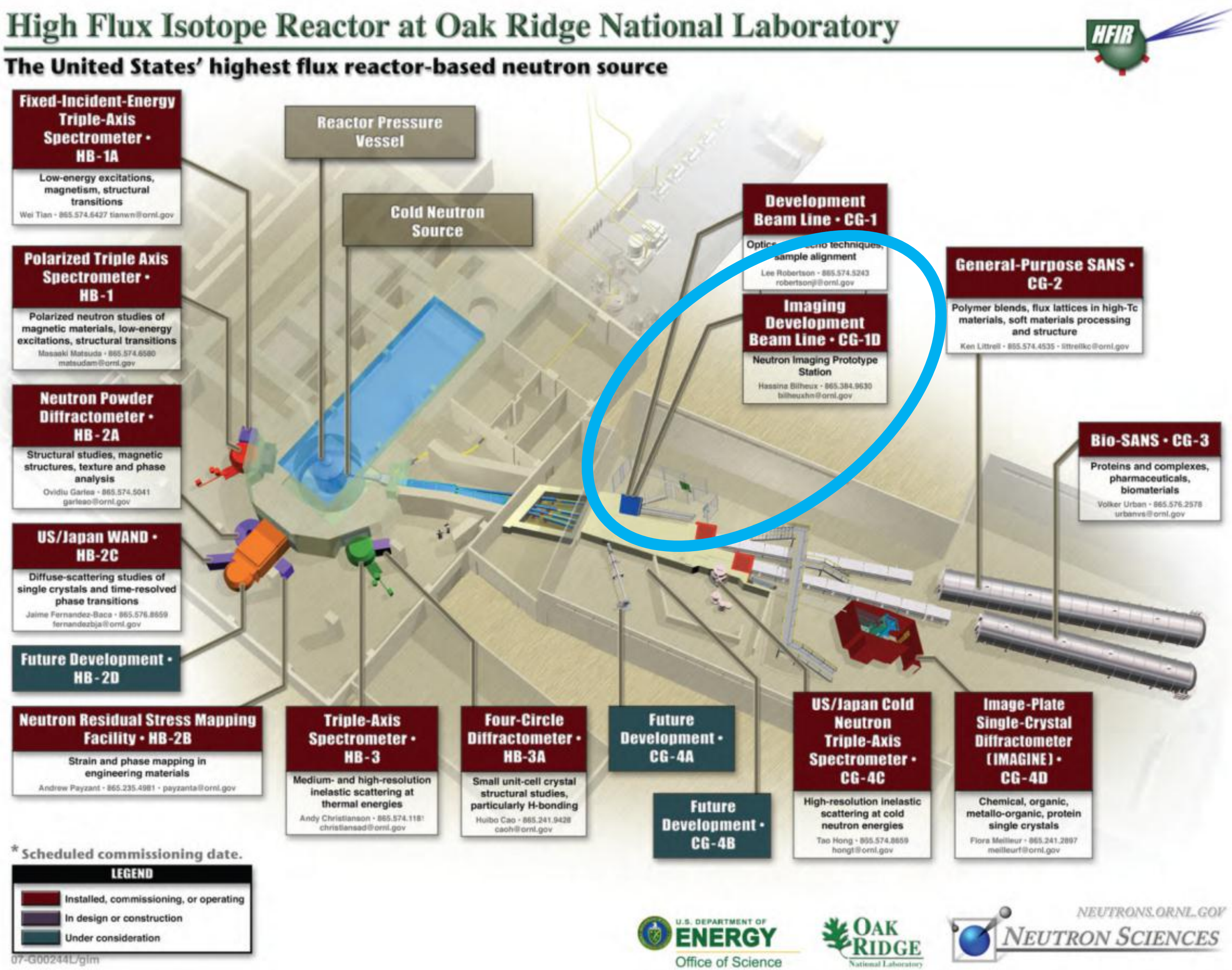
Wall channel



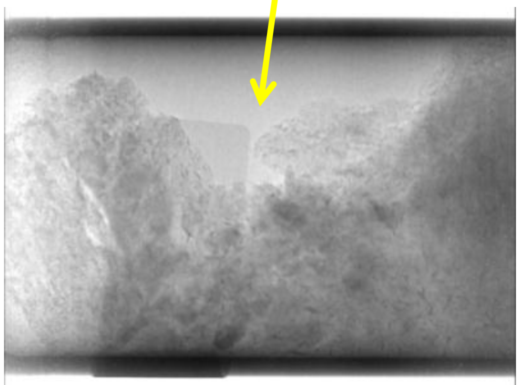




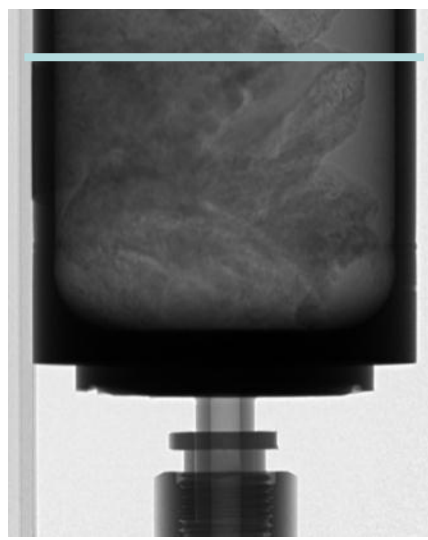
NDE: Neutron imaging was performed at ORNL's HFIR facility

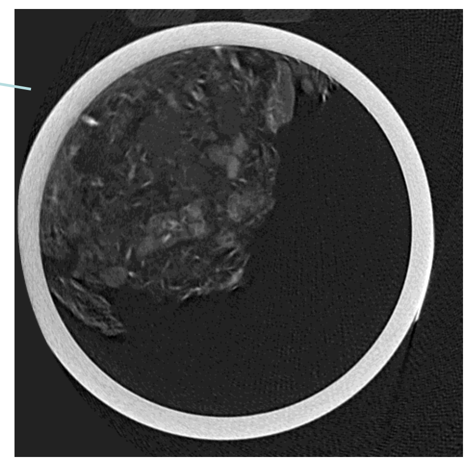


Radiography confirmed sectioning results



Voids and low density material found near inlet





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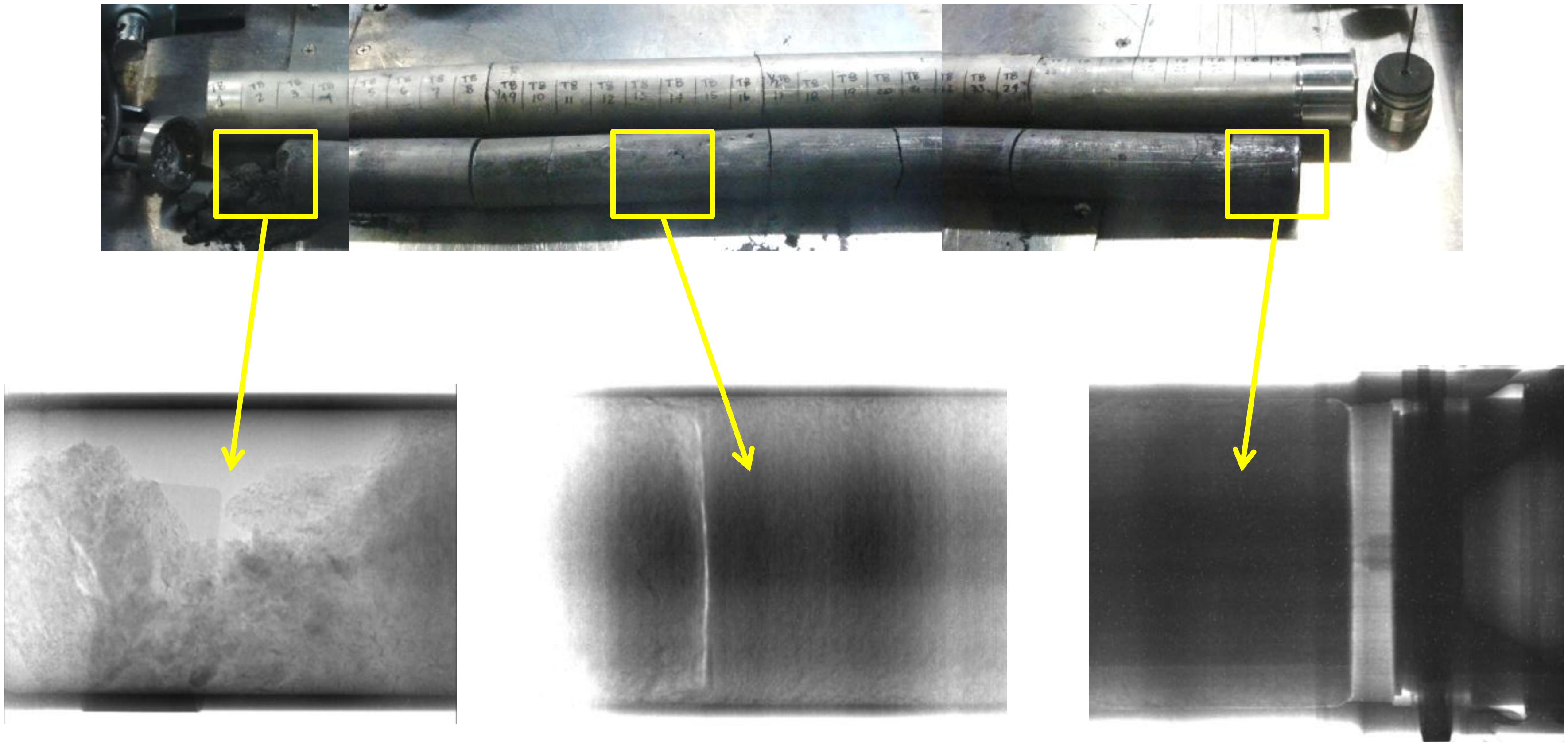

Voids and low density material found near inlet

Large transverse crack near middle

Evidence of wall channel

Results: Chemical Structure

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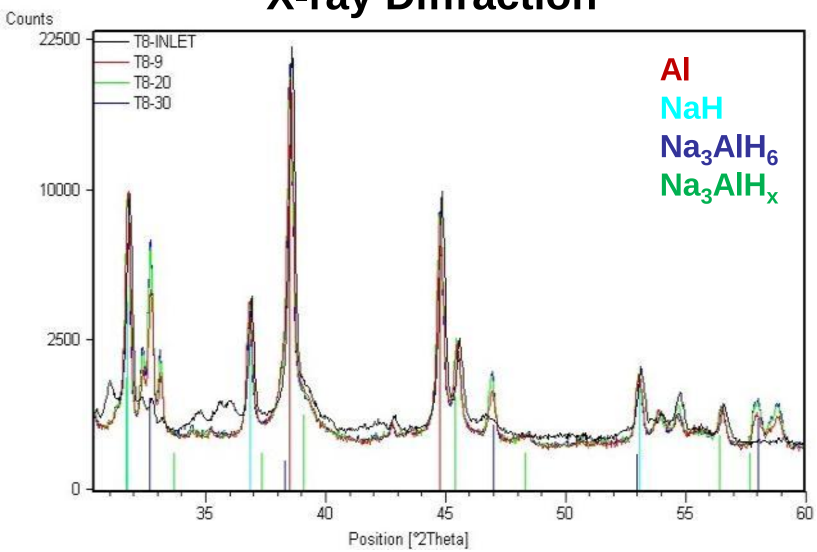
Analysis of cycled material showed "stranded" hydrogen increasingly toward far end of vessel

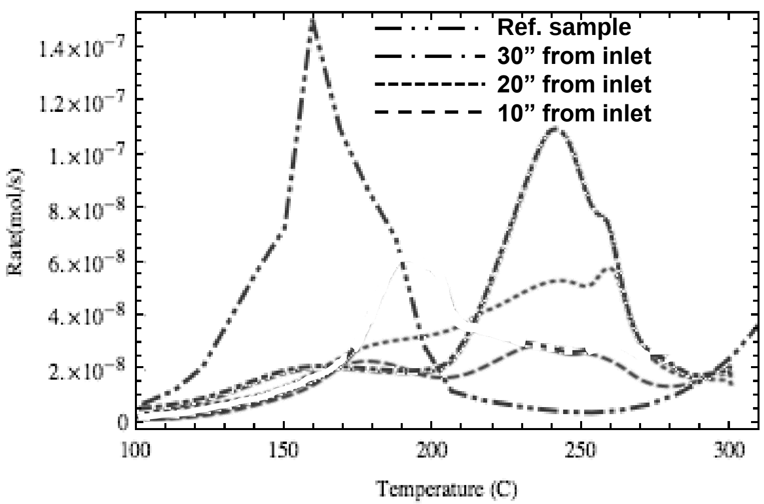
Samples taken from four locations at distances of 0, 10, 20, and 30 inches from the reactor inlet

X-ray Diffraction



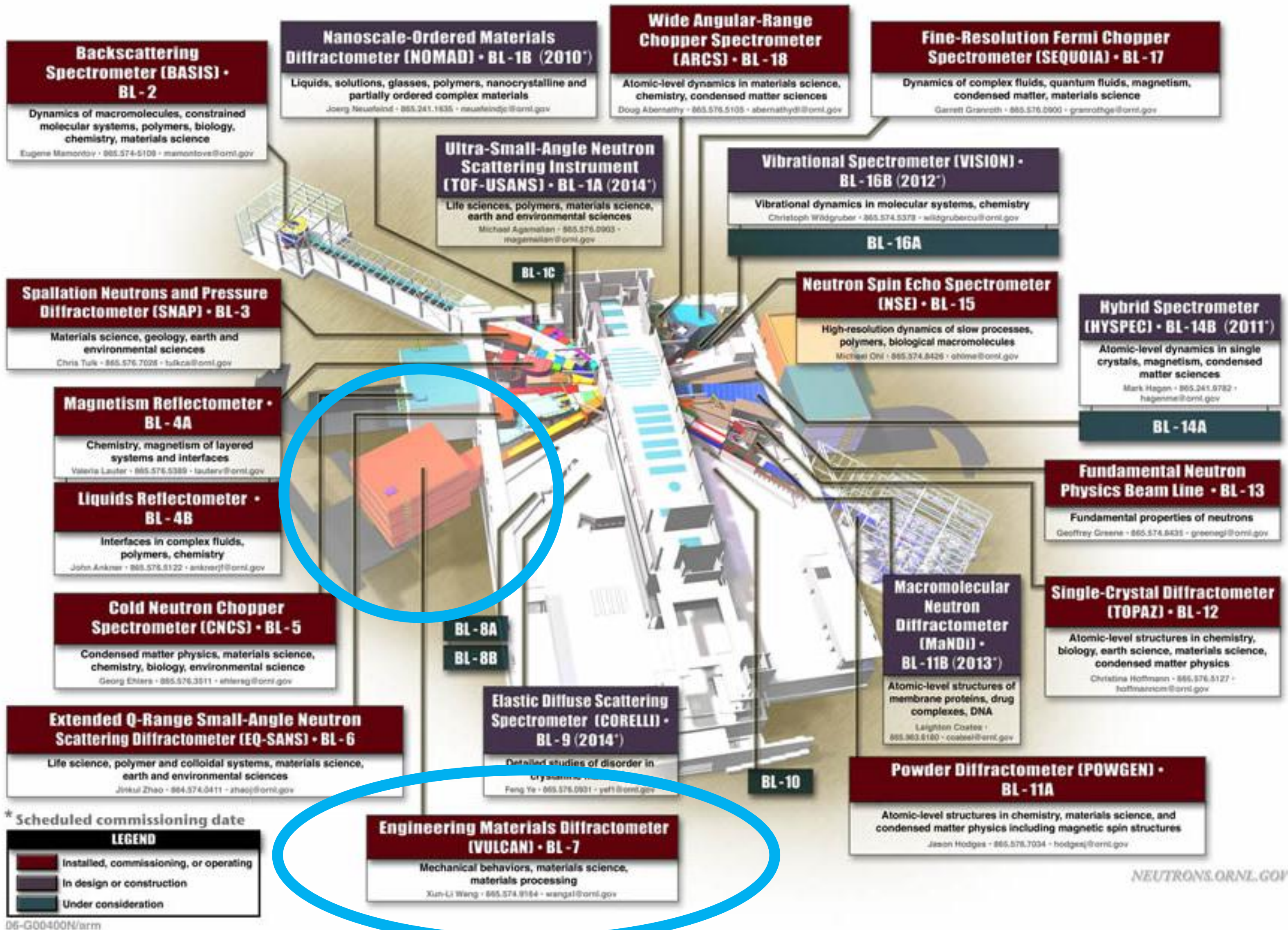
Hexahydride present in regions away from the inlet/outlet of the bed

TGA - Rate of H_2 evolution



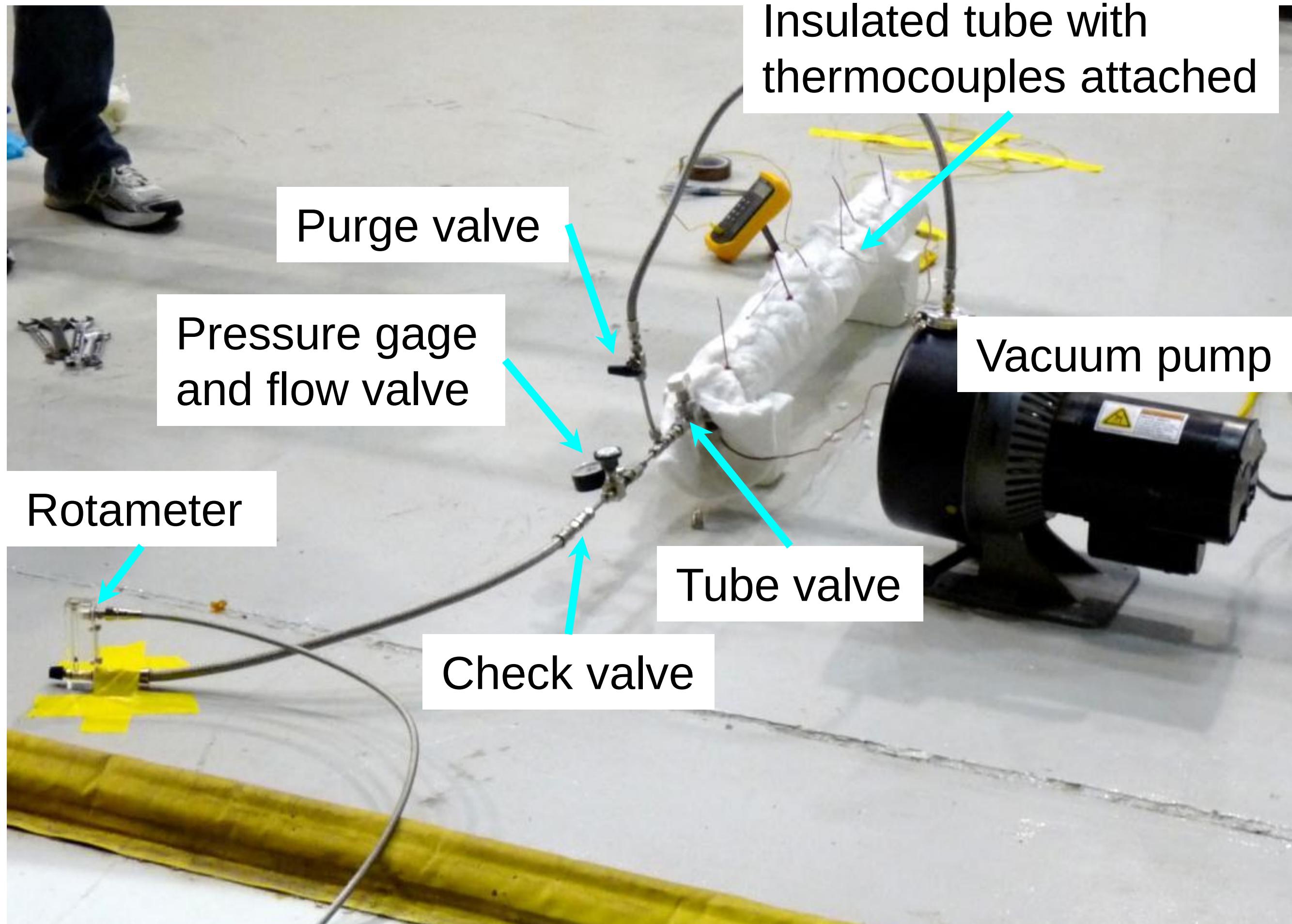
Results indicate that residual uncatalyzed Na_3AlH_6 exists in regions away from the inlet/outlet of the bed

NDE: Neutron diffraction was performed at VULCAN beamline at ORNL's SNS facility



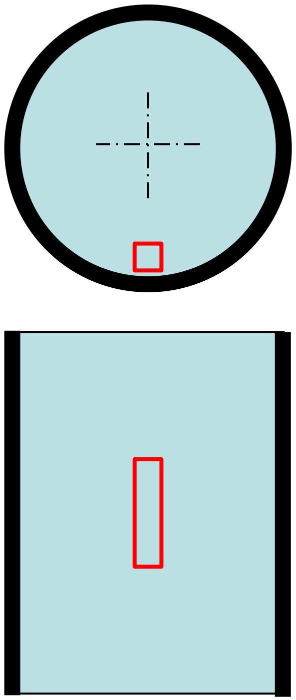
The vessel was measured in four states of fill by incrementally desorbing the H_2/D_2

Tape-type resistive heater

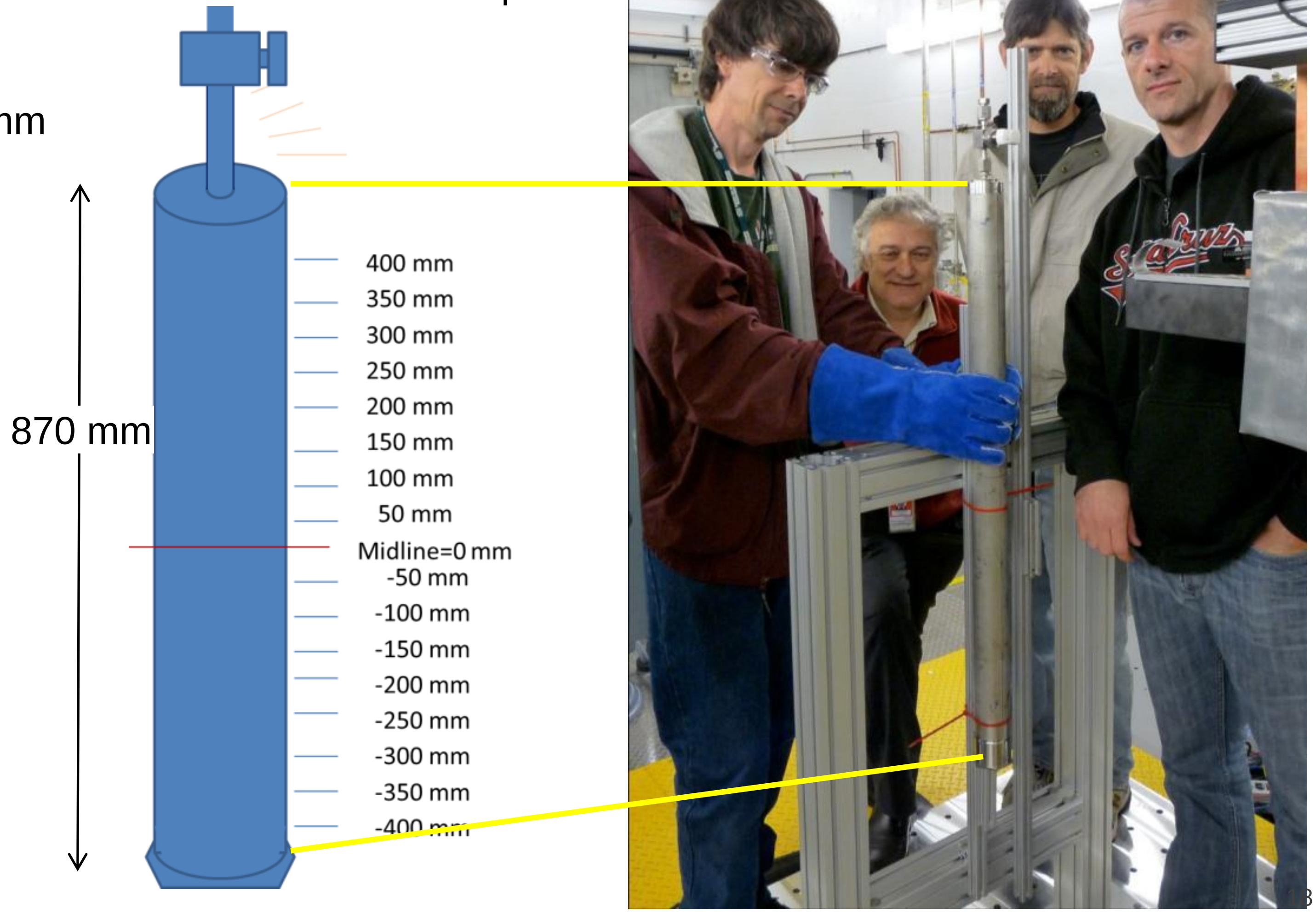


Neutron beam shape, scan locations, and scan time chosen based on experience and allotted time

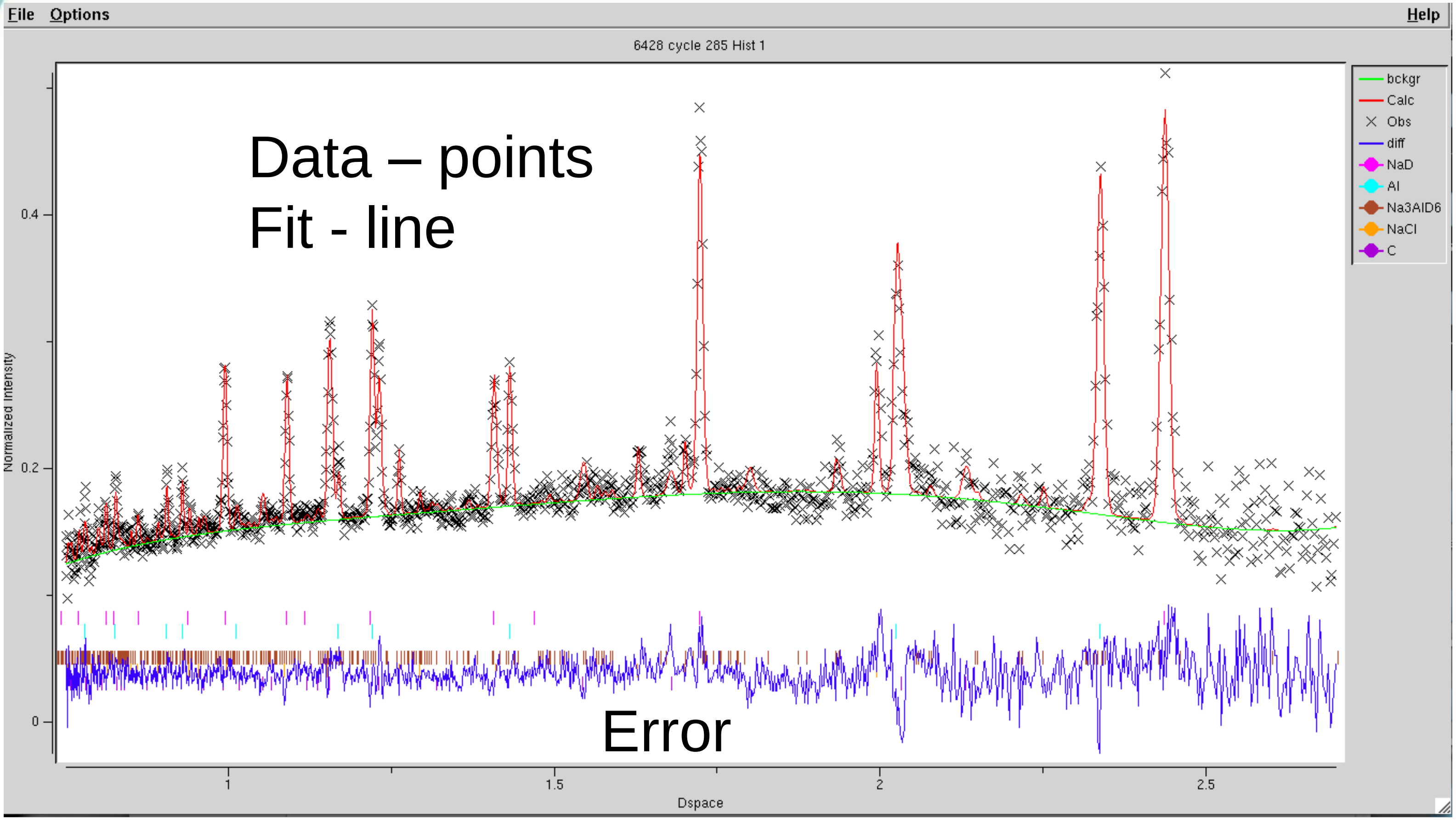
Neutron beam gage volume set by slits and detector to 5 x 5 x 20 mm



Hydride interrogated along the vessel axis in 50 mm steps



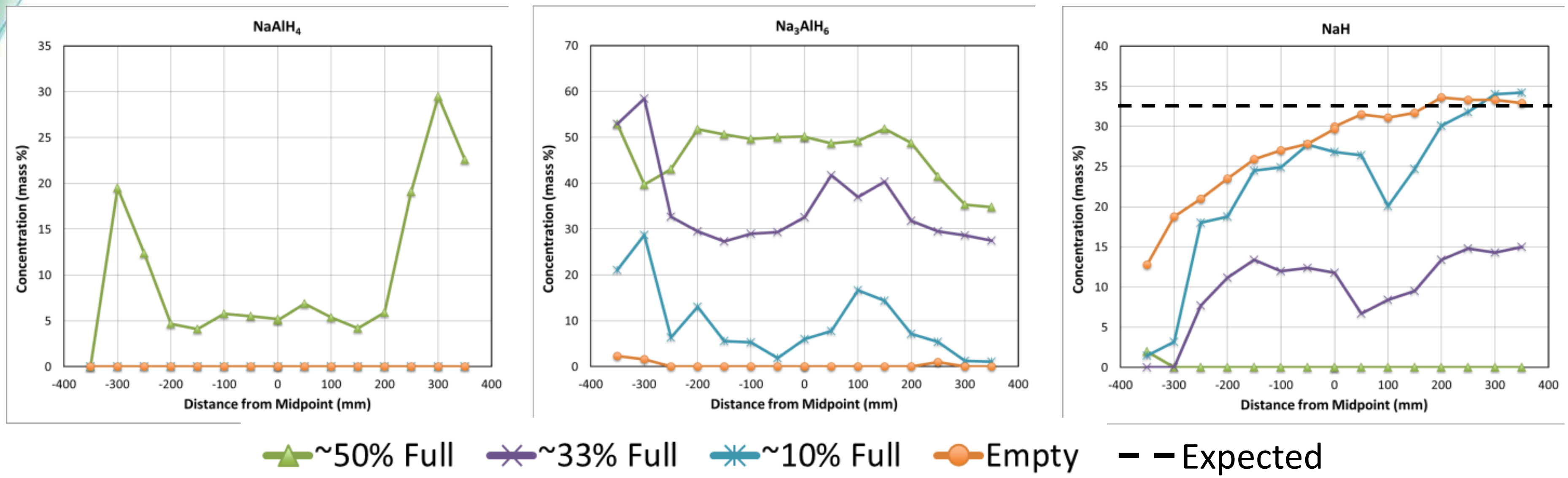
With 6 possible phases, refinement of the diffraction data was a challenge

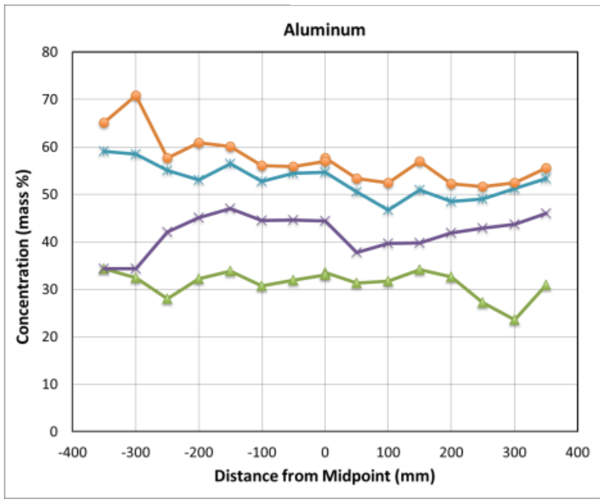


Phases
$Na(H/D)$
$Na_3Al(H/D)_6$
$NaAl(H/D)_4$
Al
C
NaCl

Plus the usual problems of finding correct reference spectra

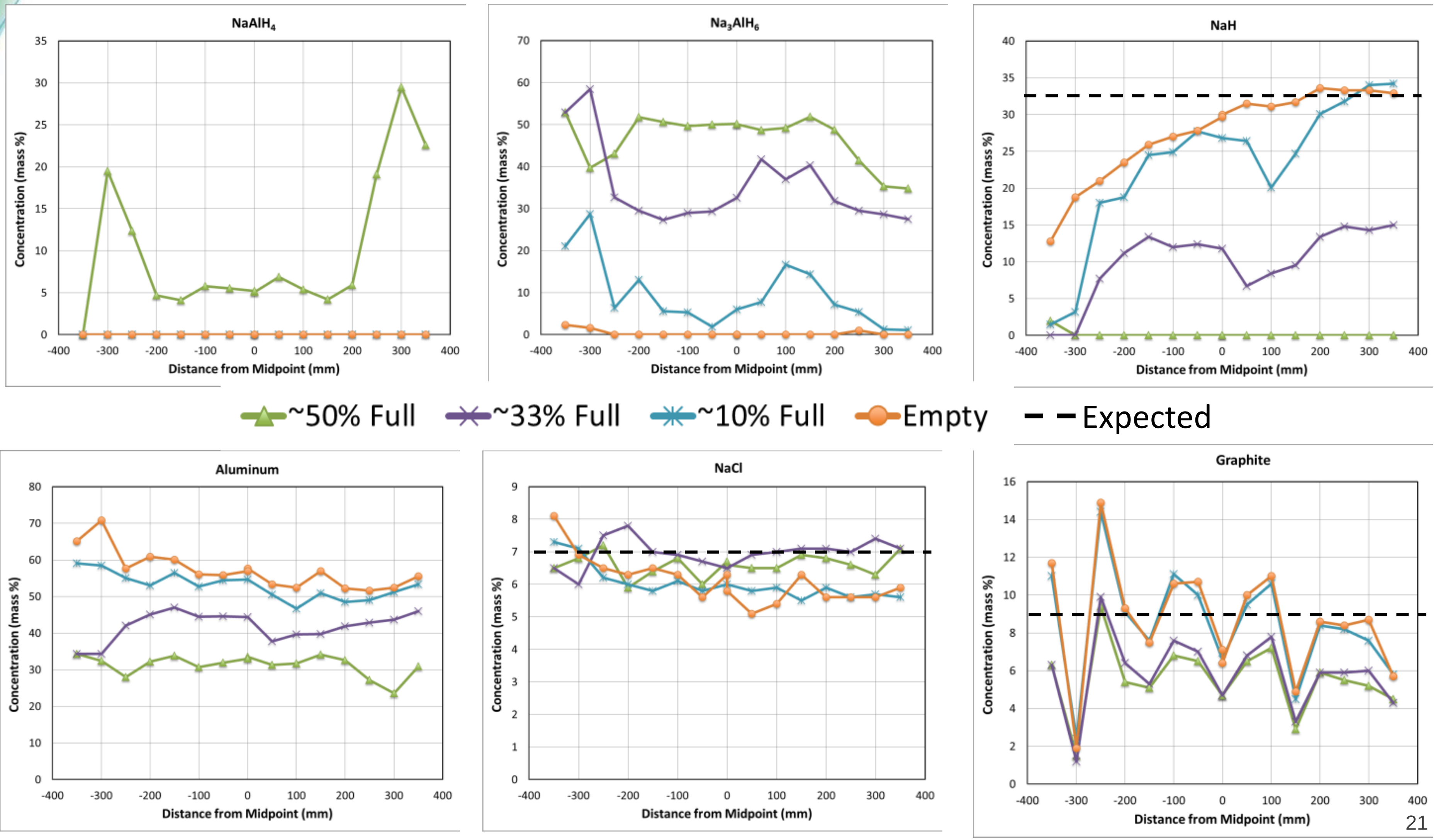
Refinement results show expected changes in species concentration with fill level; some unexpected results revealed





- Only tet and hex seen at 50% full
- Tet distribution unexpected
- Tet not seen on subsequent desorptions
- Peaks and valleys of Na species correspond, also aluminum
- Hex and NaH progression reasonable
- Non-uniform hex desorption likely due to temperature gradients

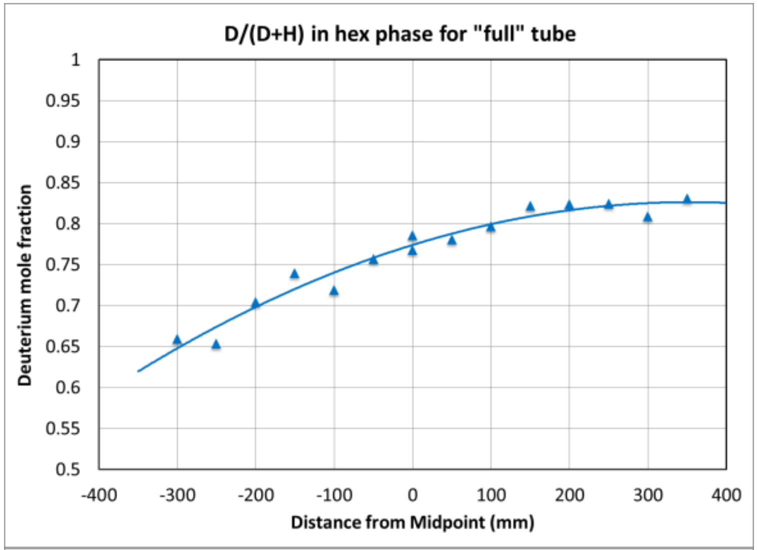
Refinement results show expected changes in species concentration with fill level; some unexpected results revealed



"Stranded" hydrogen theory supported by neutron diffraction results for NaH and D/H ratio

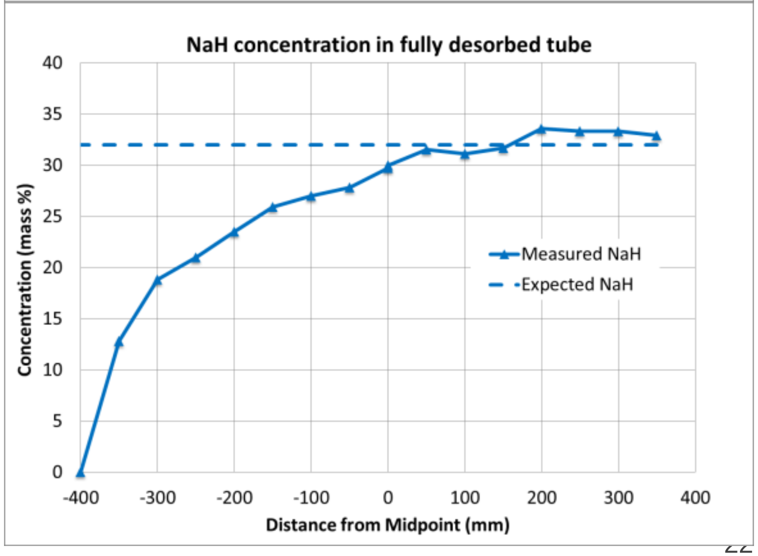
Result

- D/H ration from diffraction refinement shows increased H concentration at closed end
- NaH profile for empty state supports "stranded" hex phase
- Amount of inactive hex phase corresponds to capacity loss over 79 cycles of 0.55 wt%



Potential root causes:

- Contamination: Catalyst poisoning or reaction with Na phase
- Morphology change due to temperature or repeated cycling: catalyst segregation or particle growth/sintering



Summary and Conclusions

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General Summary: Combination of destructive and NDE methods were used successfully to explore H_2 transport and chemical species evolution in a vehicle-scale sodium alanate hydrogen storage system

Major Conclusions:

H_2 Transport:

Wall channeling model validated by tube sectioning; confirmed by neutron radiography

Both methods revealed other large-scale structures such as cracks, wormholes, and density variations that could affect H_2 transport

Capacity Degradation:

Analysis points to stranded H_2 in inactive hex phase

- Neutron imaging, TGA and D/H ratio point to stranded H_2
- XRD and neutron diffraction showed hex phase at far end of “empty” samples
- TGA showed significant H_2 evolution at T > 210 C indicative of un-catalyzed hex phase

Summary and Conclusions

Overall

Neutron-based techniques are effective NDE tools for characterizing metal hydride hydrogen storage systems

Acknowledgements

Well Deserved Thanks

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At Sandia

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At GM

- H_2-program management

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