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Investigation of Metal and Chemical Hydrides for Hydrogen Storage in Novel Fuel Cell Systems

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Project #ST134

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Overview

Timeline and Budget

- Project Start Date: 3/1/2015
- FY15 DOE Funding: $100K
- FY16 DOE Funding: $250K
- Total DOE Funds Received to Date: $350K*

* Additional Federal (ONR) Funding: $50K

Partners

- Naval Undersea Warfare Center (Newport)
- Office of Naval Research
- Ardica Technologies, LLC

Barriers

A. System Weight and Volume
B. System Cost
C. Efficiency
D. Durability
E. Charging/Discharging Rates
G. Materials of Construction
H. Balance of Plant (BOP) Components
J. Thermal Management
K. System Life-Cycle Assessment
O. Hydrogen Boil-Off
P. Understanding Physi/Chemi-sorption
S. By-Product/Spent Material Removal

Relevance

DOE Funded Activities

Objectives:

- Use engineering analyses to screen H2 storage systems against DoD targets & requirements (FY15)
- Identify suitable hydrogen storage materials and suitable vehicle demonstration platforms
- Develop a preliminary design of an integrated UUV design with a solid hydrogen storage system
- Complete detailed design of the hydrogen storage system
- Complete integrated system design

ONR/NUWC Funded Activities

Objectives:

- Design and build a small bench-scale, alane-based, hydrogen storage vessel
- Perform preliminary testing on the bench-scale, storage system
- Package and ship bench-scale vessel and alane material to the Navy NUWC
- Provide technical support to Navy NUWC for their further testing and evaluation

Impact:

- The ability to identify suitable hydrogen storage materials and use them in a viable design has implications in many other fuel cell applications.
- This project is based on the experience gained from the HSECoE and builds on the core capabilities of SRNL and positions SRNL and DOE to leverage its previous experience to new roles, which include the rapidly growing fuel cell areas for portable power and material handling equipment.
- Extension of many aspect of this program to scooters, motor cycles and even to light duty vehicles are expected.
- This project also provides the basis to extend a long-term partnership between DOE and the DOD in hydrogen and renewable energy systems.

Approach

- The overall approach of this research is to develop a methodology that incorporates engineering modeling and analyses to efficiently screen, design and select storage materials and material systems against cost and performance targets leading to an initial system design for an Unmanned Underwater Vehicle (UUV) application.
- This methodology, which was initially developed by SRNL and applied to light-duty vehicle in the Hydrogen Storage Engineering Center of Excellence (HSECoE), requires updates and modifications for it to be useful for other hydrogen and FC applications.
- More specifically in this research, this methodology will be applied to UUVs to reduce design time and lead to a more cost effective and better performing final product.
- Maintaining this capability for DOE will attract other opportunities and projects in hydrogen and other gas handling areas. The modeling analysis, to be applied to this project, integrates various hydrogen storage system options with other system components, including fuel cell and vehicle performance models to evaluate and compare the overall performance of the onboard hydrogen storage system.

Accomplishments: Material Screening Analysis Criteria

Targets and Data (Gen1 system)	*Waste heat available (Gen1 system)*
System volumetric capacity = 3% • Usable hydrogen to be stored = 2kg • Available volume = 66 L (18.5" x 15")	**Latent heat (average) from H_2O_2 reaction condensing steam = 43.9 MJ** • Mission time = 30 hours • Total mass of water available = 29 L • Steam fraction = 0.78 • Temperature = 210 °C • Pressure = 18 bar • Max (more) water sensible heat = 31.5 MJ
System gravimetric capacity = 3% • Usable hydrogen to be stored = 2kg • Storage system weight = 66 kg	
Cost = +1000 $/kg of hydrogen	Heat (average) from FC byproduct water = 4.08 MJ • Mission time = 30 hours • Total mass of water available = 17.7 L • Temperature = 80 °C
H_2 average flow = 1.1 g/min • Based on FC efficiency of 50%	
H_2 peak flow = 2.1 g/min • Based on FC efficiency of 50%	Heat (average) from FC cooling water = 60.48 MJ • Mission time = 30 hours • Total mass of water available = variable • Temperature = 80 °C
H_2 delivery pressure = 2-20 bar	

Targets and Data (Gen2 system)	*Waste heat available (Gen2 system)*
System volumetric capacity = 5% • Usable hydrogen to be stored = 3.2kg • Available volume = 66 L (18.5" x 15")	**Latent heat (average) from H_2O_2 reaction condensing steam = 43.9 MJ** • Mission time = 30 hours • Total mass of water available = 29 L • Steam fraction = 0.78 • Temperature = 210 °C • Pressure = 18 bar • Max (more) water sensible heat = 31.5 MJ
System gravimetric capacity = 5% • Usable hydrogen to be stored = 3.2kg • Storage system weight = 66 kg	
Cost = 1000 $/kg of hydrogen	Heat (average) from FC byproduct water = 4.08 MJ • Mission time = 30 hours • Total mass of water available = 17.7 L • Temperature = 80 °C
H_2 average flow = 1.8 g/min • Based on FC efficiency of 50%	
H_2 peak flow = 3.8 g/min • Based on FC efficiency of 50%	Heat (average) from FC cooling water = 60.48 MJ • Mission time = 30 hours • Total mass of water available = variable • Temperature = 80 °C
H_2 delivery pressure = 2-20 bar	

Using military hydrogen storage targets similar to DOE targets – SRNL evaluated hydrogen materials against near-term (Gen1) and long-term (Gen2) application performance requirements.

Accomplishments: Material Screening Analysis

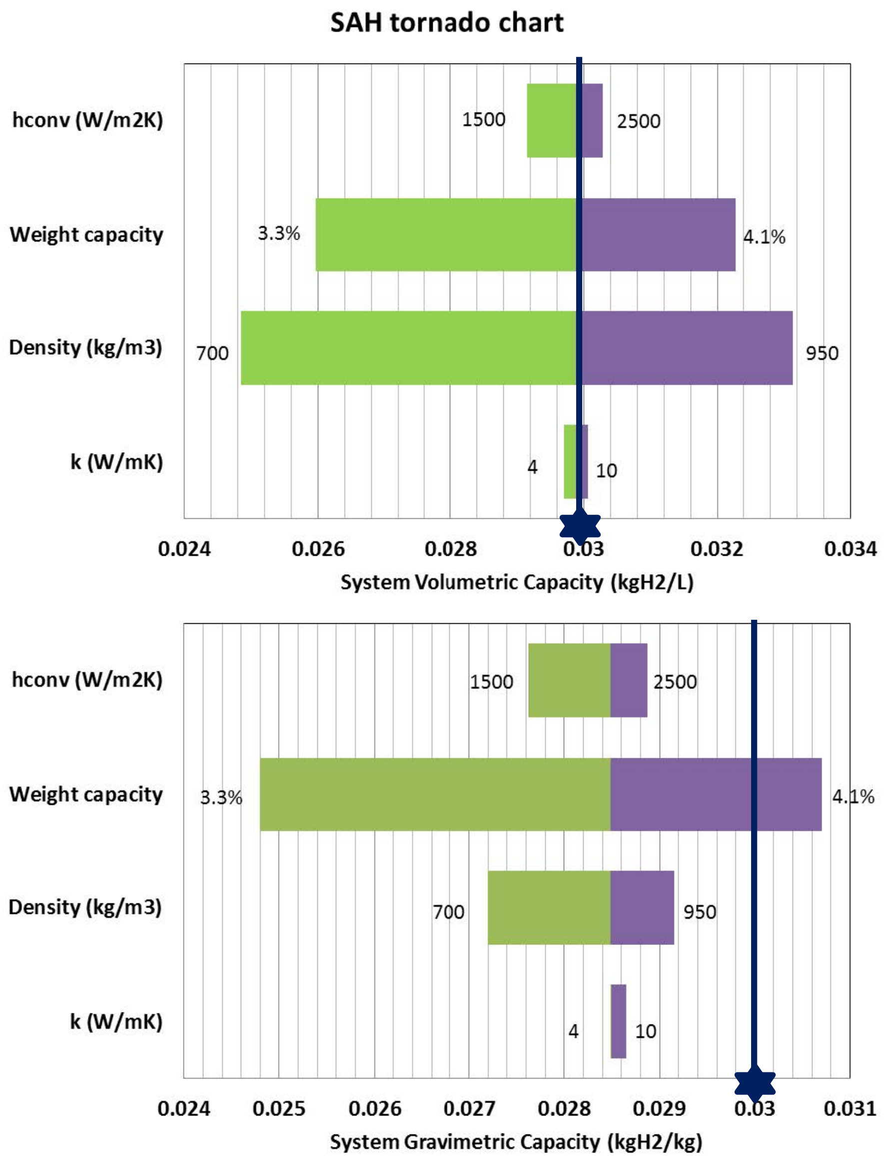
- **Material classes**
  1. Reversible low T MH (AB_5, AB, $NaAlH_4$)
  2. Reversible high T MH (Mg family materials)
  3. Non reversible MH (Alane, Mg alanate, LiMg alanate)

Gen1

Gen2

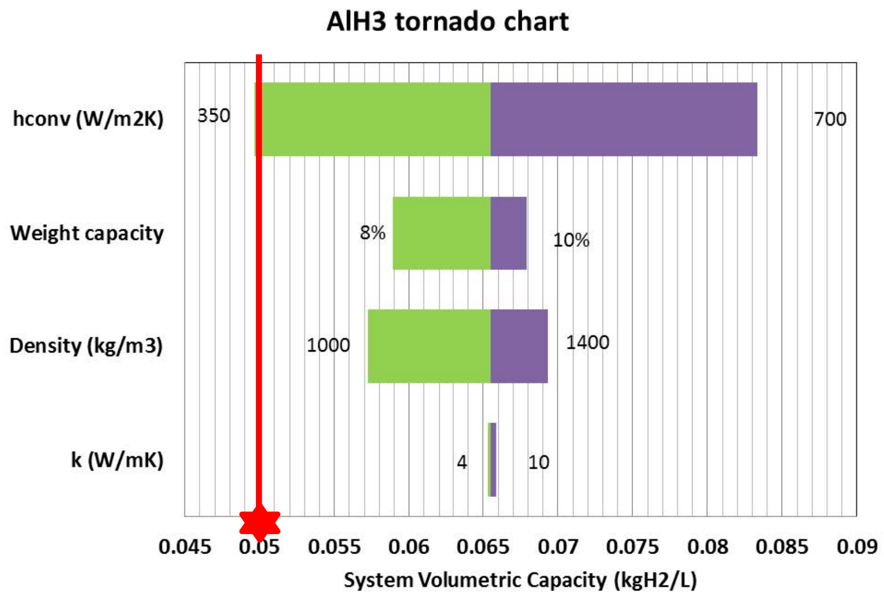
MH material	Operating T(°C)/P(bar)	Matl cost ($/kg)	Matl wf (kg_{H2}/kg_{MH})	Matl vf (kg_{H2}/L)	Enthalpy (kJ/mol_{H2})	Waste heat (kJ/mol_{H2})	Comment
AB_5 ($MmNi_5$)	50/12	35	1.1%	4.4%	30.5	64.1	Too low wf
AB (TiFe)	50/10	7	1.8%	4.5%	28	64.1	Too low wf
$NaAlH_4$	120/45	3.5	3.8-4%	3.3-3.5%	40	53.9	
Mg	360/10	4	6%	5.2%	75	-	Additional H2 to be burned
$Mg_2Ni_{0.75}Cu_{0.25}$	280/10	8.2	3%	6%	53	-	Additional H2 to be burned
AlH_3	80-120/25	*	9.5%	12.6%	11	35.3 (Gen1Sc=56.5)	Currently expensive
$Mg(AlH_4)_2$	130-170/30	*	8%	8%	1.5	31.4 (Gen1Sc=50.2)	Inexpensive matl; Step 1 + Hydrolysis
$LiMg(AlH_4)_3$	150/30	*	8%	8%	13.1	31.4 (Gen1Sc=50.2)	Two step material + hydrolysis
Targets (Gen1) **(Gen2)**	**P=2-20 bar** **P=2-20 bar**	**+1000** **1000**	**>3%** **>5%**	**>3%** **>5%**	-	-	

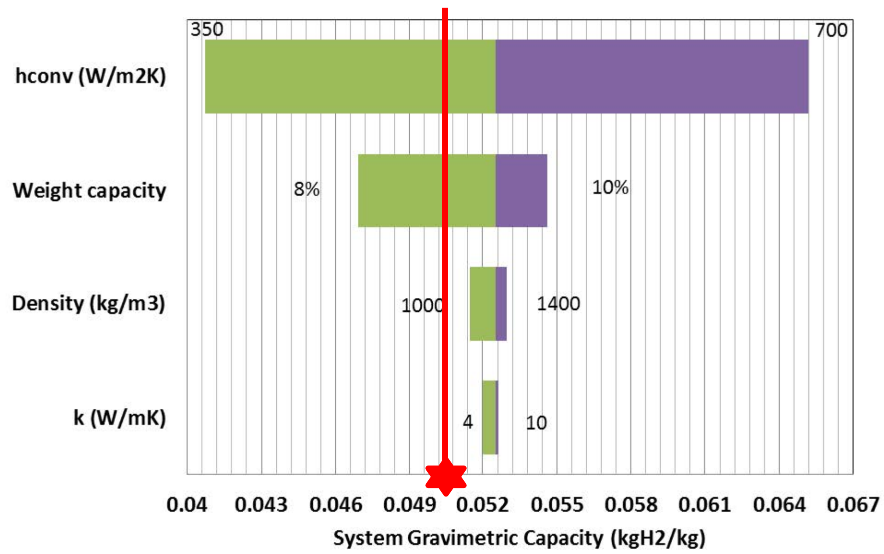
Accomplishments: $NaAlH_4$ material performance sensitivity analysis (Gen1)



- **The material shows good performance**
  - Gen1 target volume capacity (3%) achieved by mini-channel heat exchanger or enhanced heat transfer systems
  - It approaches the Gen1 gravimetric target (3%)
- **Significant influence of the material properties on the performance**

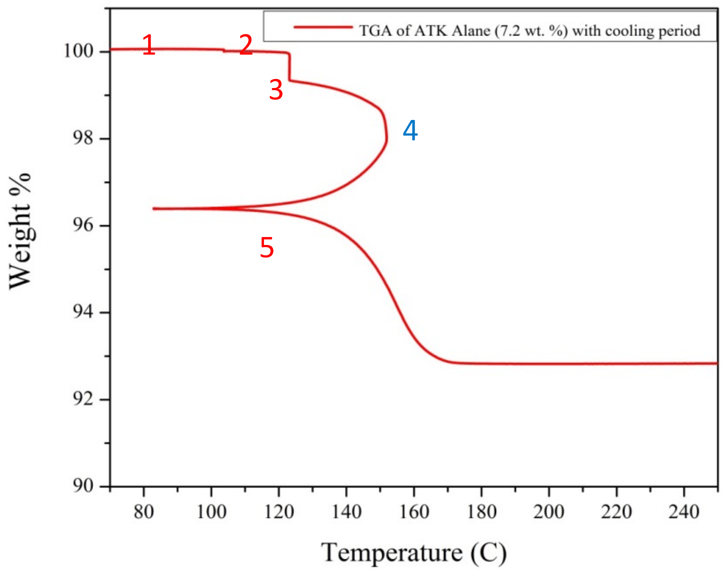
Accomplishments: AlH_3 material performance sensitivity analysis (Gen2)



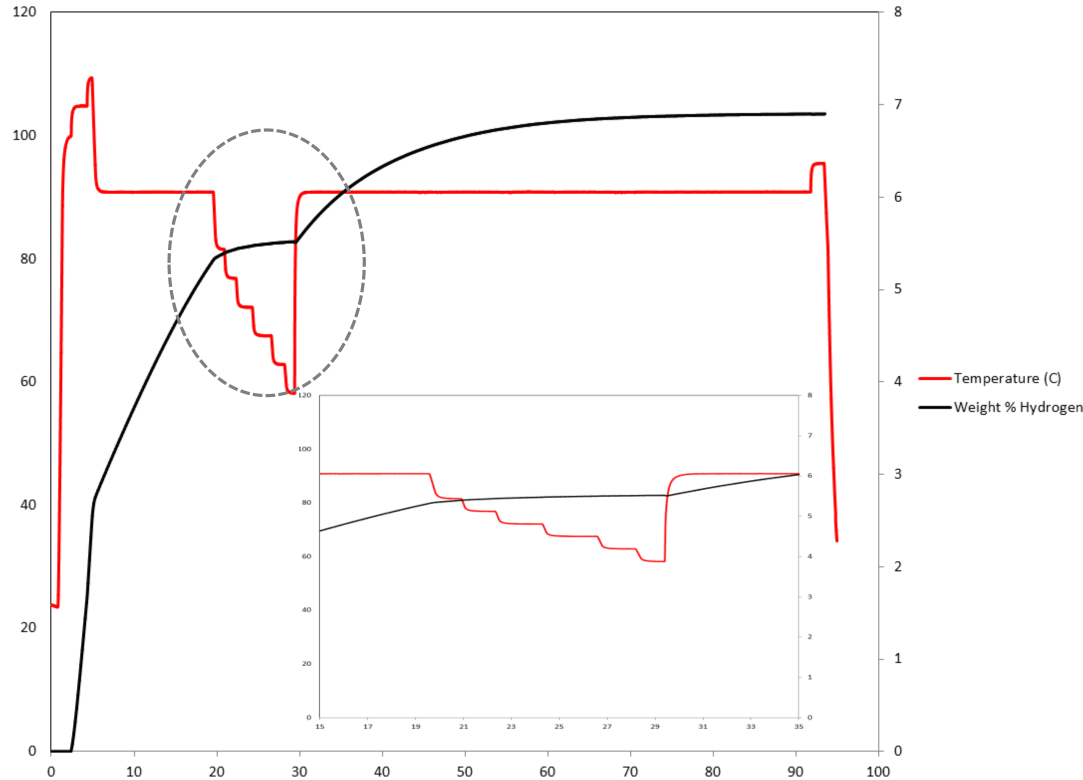


- **The material with 'normal' shell & tube, heat exchangers shows good performance**
  - Gen2 target volume capacity (5% kg/L) achieved
  - Gen2 gravimetric capacity (5%) achieved
- **Significant influence of the heat exchanger properties (mainly convective heat transfer)**
- **Main issues → making a lower cost material**

Accomplishments: SRNL Alane Decomposition – TGA/PCT Results



TGA of ATK α-Alane with 7.2 wt. % H_2 capacity



PCT/Sieverts' test with active heating no cooling

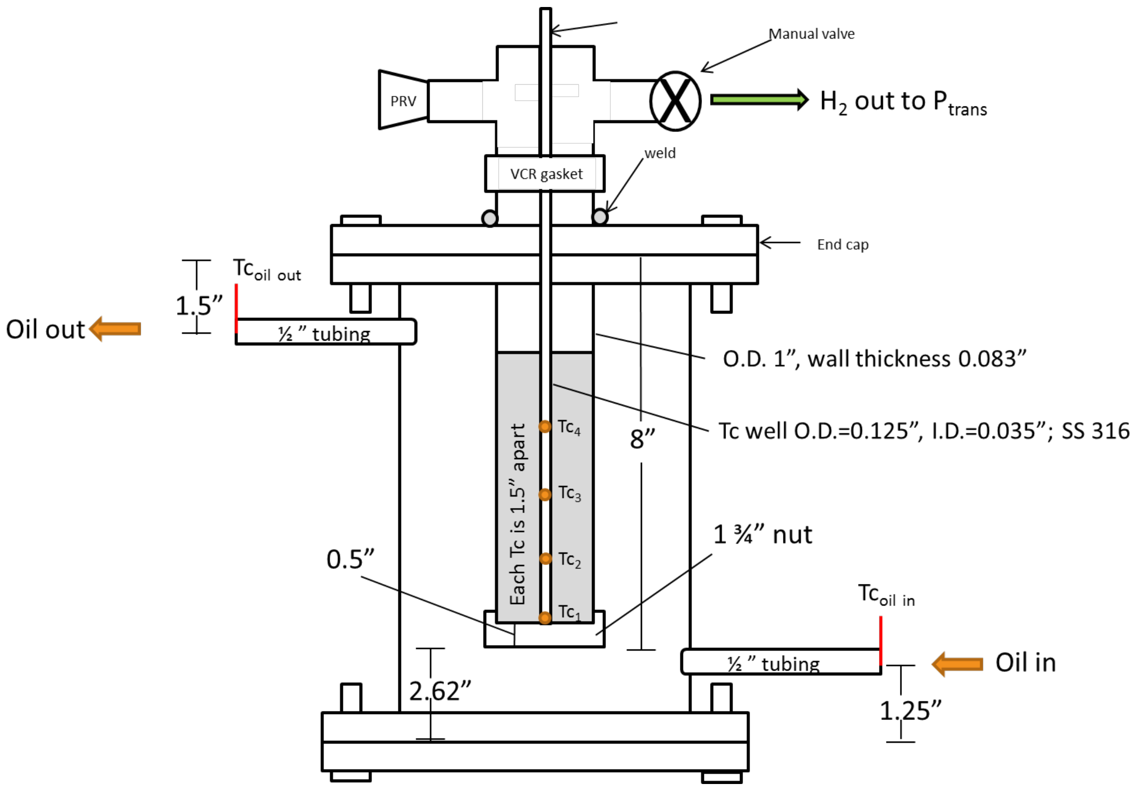
__Heating Conditions:__

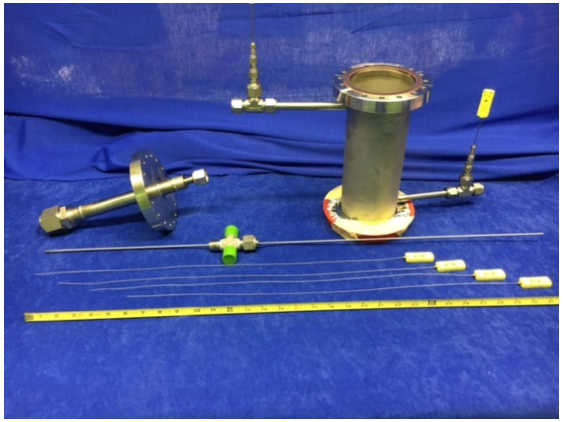
1) Heating 30°C to 100°C
2) Heating100°C to 120°C
3) Heating 120°C to 150°C
4) Cooling 150°C to 80°C
5) Heating 80°C to 300°C

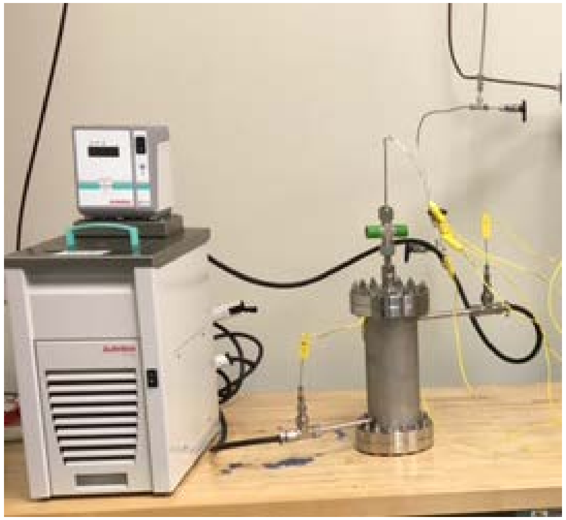
Even with passive cooling the rate of hydrogen release is significantly slowed and can be stopped.

Perkin Elmer Pyris 1 Thermogravimetric Analyzer

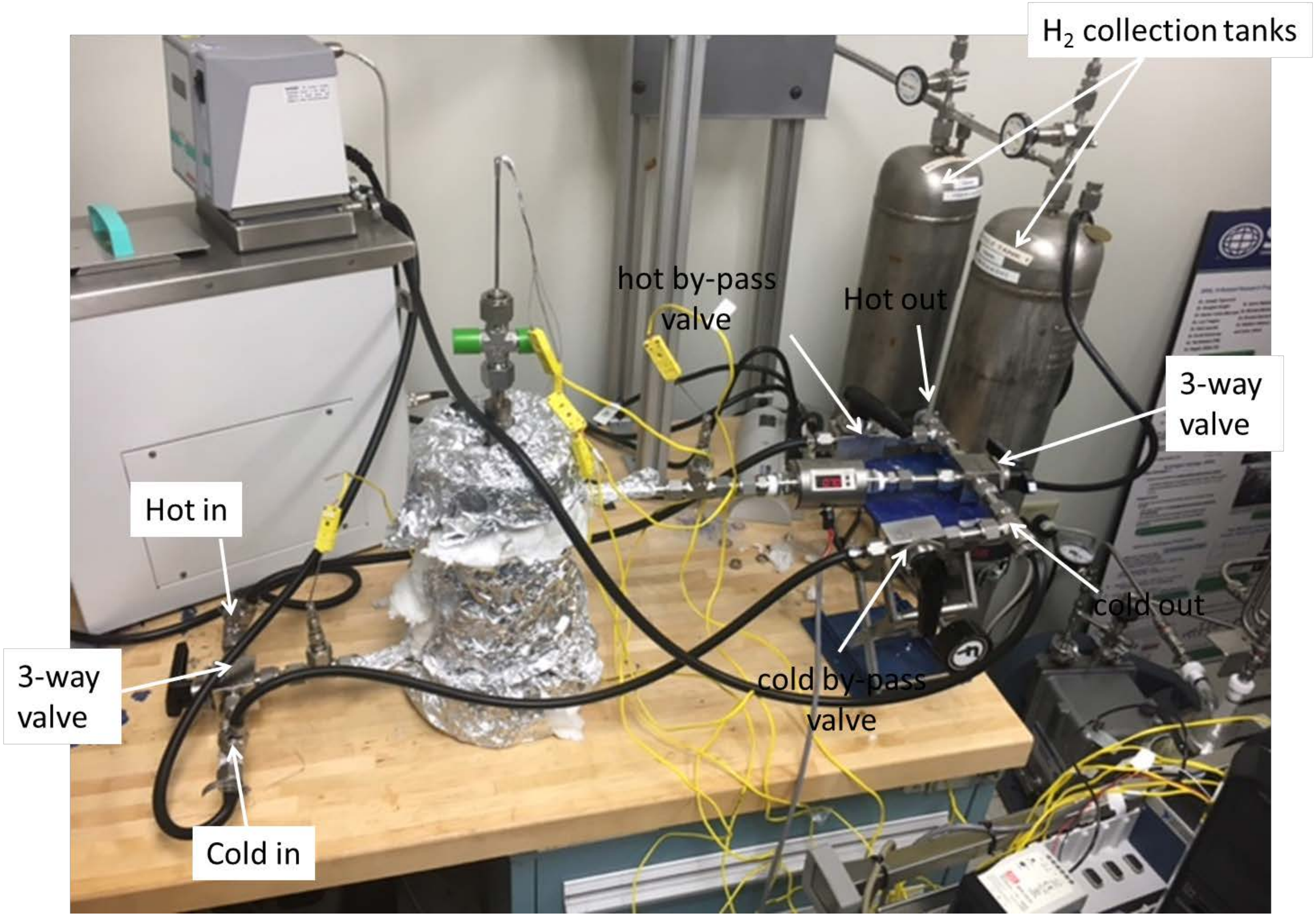
Accomplishments: SRNL Alane Test Vessel for ONR



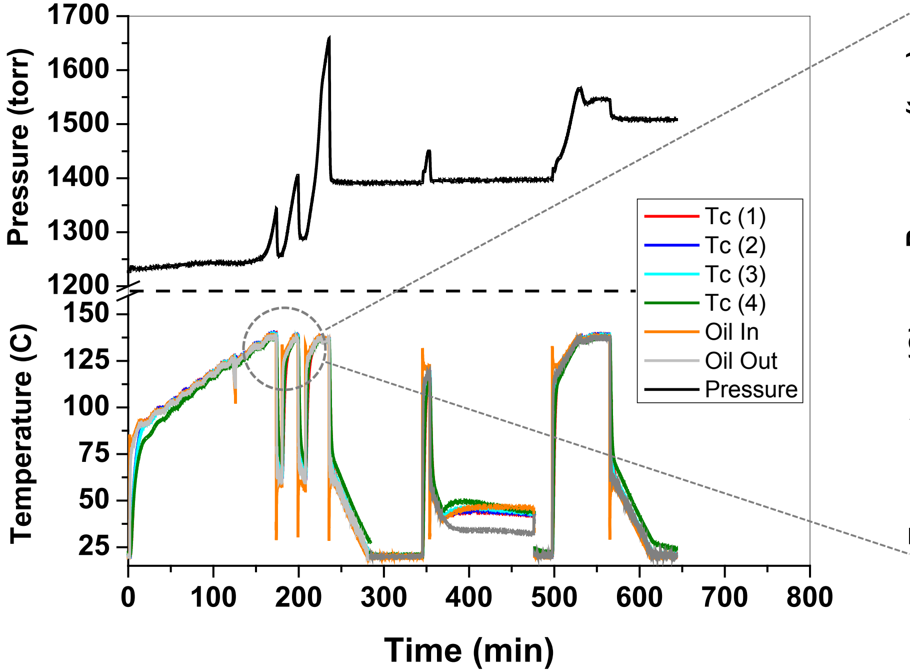


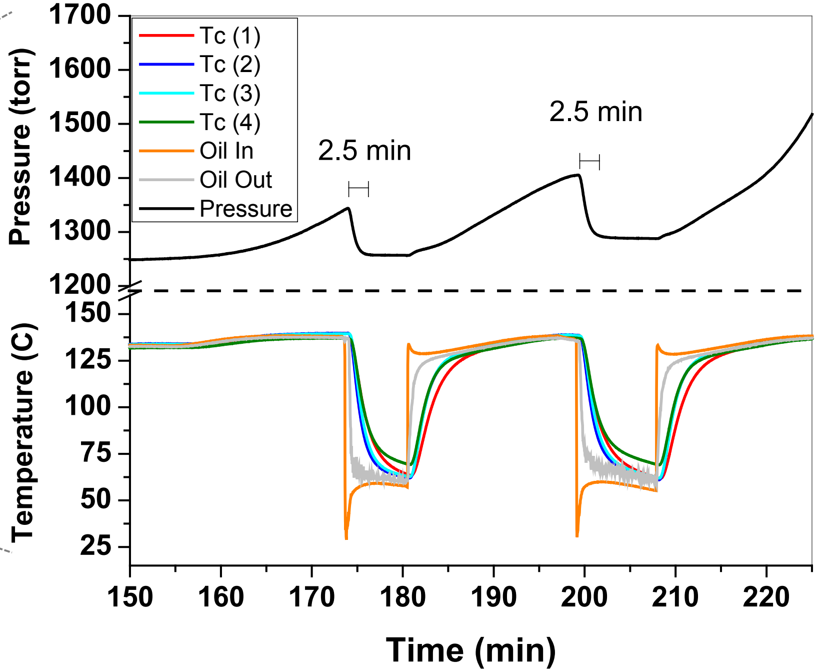


Accomplishments: SRNL Alane Test Vessel setup



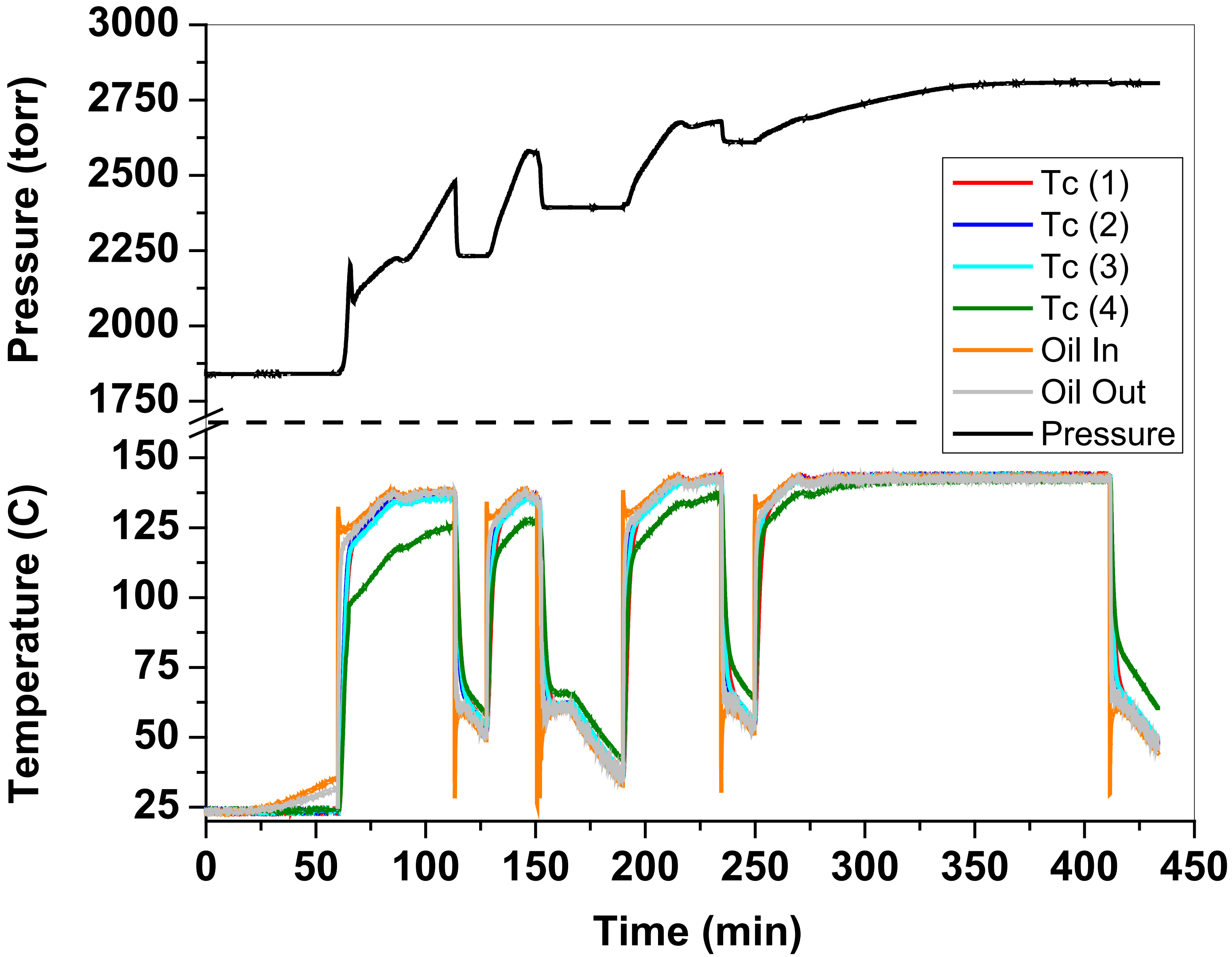
Accomplishments: SRNL Alane Test Vessel Operation with Alane





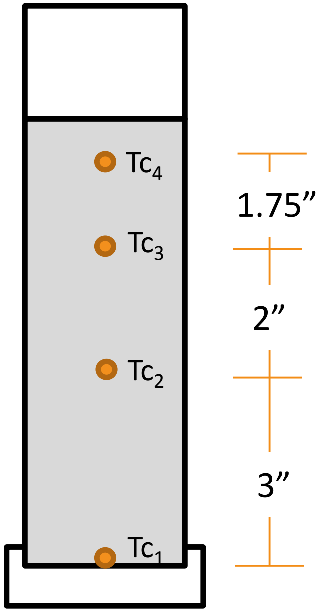
- H_2 is released at ~133°C.
- H_2 release can be readily stopped via the cooling loop set at 20°C.

Accomplishments: SRNL Alane Test Vessel Results

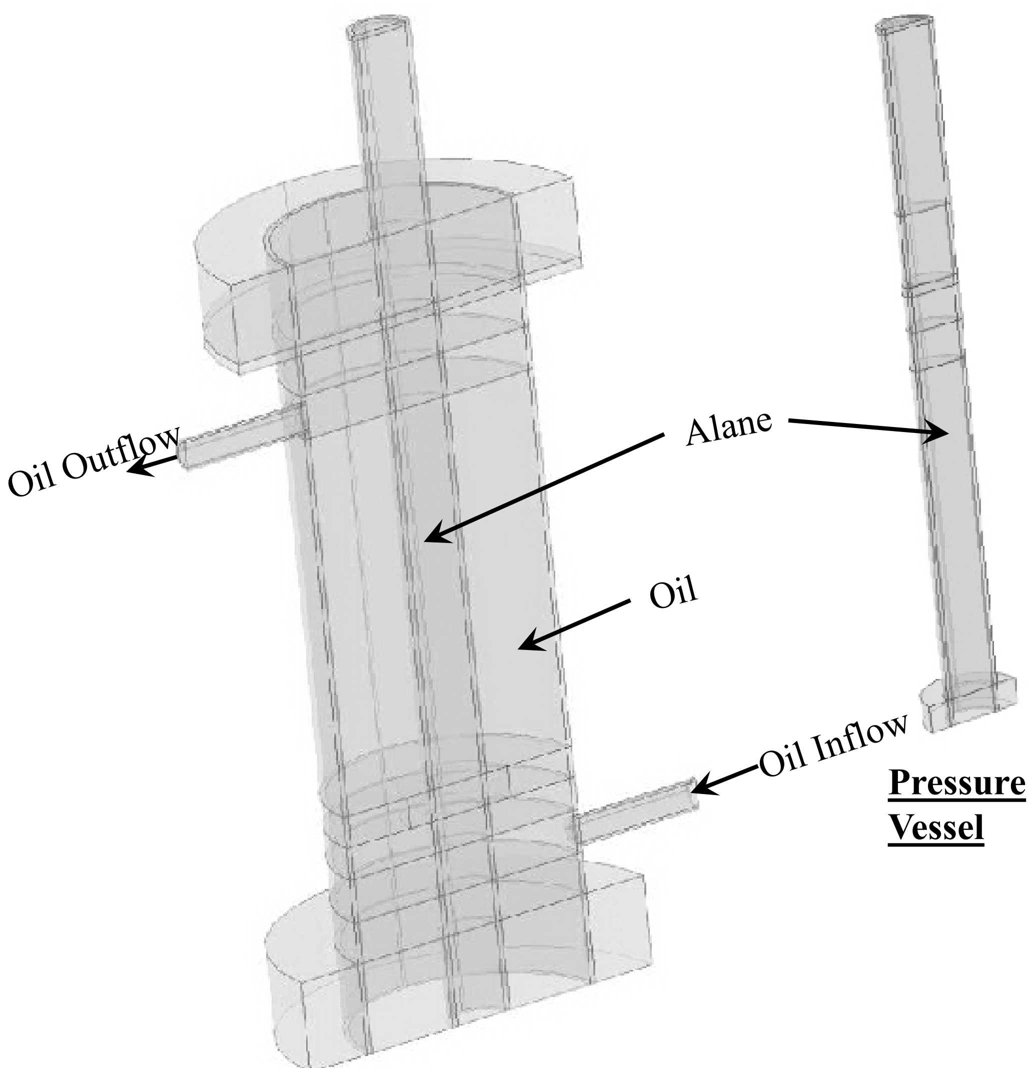


56.3g of AlH_3 in 70 mL volume. Sample contained 6.5 wt% H_2 based on TGA.

T_c placement for this test

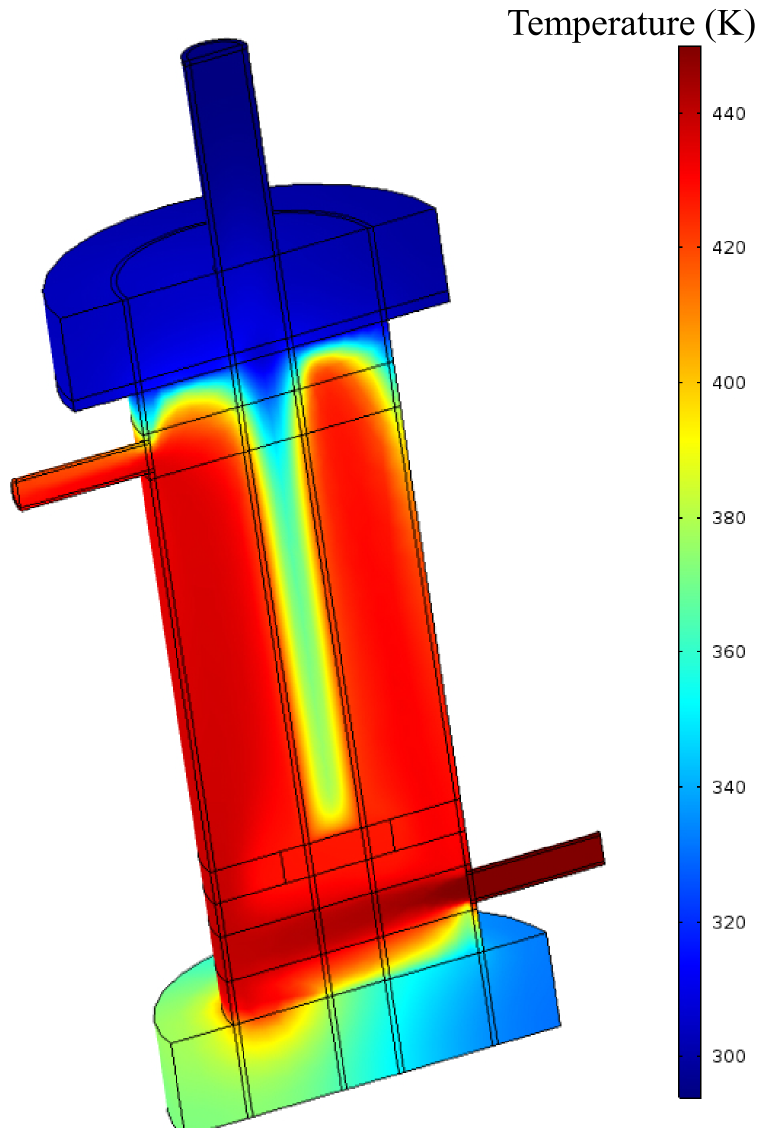


Accomplishments: Storage System Heat Transfer Modeling



Complete Assembly

Pressure Vessel

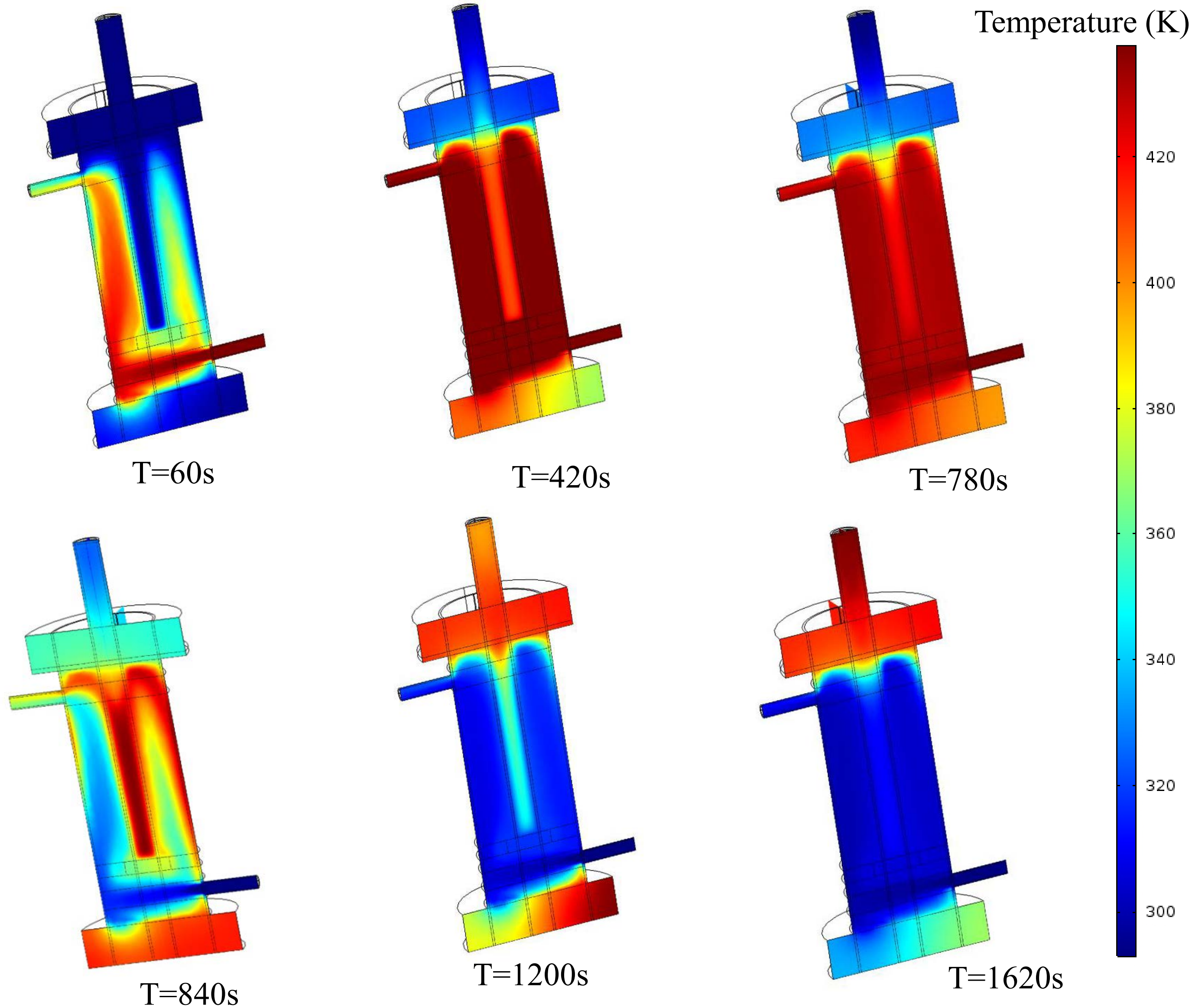


Temperature Profile at 240s

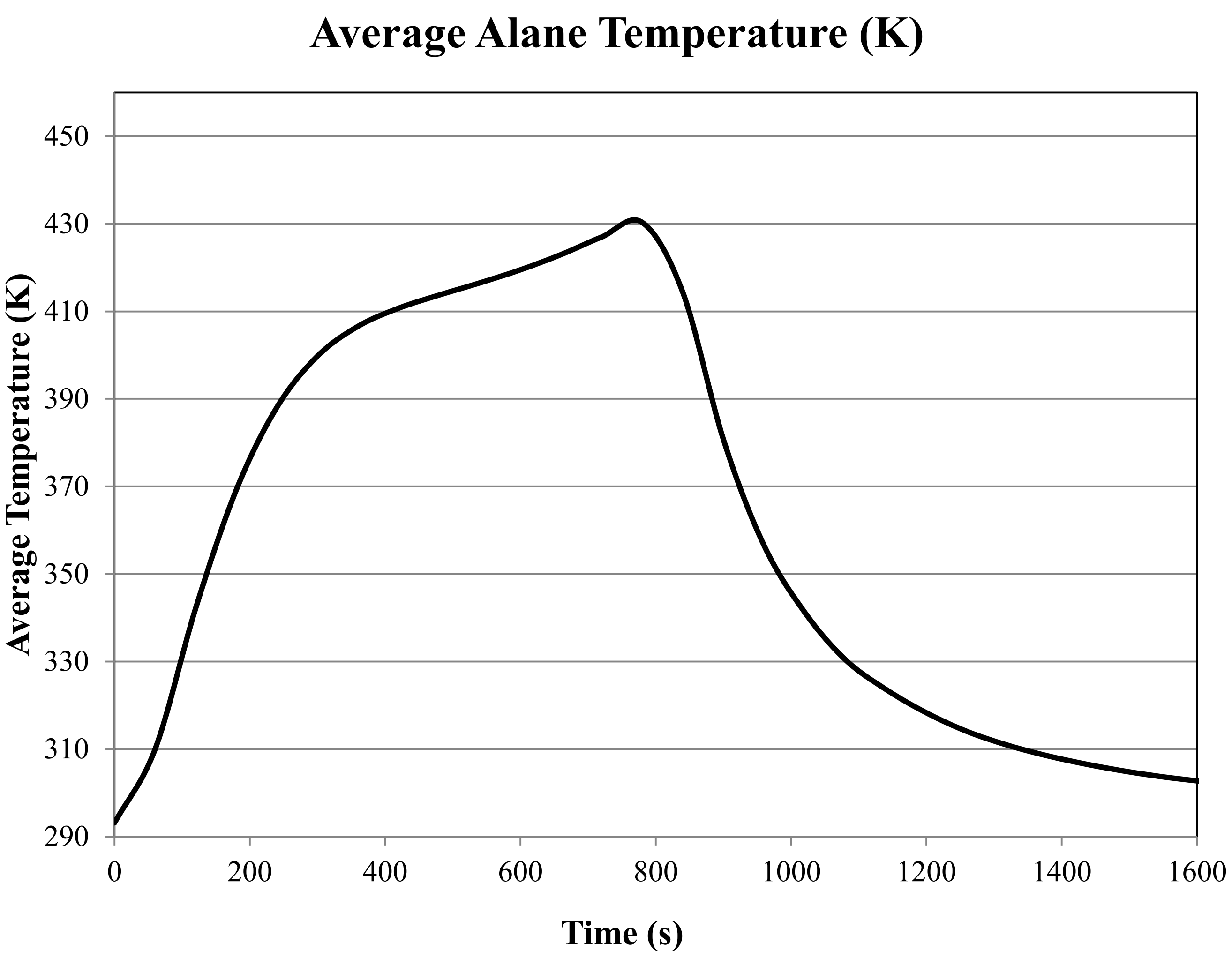
Accomplishments: Storage System Modeling

Initial Temperature=293K
Oil Inlet Temperature=450K

Oil Inlet Temperature=293K



Accomplishments: Storage System Modeling



T=840s

Summary and Path Forward

- Completed an engineering analysis to screen the most attractive solid-state hydrogen storage materials for UUV applications
- Alane (AlH_3) was selected as the most attractive candidate
- Testing was performed to demonstrate AlH_3 hydrogen storage and delivery performance including steady-state and transient operations
- Delivered AlH_3 material and test module to NUWC for further Navy testing
- Ongoing systems and detailed modeling for UUV platforms are underway along with material safety testing (Ardica Technologies)
- Preliminary analyses indicate *2 to 3 times the energy storage compared to battery systems*
- End of year objective is to develop a preliminary prototype alane-based UUV system design & system moedl for potential Navy applications
- Long-term path forward is to work with the Navy to develop a final design, fabrication and testing of a prototype UUV system.

Collaborations and Technology Transfer Activities

- Naval Undersea Warfare Center (Newport)
  - UUV energy system integrator
  - End-user and system tester/evaluator
- Office of Naval Research
  - Sponsor
- Ardica Technologies, LLC
  - Fuel cell portable power system developer and manufacturer
  - Developer for DoD Army alane-based soldier power system
  - DOE CRADA Partner with SRNL to lower the manufacturing and recycling cost of alane.

No new patents to date but SRNL patent # US 8470156 B2 is the basis for the current DOE CRADA between SRNL and Ardica and future IP and/or Tech Transfer is anticipated

Remaining Challenges and Barriers

- Efficiently integrating alane-based hydrogen storage vessel design with fuel cell, hydrogen generator (hydrogen peroxide) and BOP.
- Meeting system volume and weight requirements to meet Navy UUV specifications and maintaining neutral buoyancy and achieving all performance objectives.
- Demonstrating onboard alane material storage and handling safety
- Supporting the Navy to provide a suitable cost supply of alane to meet future missions and applications.