Savannah River National Laboratory™

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Investigation of Solid State Hydrides For Autonomous Fuel Cell Vehicles

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Savannah River National Laboratory

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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*

FY 17 DOE Funding: $250K

***Additional Federal (ONR) Funding:** $50K FY15, $100K FY16

Partners

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

Relevance

DOE Funded Activities

Objectives:

- Screen H_2 storage systems against DoD targets and requirements that are suitable for vehicle demonstration platforms
- Complete a detailed design of the hydrogen storage system for use in an integrated system design
- Develop a preliminary design of an integrated UUV platform with a non flow through fuel cell

ONR/NUWC Funded Activities

Objectives:

- Design, build, and test a small bench-scale, alane hydrogen storage vessel
- 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 experience gained from the HSECoE and the core capabilities of SRNL and DOE were leveraged to develop a unique hydrogen storage system for new fuel cell applications
- Extension of this program to other unmanned and manned platforms is likely
- *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, initially developed by SRNL and applied to light-duty vehicle in the Hydrogen Storage Engineering Center of Excellence (HSECoE), was adapted for other hydrogen and FC applications
- 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

Naval Undersea Warfare Center (NUWC) Division Newport

Naval Undersea Warfare Center, is the Navy's full-spectrum research, development, test and evaluation, engineering, and fleet support center for submarine warfare systems and many other systems associated with the undersea battlespace.

Christian Schumacher and Dr. Joseph Fontaine

REMUS 600

Navy NUWC changes proposed project from 22" UUV to 12.75" Remus Platform

Advantages:

- Smaller, less expensive and readily available commercial platform
- Reduced requirements for alane material
- Ability to break hull to accommodate canister refueling

Example Mission: Bottom Mapping Survey

Target Mission

Constant Power: 250W

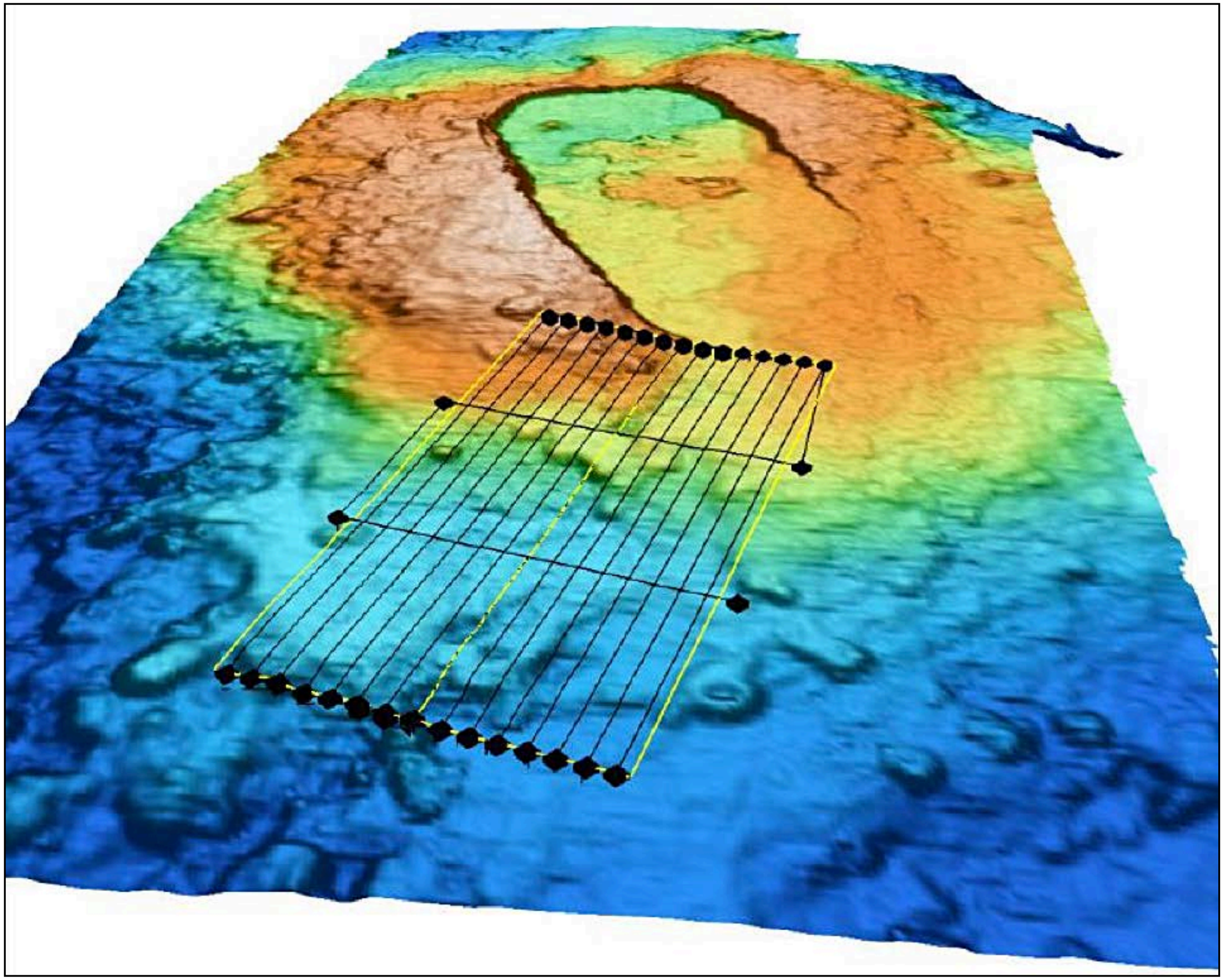
- 100W Propulsion
- 100W Hotel Load
- 50W Sensors

No Transients

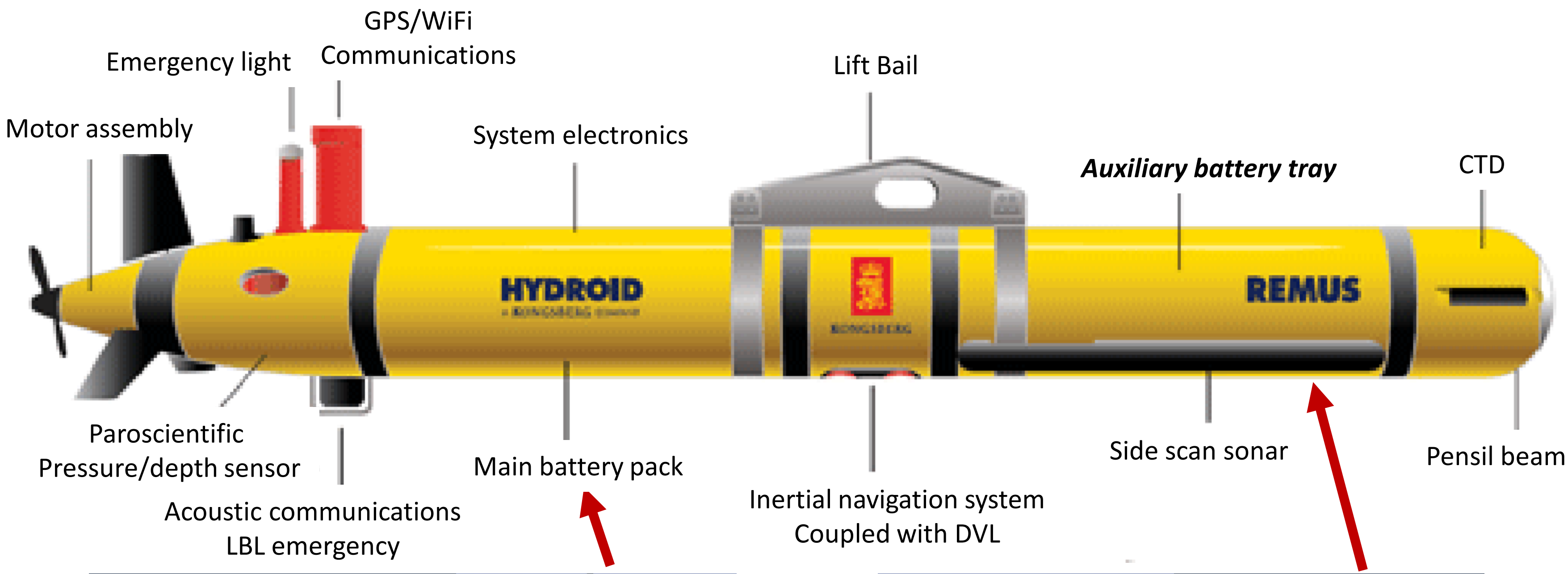
- Simple Design

Assume Auxiliary Battery

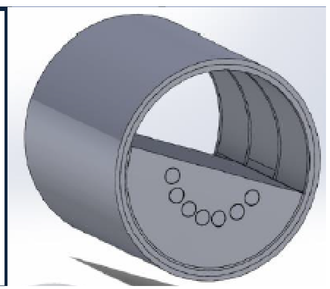
- Neglect Start-up
- Neglect Shut-down

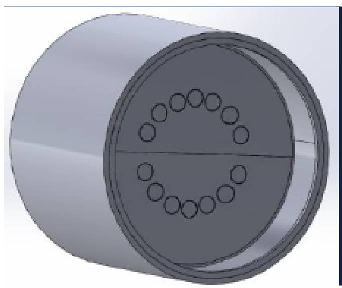


REMUS 600



Keep:
Main Battery Sec
~ 36" in Length





Replace:
Aux Battery Tray
~ 45" in Length

Replace auxiliary battery tray with a hydrogen storage material, fuel cell, and oxidant system

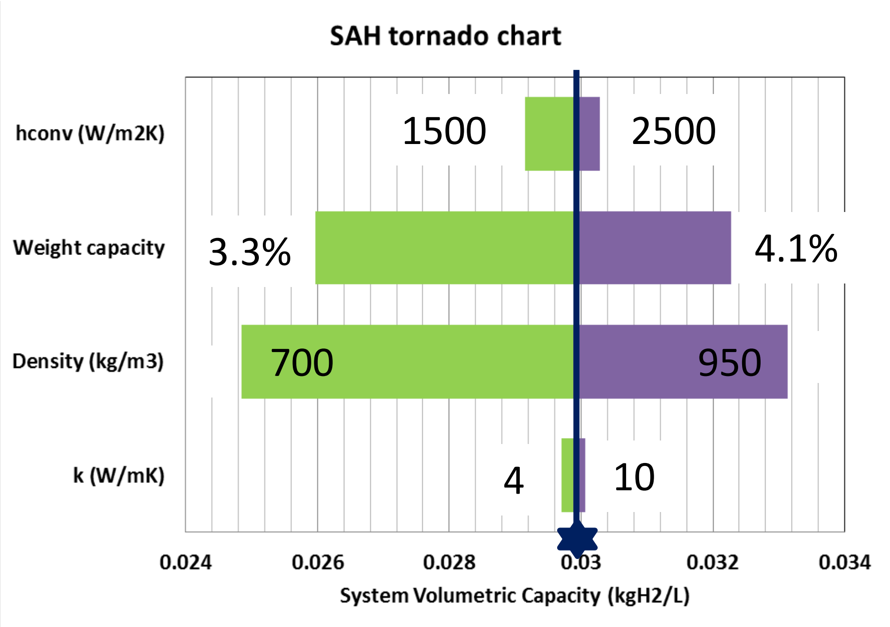
Accomplishments: Material Screening Analysis Criteria

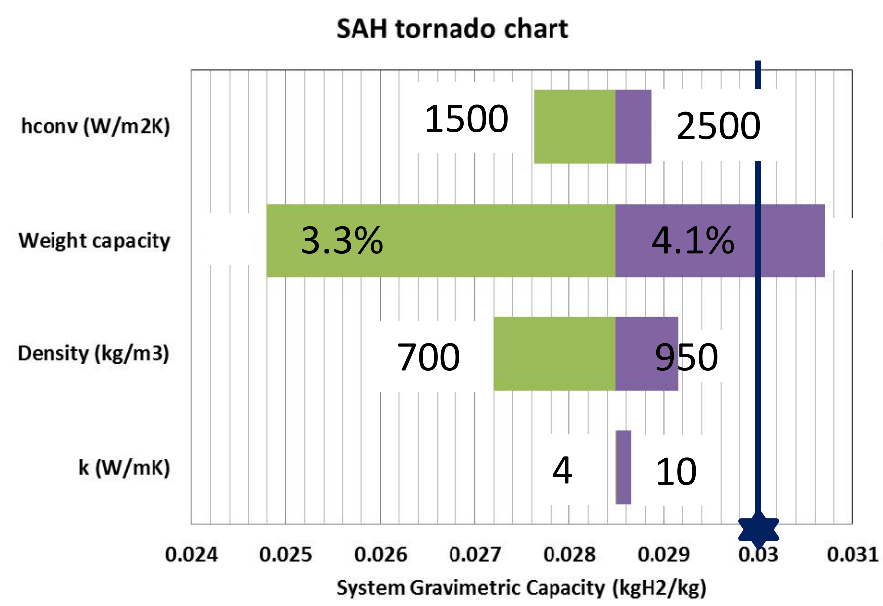
<table>
<tr><th>Targets and Data (Gen1 system)</th><th>Waste heat available (Gen1 system)</th></tr>
<tr><td>System volumetric capacity = 3%
• Usable hydrogen to be stored = 2kg
• Available volume = 66 L (18.5” x 15”)</td><td rowspan="2">Latent heat (average) from H_2O_2 reaction condensing steam = 43.9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

<table>
<tr><th>Targets and Data (Gen2 system)</th><th>Waste heat available (Gen2 system)</th></tr>
<tr><td>System volumetric capacity = 5%
• Usable hydrogen to be stored = 3.2kg
• Available volume = 66 L (18.5” x 15”)</td><td rowspan="2">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</td></tr>
<tr><td>System gravimetric capacity = 5%
• Usable hydrogen to be stored = 3.2kg
• Storage system weight = 66 kg</td></tr>
<tr><td>Cost = 1000 $/kg of hydrogen</td><td rowspan="2">Heat (average) from FC byproduct water = 4.08 MJ
• Mission time = 30 hours
• Total mass of water available = 17.7 L
• Temperature = 80 °C</td></tr>
<tr><td>H_2 average flow = 1.8 g/min
• Based on FC efficiency of 50%</td></tr>
<tr><td>H_2 peak flow = 3.8 g/min
• Based on FC efficiency of 50%</td><td rowspan="2">Heat (average) from FC cooling water = 60.48 MJ
• Mission time = 30 hours
• Total mass of water available = variable
• Temperature = 80 °C</td></tr>
<tr><td>H_2 delivery pressure = 2-20 bar</td></tr>
</table>

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

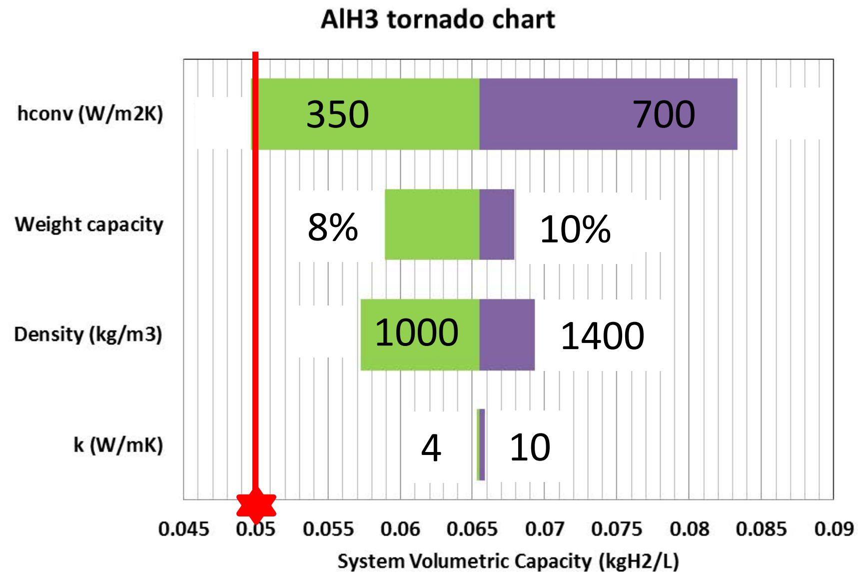
Accomplishments: $NaAlH_4$ material performance sensitivity analysis (Gen1)

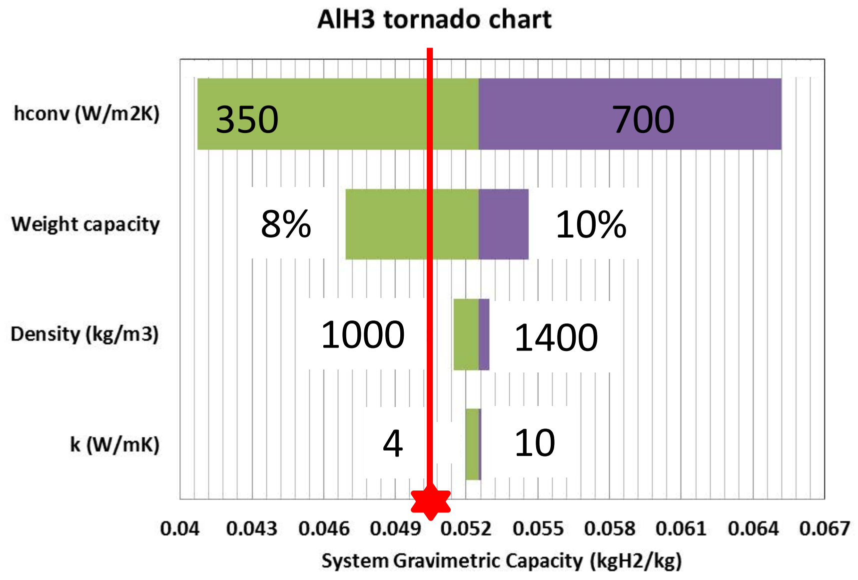




- **The Material Shows Good Performance**
  - Gen1 target volume capacity (3%) achieved by mini-channel heat exchanger or enhanced heat transfer systems
  - It approaches the Gen1 gravimetric target (3%)
- **Significant Influence of the Material Properties on the Performance**

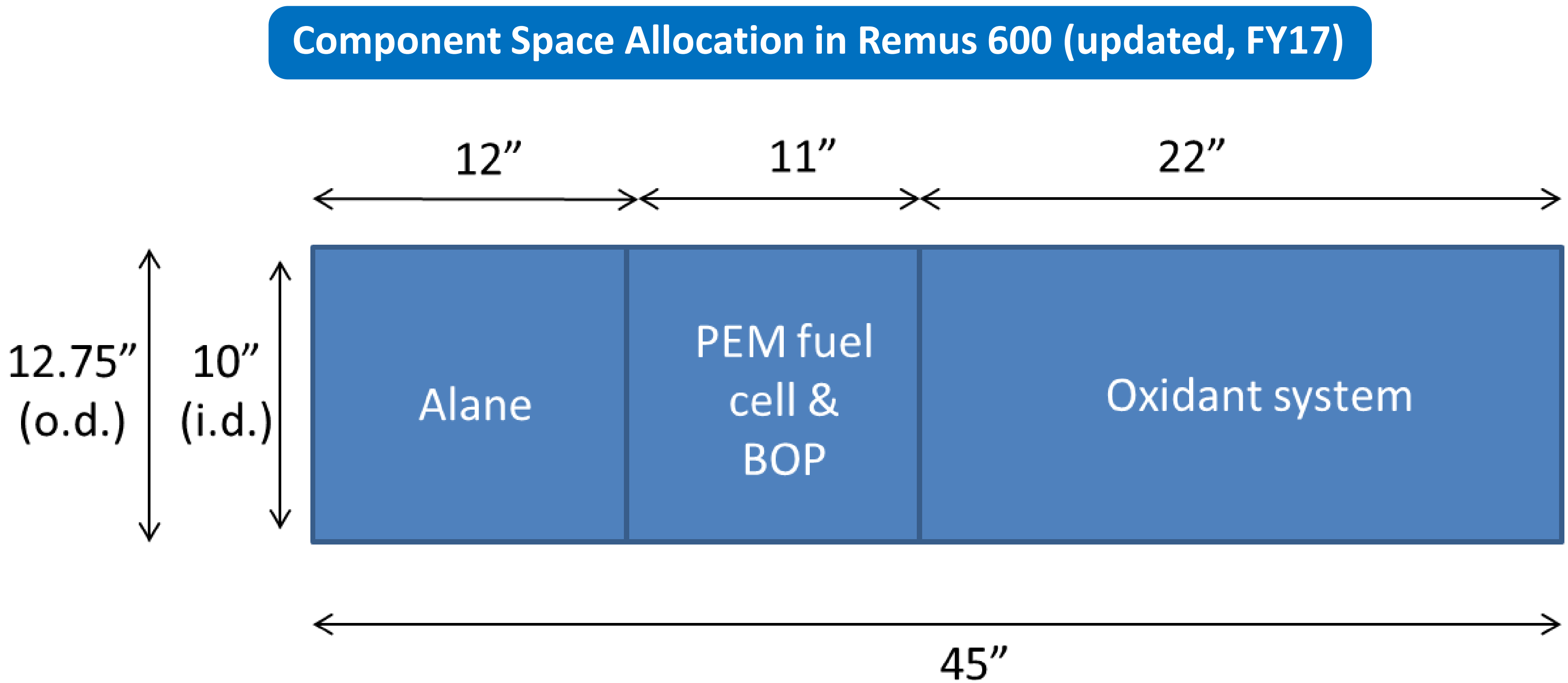
Accomplishments: AlH_3 material performance sensitivity analysis (Gen2)





- **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**

Space Allocation for System



- This system will utilize heat from the oxidant system to drive the thermal desorption of hydrogen from alane to drive a fuel cell
- The ultimate goal is to ***achieve a 2 x increase in the vehicle operation range/time***

Preliminary sizing of the alane reactor

System assumptions and constraints	
Mass of hydrogen	1.13 kg
Hydrogen flow rate	0.2 g/min for 96 hours
Start up/shut down	10 min
Max diameter	10 in
Length	9.0 - 13.1 in
Heat transfer fluid	Pressurized water
Inlet/Outlet T	150/130 °C
Pressure	10 bar

Alane properties	
ΔH	7.6 kJ/mol H_2
Cp	1340 J/kgK
k	7 W/mK
wf	10%
Bulk density	1000 kg/m^3

Results	
Reactor Diameter	10 in
Reactor Length	10.6 in
Total Power Required	890 W
Thermal Energy for start up/shutdown	146 Wh
Thermal Energy for desorption	1200Wh
Total Required Power	890 W
Power required for desorption	13 W

- This study determined the alane reactor size and accounted for the mass and energy balance of the reactive system along with a heat transfer system (shell and tube)
- ***The alane vessel will fit in the space allotted in the REMUS 600***

Alane, oxidant system, and fuel cell interfaces

Alane
-7 kJ/mol of H_2
11.3 kg
3917.9 kJ (1.089 kW-hrs)

H_2 gas
559.7 mol
1.13 kg

PEM Stack
250W Avg.
96 hr, 24 kW-hrs
0.8V, Ɛ=0.6
100W waste heat

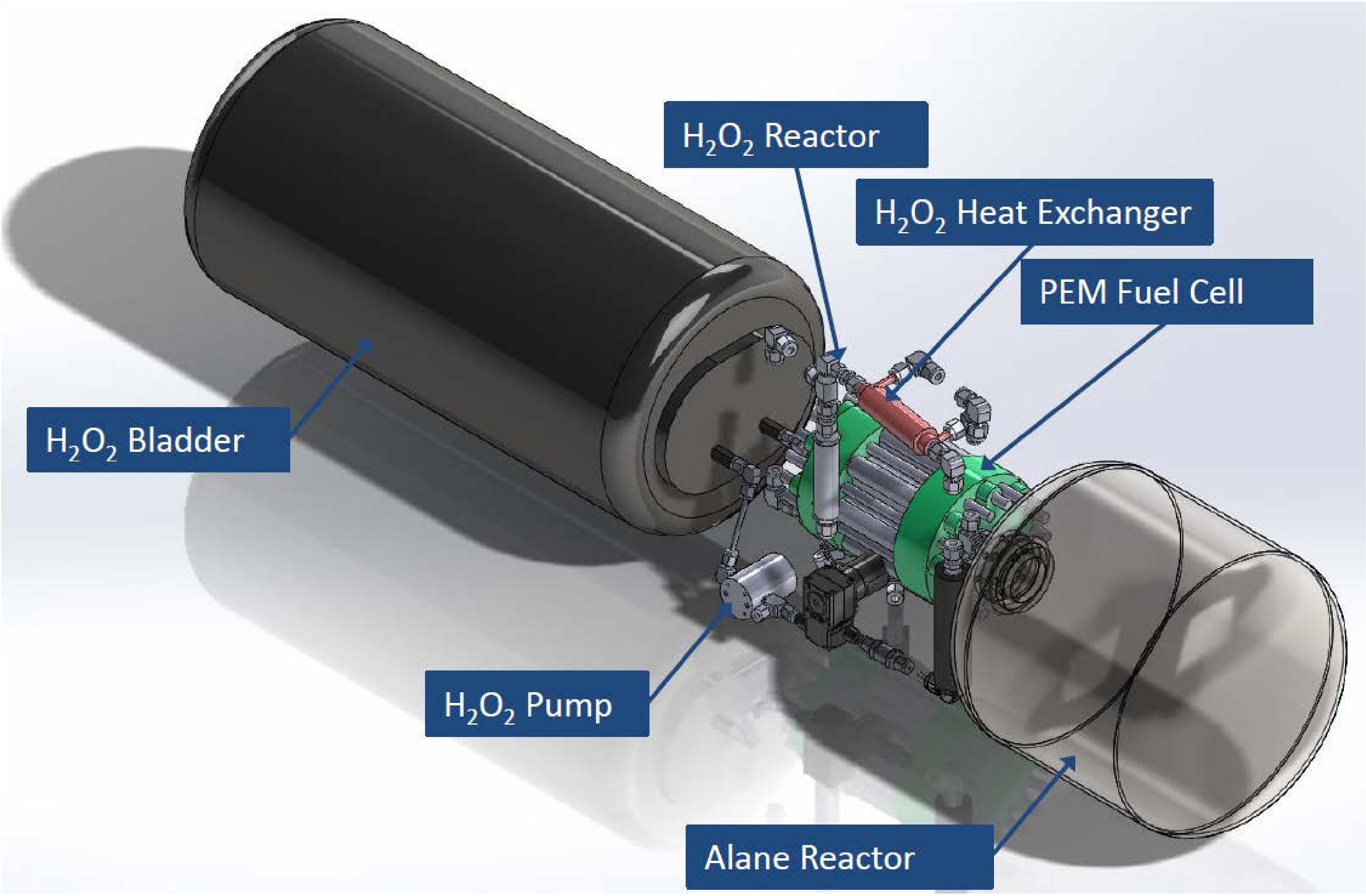
Cooling water
100W * 3600s/hr =
34,560 kJ (9.6 kW-hrs)
96 hr, 24 kW-hrs

Hydrogen peroxide
(60 wt%) 46.7 kJ/mol @
265 psia, 200°C
1264.2 mol
34.9 kg

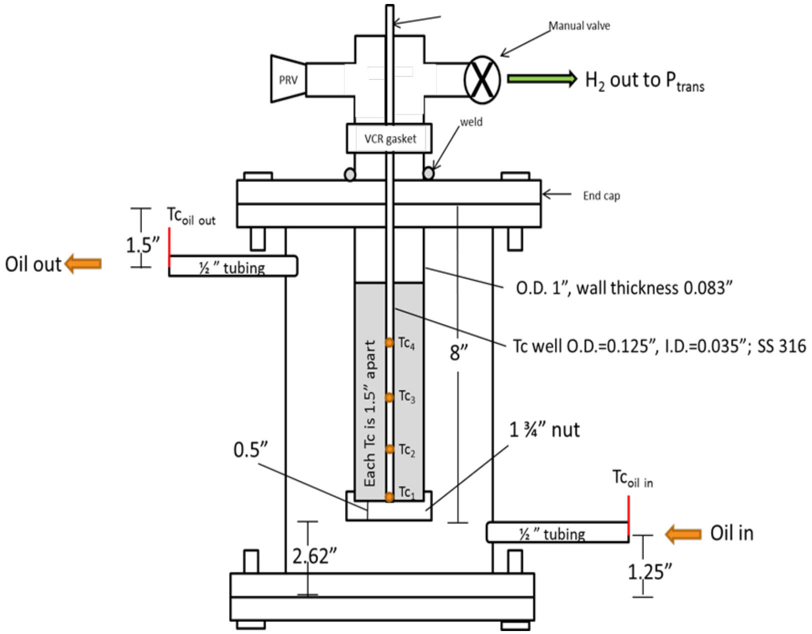
O_2 gas
279.8 mol
8.95 kg

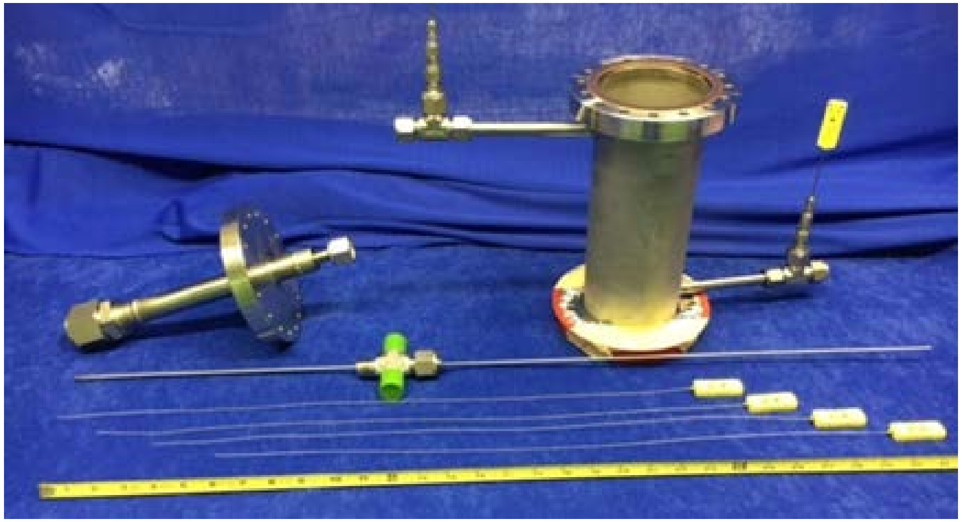
By-product water ~200°C
1264.2 mol
22.78 kg
59038.1 kJ (16 kW-hrs)

Solid Model of System

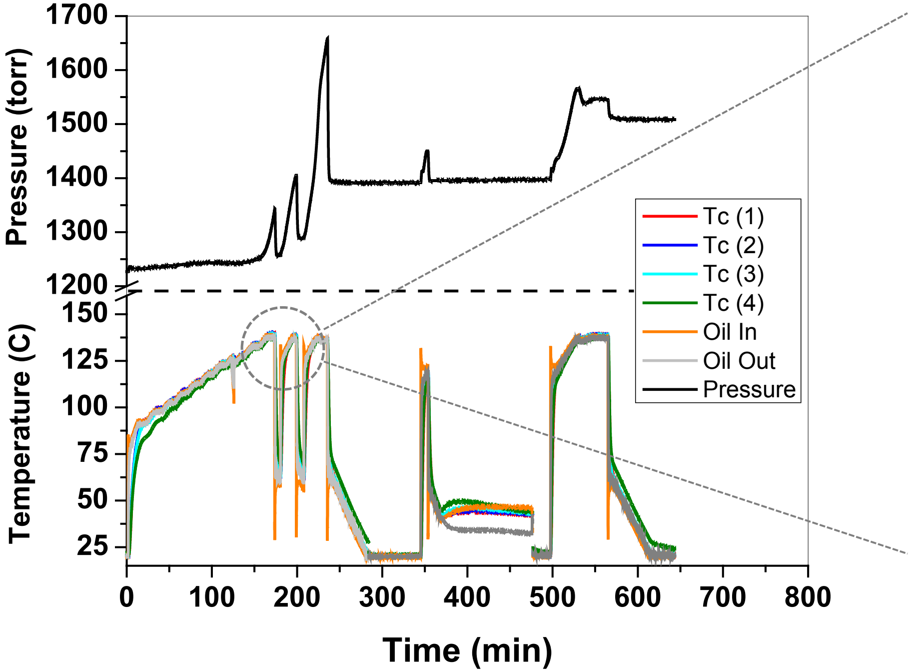


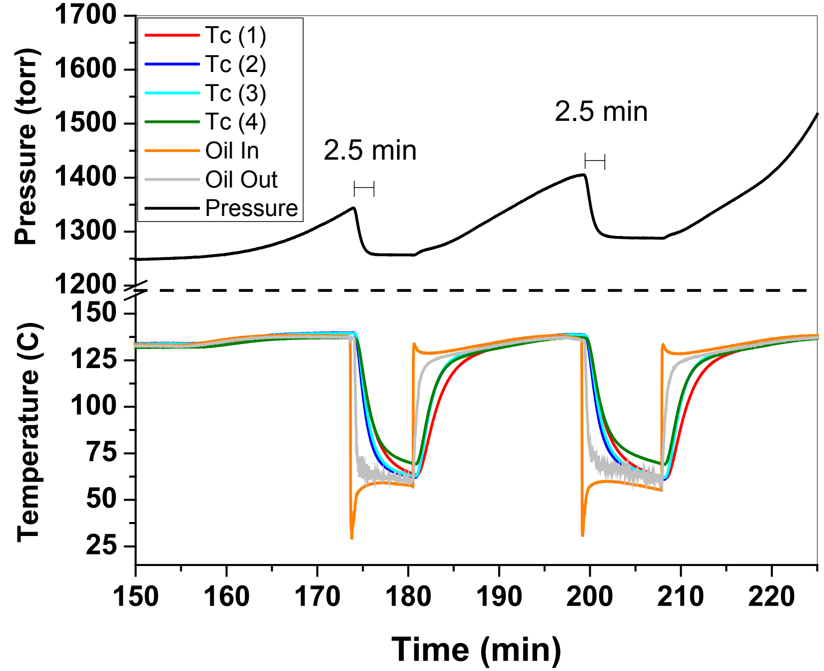
Accomplishments: SRNL Alane Test Vessel Setup





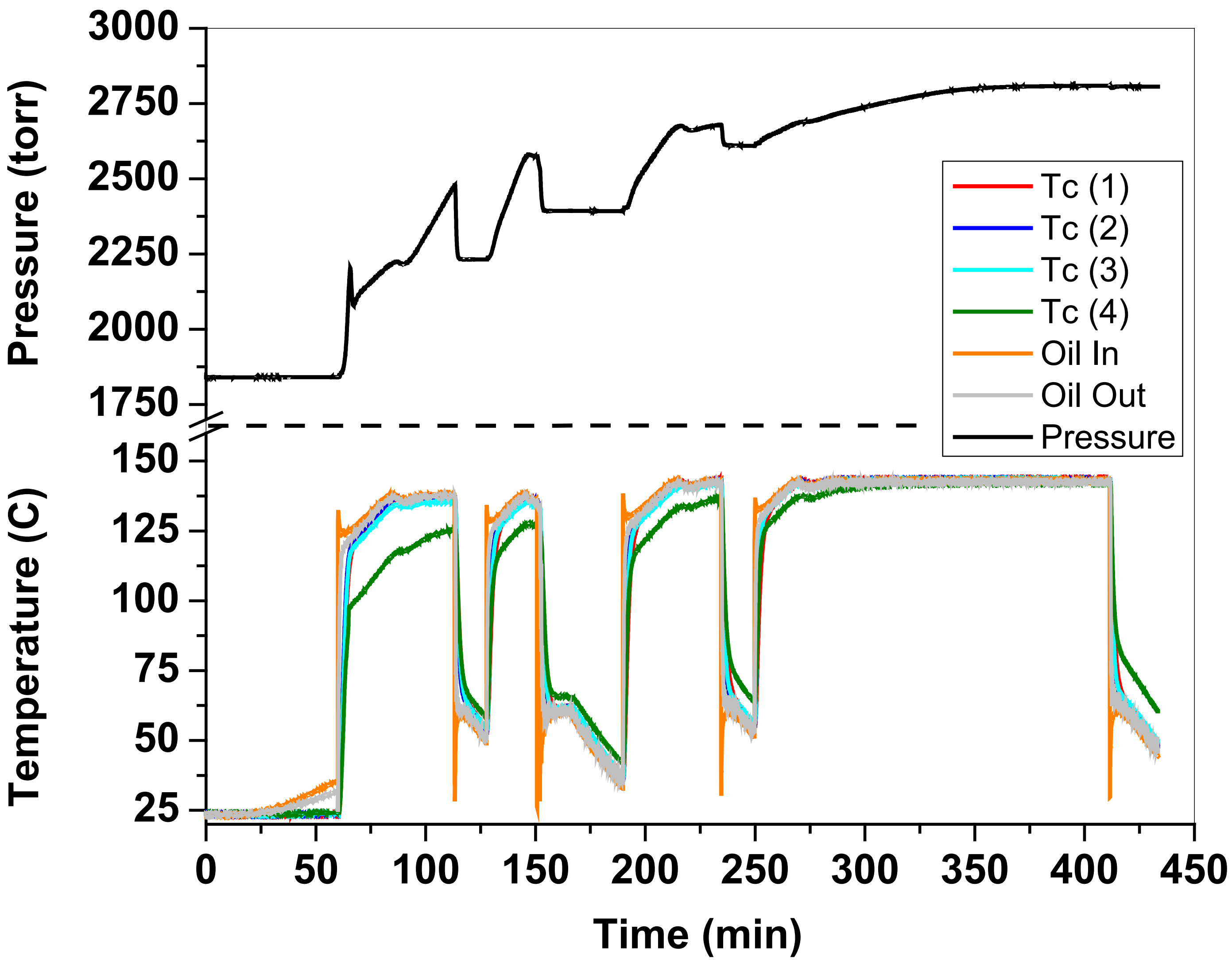
Accomplishments: SRNL Alane Test Vessel Operation with Alane (ATK alane)



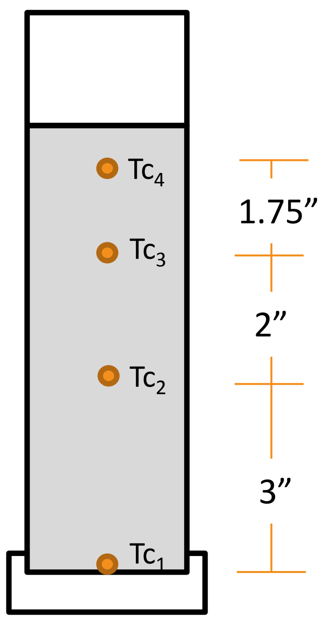


- H_2 is released at ~133 °C.
- H_2 release can be readily stopped via the cooling loop set at 20 °C.

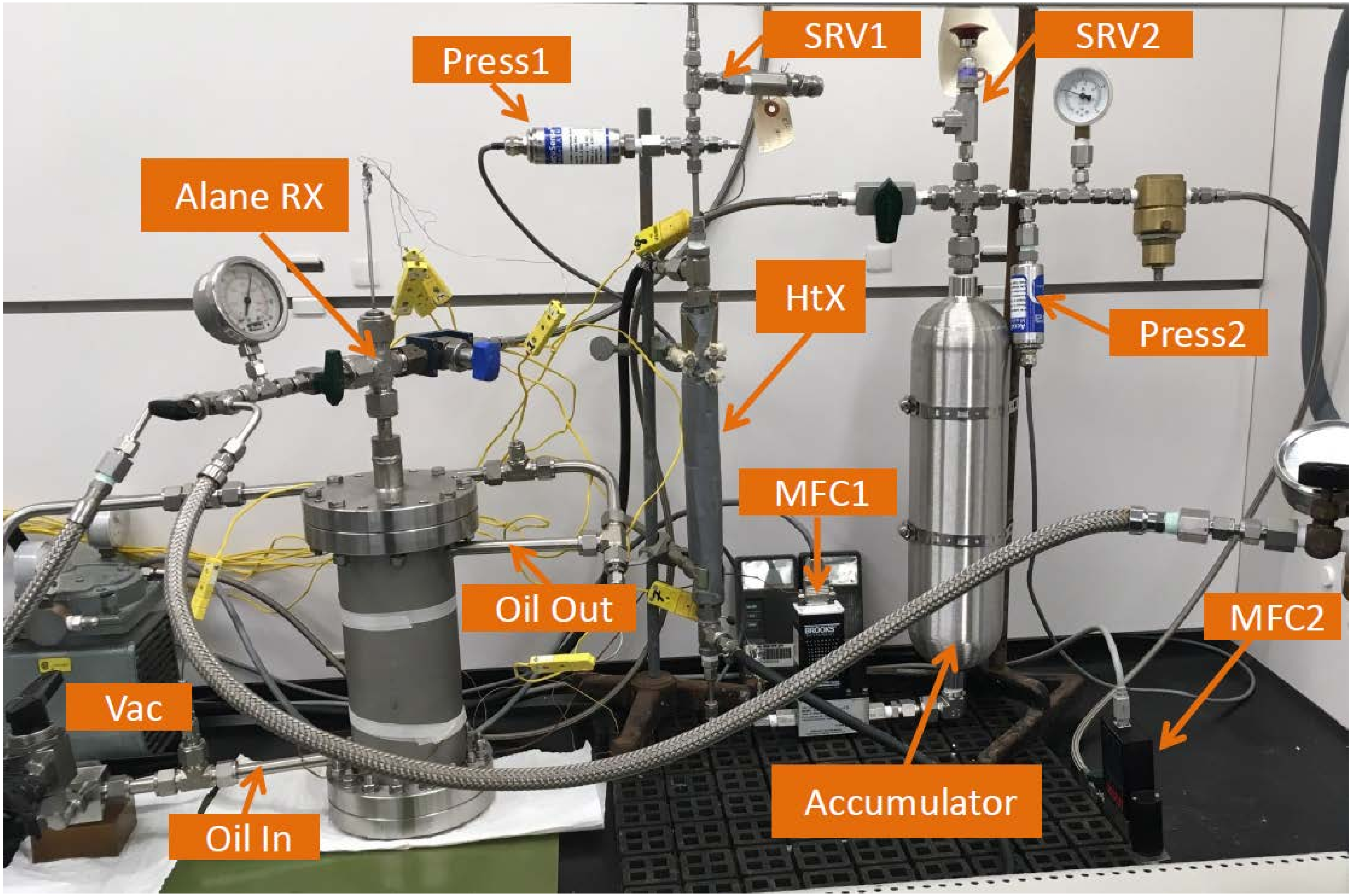
Accomplishments: SRNL Alane Test Vessel Results (Ardica alane)



56.3g of AlH_3 in 70 mL volume

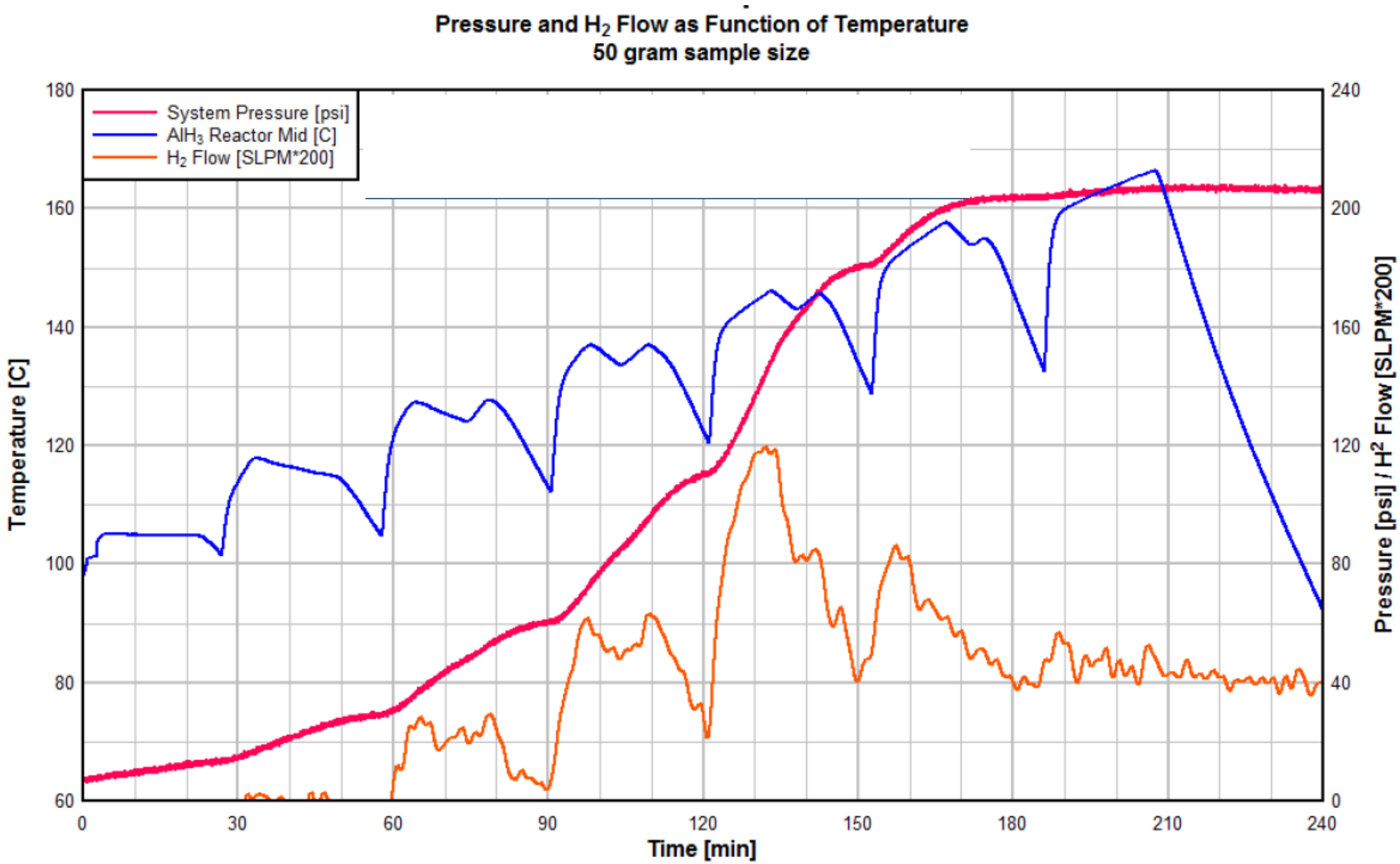


NUWC Set-up and Testing



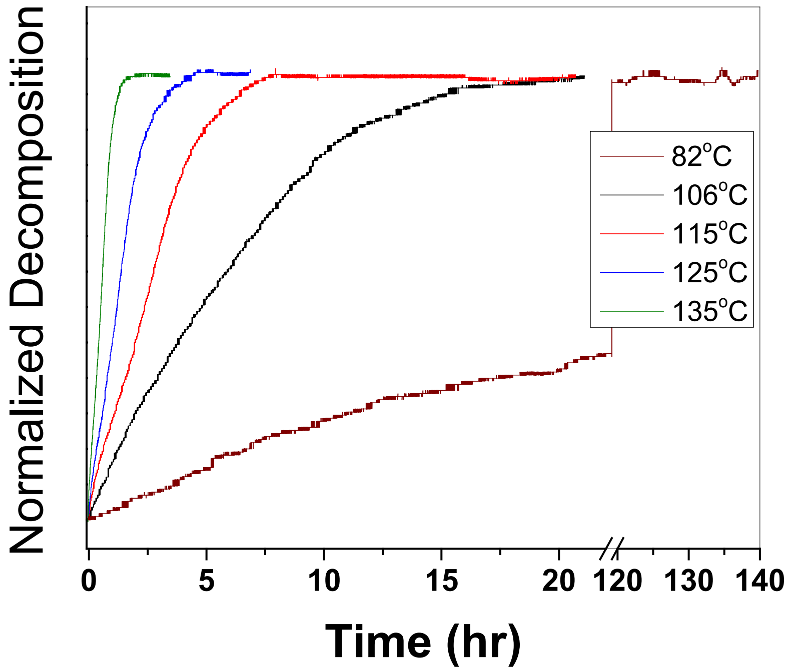
NUWC Set-up and Testing Verification

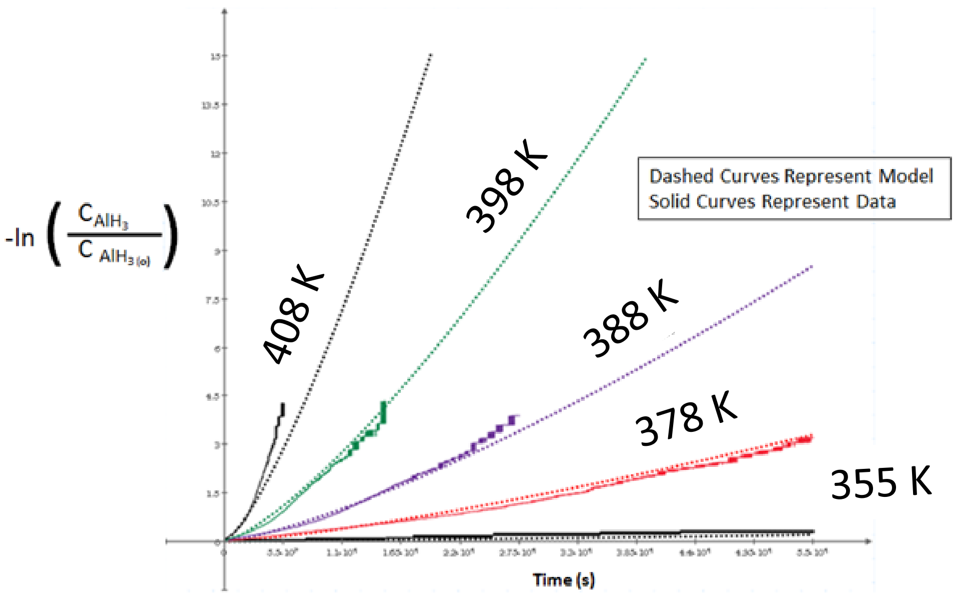
Alane Decomposition



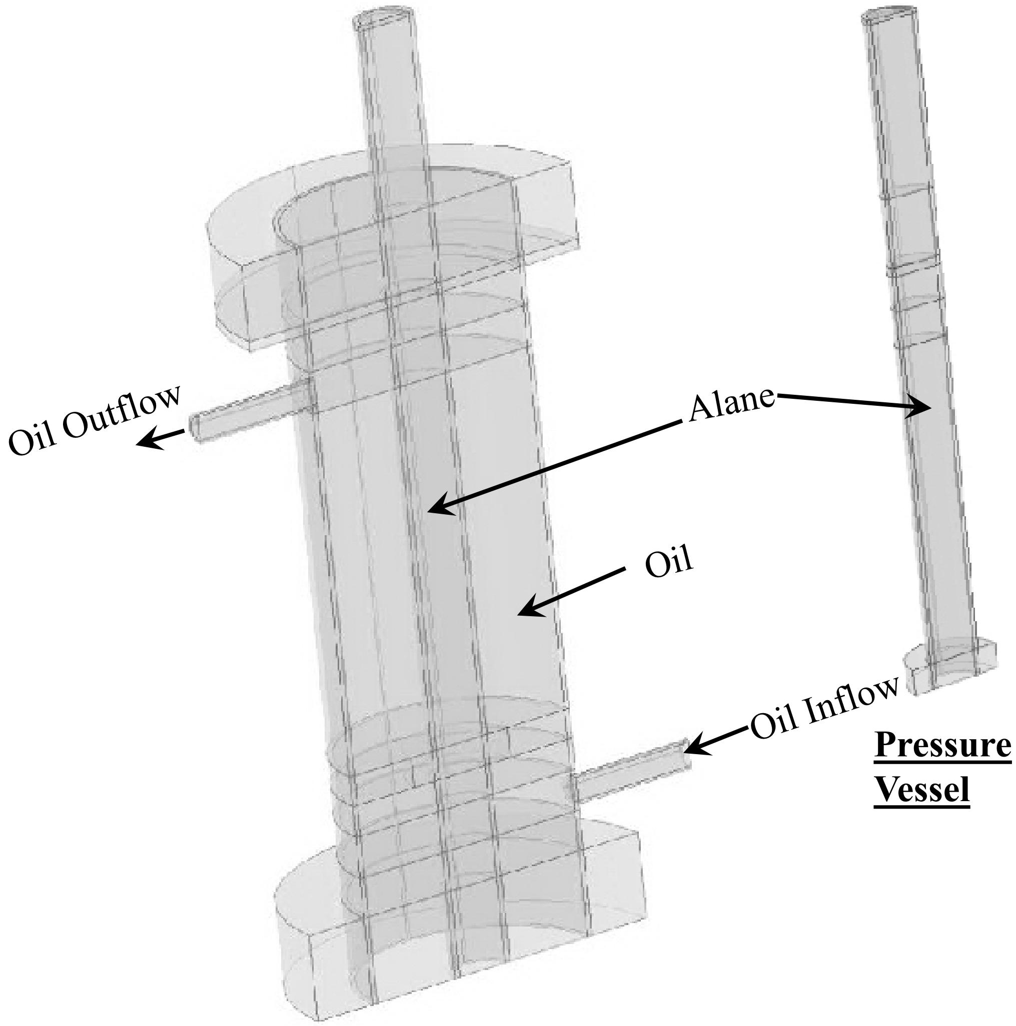
Accomplishments: Alane Kinetic Modeling (ATK alane)

Isothermal Desorption of Alane With 1 bar H_2 Back Pressure



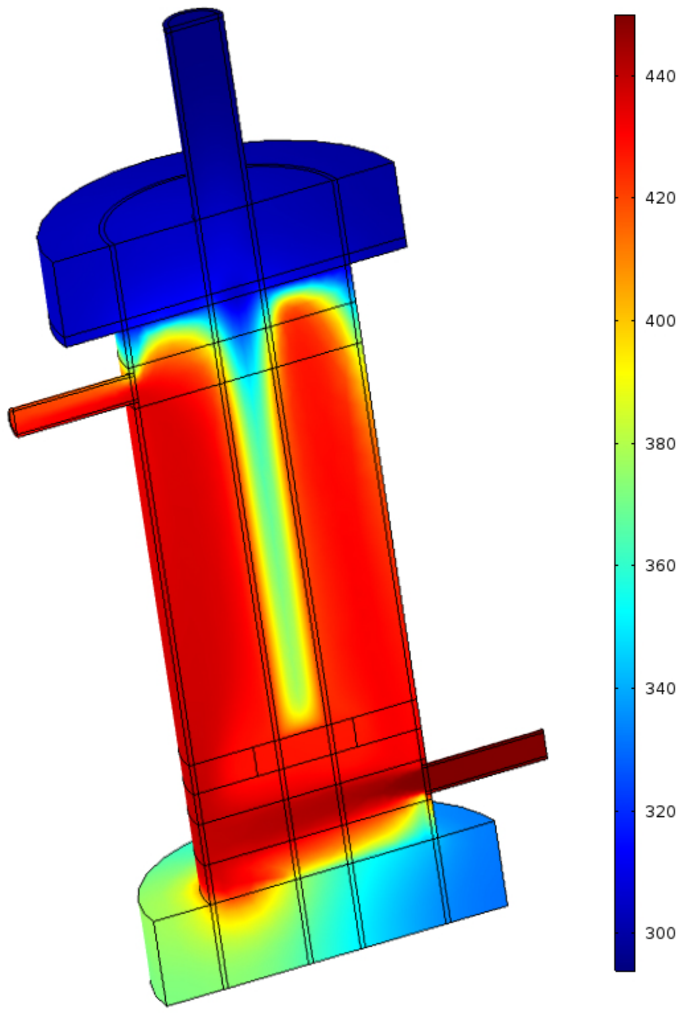


Accomplishments: Storage System Heat Transfer Modeling



Pressure Vessel

Complete Assembly

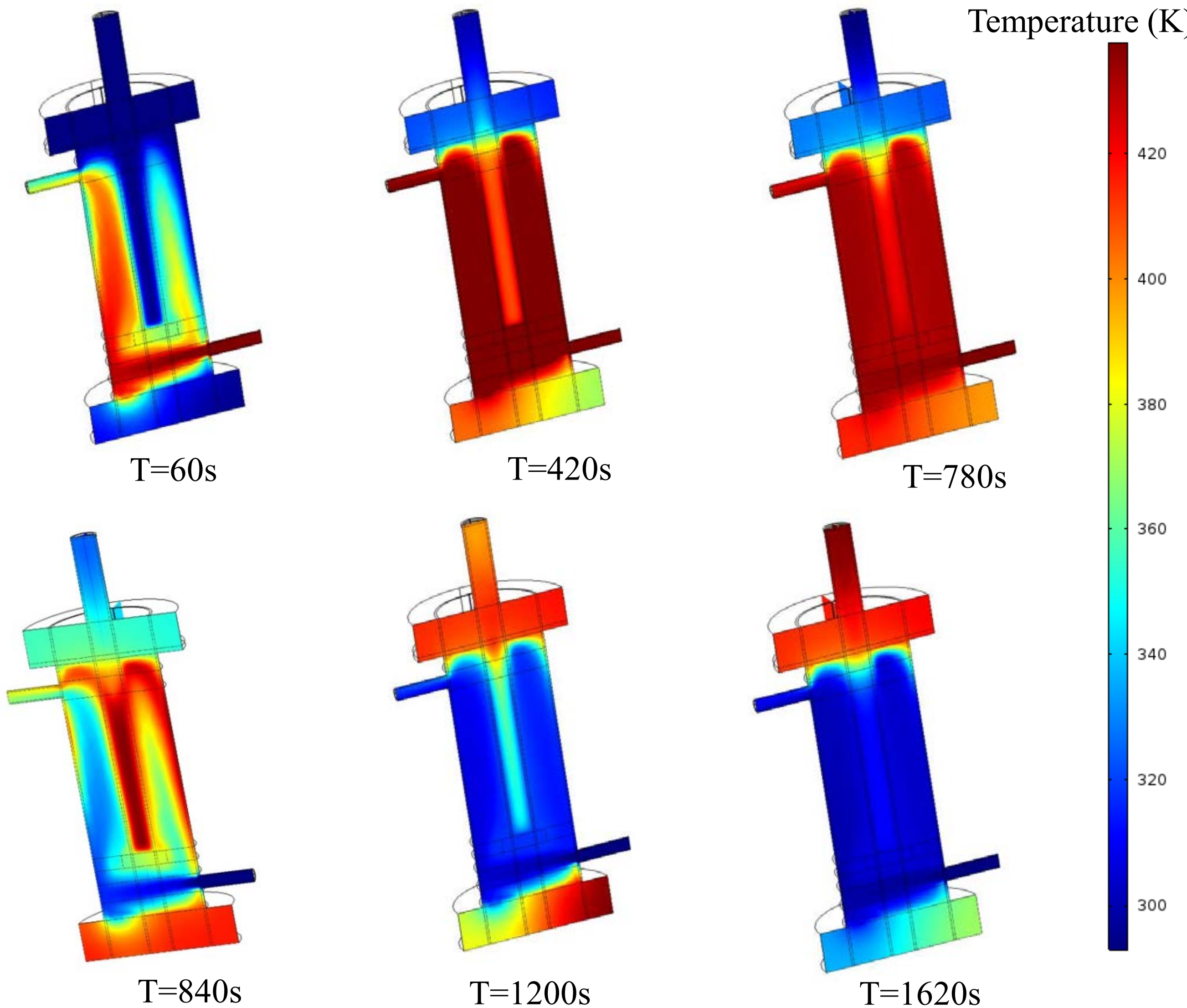


Temperature Profile at 240s

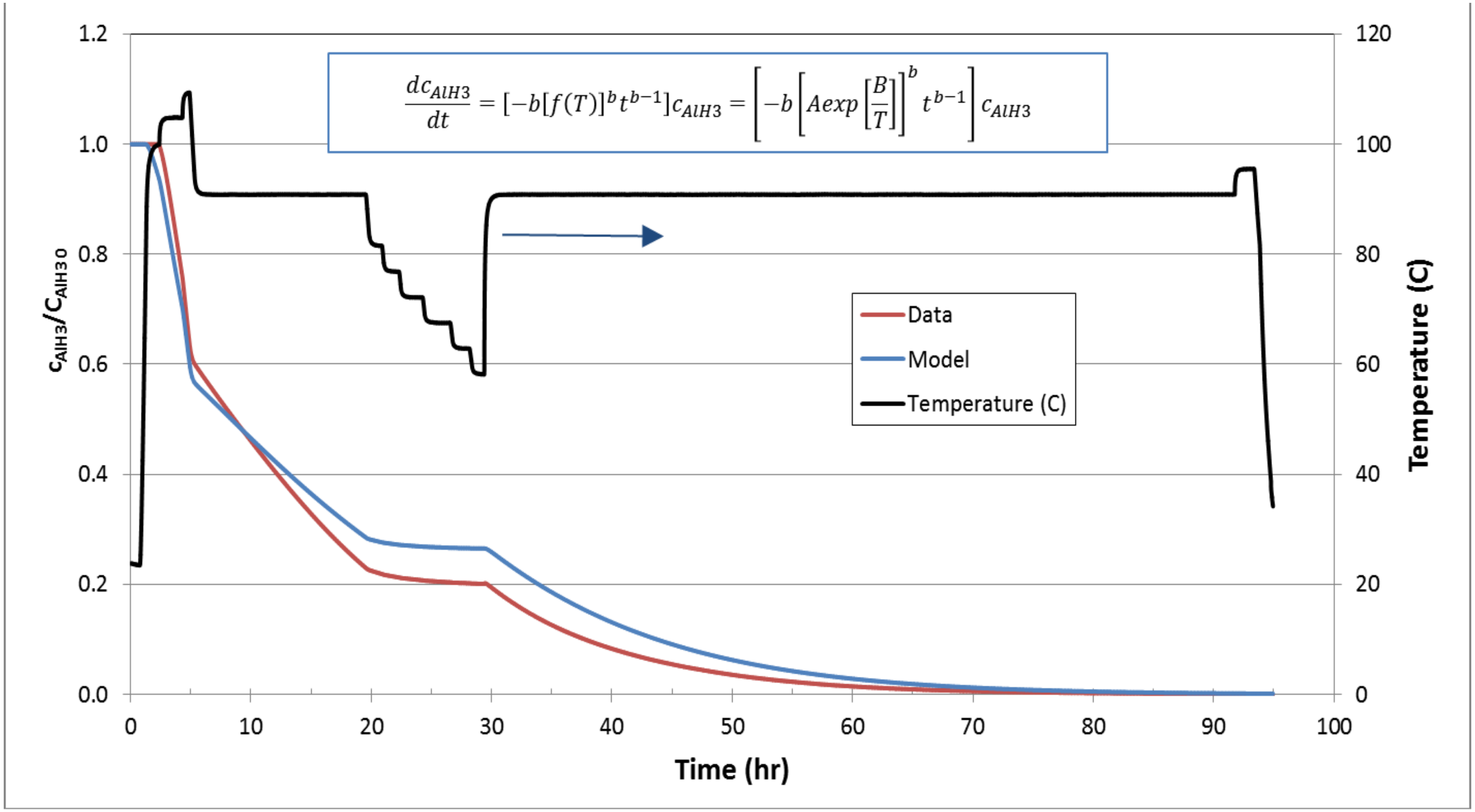
Accomplishments: Storage System Modeling

Initial Temperature = 293K
Oil Inlet Temperature = 450K

Oil Inlet Temperature = 293K



Accomplishments: Modeling Temperature Transients



Response to Reviewer Comments

- Project not reviewed in 2016.

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 times the energy storage compared to battery systems***
- End of year objective is to develop a prototype alane-based UUV system design & system model 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

UUV operations off the coast of Bahrain in 2013. Credit: Specialist 2nd Class Michael Scichilone/US Navy/Released

Backup slides

Material Screening Analysis

Material Classes

1. Reversible low T MH (AB_5, AB, $NaAlH_4$)
2. Reversible high T MH (Mg family materials) — Gen1
3. Non reversible MH (Alane, Mg alanate, LiMg alanate) — 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%**	-	-	