Quantifying and Addressing the DOE Material Reactivity Requirements with Analysis and Testing of Hydrogen Storage Materials and Systems

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United Technologies Research Center (UTRC)

& Combustion Research Center

Kidde-Fenwal

DOE Hydrogen Program

Annual Merit Review and Peer Evaluation

Arlington, VA

May 9-13, 2011

Project ID# ST012

Overview

- **Timeline**
  - Start: June 2007
  - End: September 2011
  - Percent complete: 85% (spending)
- **Budget Data**
  - $1.34M Total Program
    - $1.07M DOE
    - $0.27M UTRC
  - FY10: $384K
  - FY11: $0K
- **Barriers**
  - F. Codes & Standards
  - A. System Weight & Volume
- **Target**
  - EH&S: “Meets or exceeds applicable standards”
- **Partners**
  - Kidde-Fenwal: dust cloud testing

    Kidde Fenwal
  - Multiple collaborators:

    SNL, SRNL, IEA HIA Task-31, Lincoln Composites, NFPA-2, HSECoE

Collaborations

Other DOE Reactivity Projects

- Savannah River National Lab
- Sandia National Labs

IEA HIA Task 22 / IPHE Project (with SRNL & SNL)

- FZK (Germany, Government lab)
- AIST (Japan, Government lab)
- UQTR (Canada, University)

Additional Collaborations

- DOE Hydrogen Program Codes & Standards
- DOE Hydrogen Program Safety Panel
- NFPA-2 Hydrogen Technology Committee
- Lincoln Composites
- IEA HIA Task 31
- HSECoE

Project Objectives & Associated Tasks

High-Level Objectives

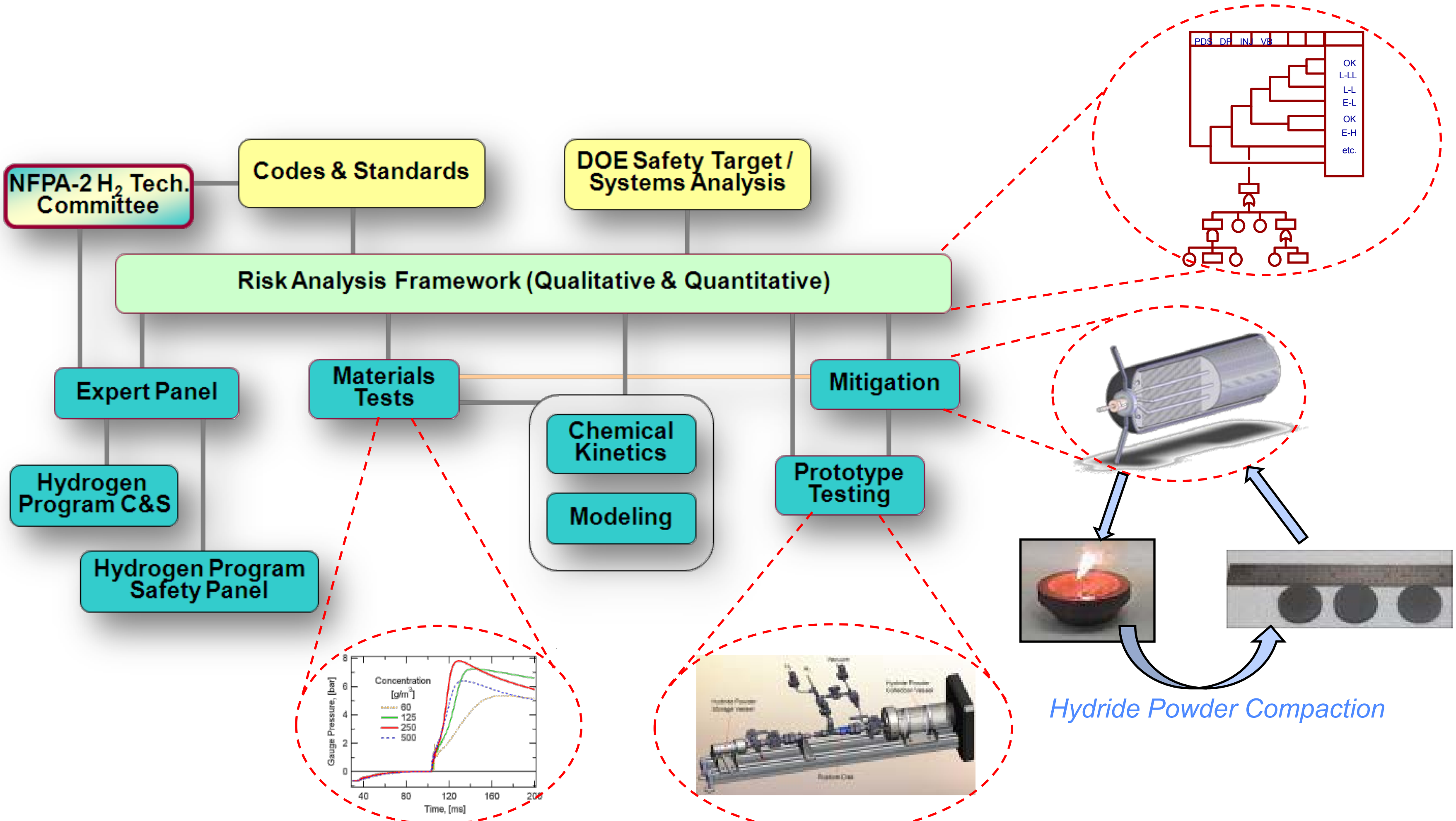
- Contribute to quantifying the DOE On-Board Storage Safety Target: "Meets or exceeds applicable standards."
- Evaluate reactivity of key materials under development in the materials Centers of Excellence.
- Develop methods to reduce risks.

Primary Tasks

- Risk analysis (Task 1.0)
  - Qualitative risk analysis (QLRA) for a broad range of scenarios
  - Quantitative risk analysis (QRA) for key scenarios
- Material testing
  - Dust cloud: standard and modified ASTM procedures (Task 2.0)
  - Reaction kinetics: air exposure / time resolved XRD (Task 3.0)
- Risk mitigation
  - Material-based risk mitigation tests (Task 4.0)
  - Atomic and thermodynamic modeling of hydrides oxidation and hydration reactions (Task 4.0)
  - Subscale prototype test (Task 5.0)

Approach

Materials testing and modeling results are used to supplement the Risk Analysis (RA) Framework which serves as the basis for risk-informed safety C&S.



Hydride Powder Compaction

Dust Cloud Test

Fast Depressurization

Materials & Systems

Examine hydrogen storage candidate materials and related system configurations which are being developed within the DOE Hydrogen Program.

Current Focus Materials:

- $NaAlH_4$
- Activated carbon (AX-21)
- AlH_3
- NH_3BH_3
- $2LiBH_4 + MgH_2$
- $3Mg(NH_2)_2.8LiH$
- Others – refer to HSCoE "Candidate Materials Matrix"

Tier 1 ($NaAlH_4$, Activated carbon (AX-21), AlH_3, NH_3BH_3)

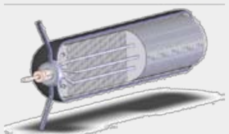
General System Classes:

- On-board reversible hydride bed systems (guided by $NaAlH_4$ prototypes)
- On-board reversible adsorbant systems (activated carbon)
- Off-board regenerable based systems (alane & ammonia borane)

Overview of Technical Accomplishments

- **Quantitative Risk Analysis (QRA)**
  - On-board reversible storage system fault tree (FT) model.
  - Fault tree model for hydrogen permeation / leakage from storage vessels.
  - Fault tree model for solid AB off-board regenerable storage system.
  - Fault tree model of on-board solid AB thermolysis reactor failure.
- **Qualitative Risk Analysis (QLRA)**
  - Critical risks and failure mechanisms of a baseline design of an on-board reversible hydrogen storage system.
  - Critical risks and failure mechanisms of a baseline design of an off-board regenerable alane-based storage system.
- **Risk Mitigation**
  - Atomic and thermodynamic modeling of $NaAlH_4$ oxidation and hydration reactions.
- **Experimental Studies**
  - Material reactivity risk mitigation tests.
  - Fast blowdown (depressurization) tests.
  - Dust cloud combustion tests.
  - Mechanical impact sensitivity tests.
  - Hot surface contact tests.
  - X-Ray diffraction analysis.

QLRA: Safety-Significant Failure Mechanisms of On-Board Reversible Storage Systems



Storage vessel & TPRD are the most safety-significant components in the on-board H2 storage system

Safety-Significant Failure Mechanisms that Challenge Vessel Integrity of On-Board Reversible Storage Systems

- **1. Catastrophic Failure of the Hydride Storage Vessel**
  - **1.1 Vessel Rupture Caused by Vehicular Collision**
  - **1.2 Vessel Burst Due to External Fire & TPRD Fails to Vent**
- **2. Hydrogen Permeation or Leakage Leading to Early/late Ignition and/or Explosion**
  - **2.1 Pipe Break**
  - **2.2 TPRD Spurious Venting**
  - **2.3 Loose Joints, Fittings, etc**
  - **2.4 Hydrogen Permeation / Diffusion**
- **3. Fluid Intrusion into Storage Vessel Leading to Chemical Reaction with Hydride Material**
  - **3.1 Water Intrusion into Storage Vessel Leading to Chemical Reaction with Hydride Material**
  - **3.2 Air Intrusion into Storage Vessel Leading to Chemical Reaction with Hydride Material**

Overview of Risk Mitigation Tests

Figure 1: Mechanical Impact Sensitivity Test ($NaAlH_4$)

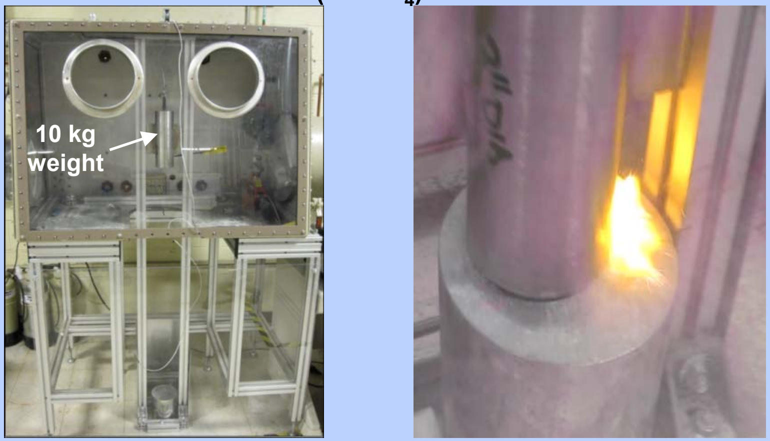


Figure 2: Storage Vessel Fast Depressurization Rig.

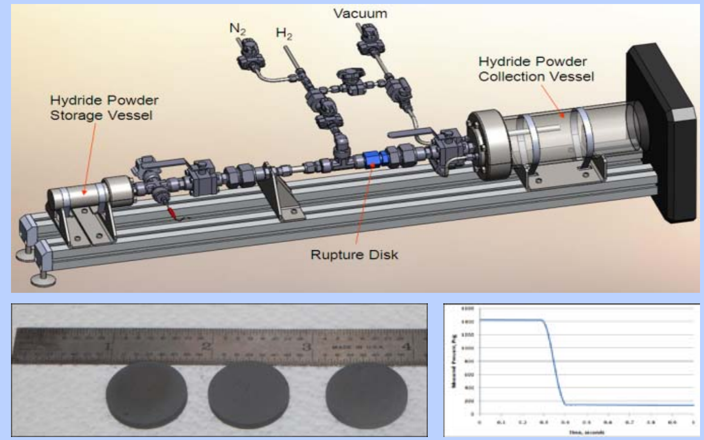
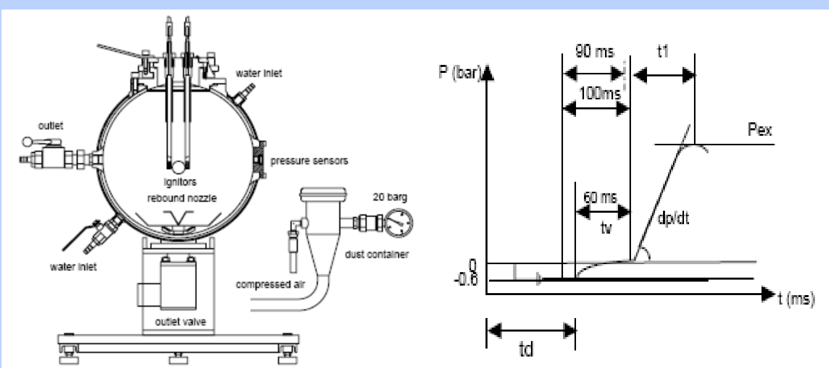


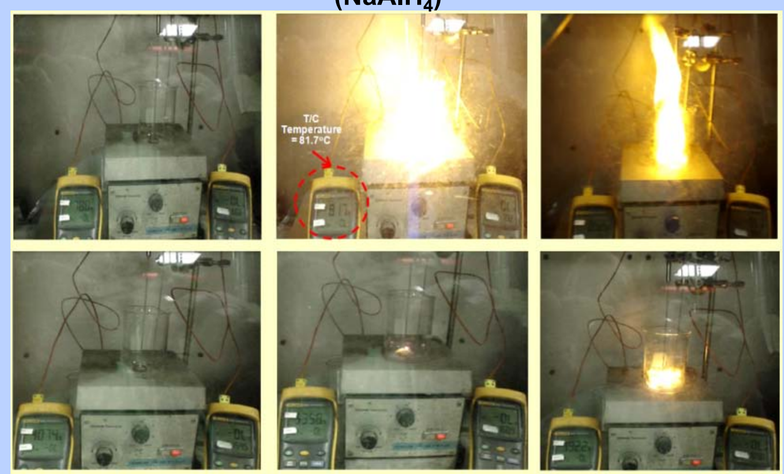
Figure 3: Dust Cloud Explosibility and Ignition Properties



Kühner 20-liter spherical explosion test apparatus.

Pressure / time Profile of dust explosion in a 20-liter vessel.

Figure 4: Hydride Powder Compact Contact with Hot Surface ($NaAlH_4$)



Overview of Risk Mitigation Tests (cont'd)

Figure 5: Material's State-Dependent Pyrophoricity

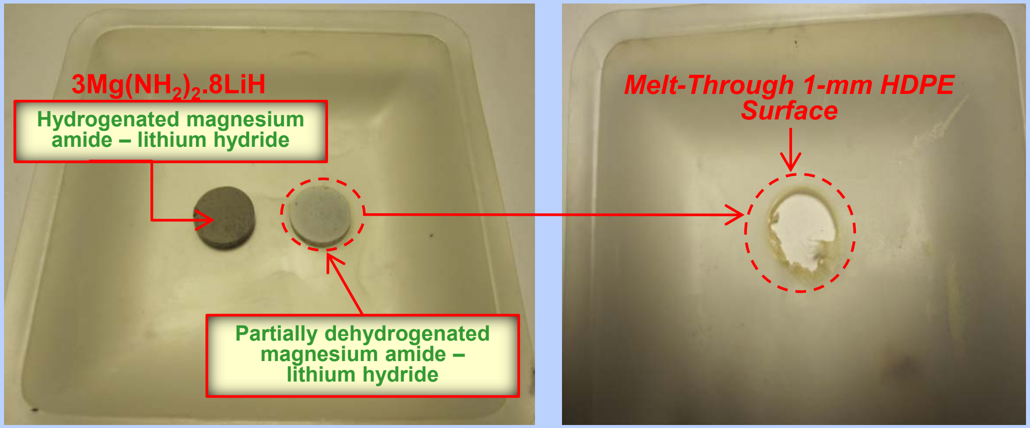


Figure 6: Powder ($NaAlH_4$) Pyrophoricity

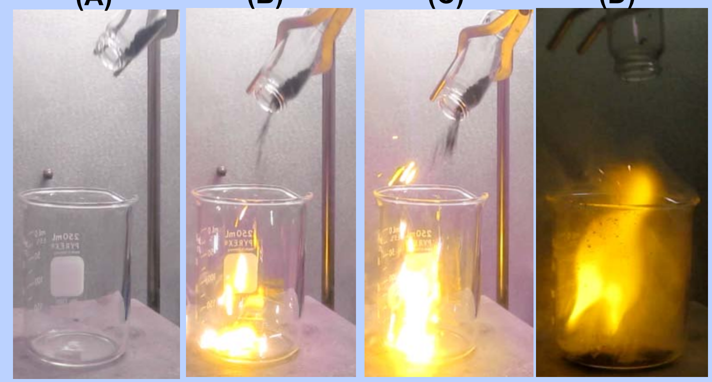


Figure 7: X-Ray Diffraction (XRD)

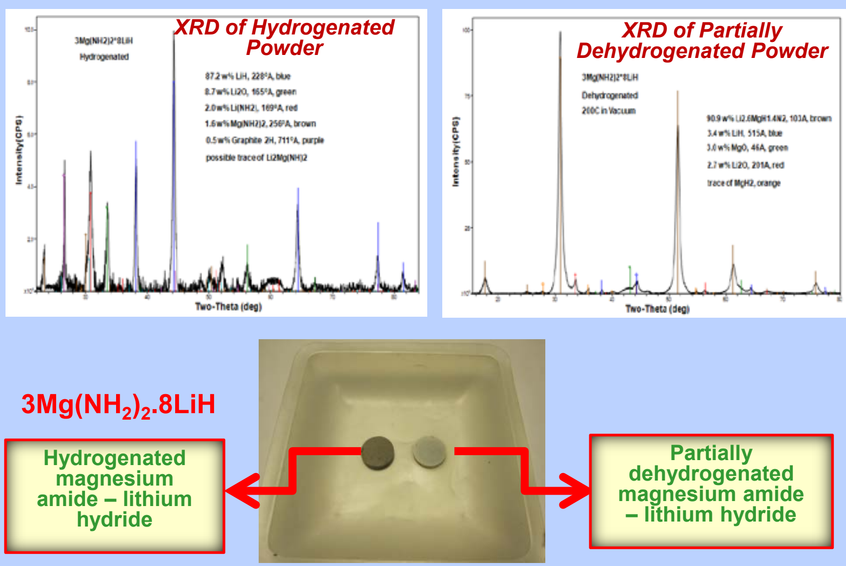
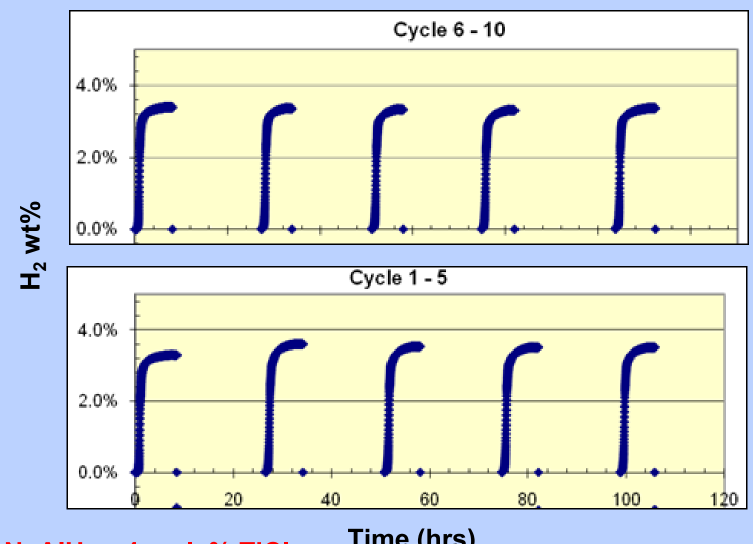


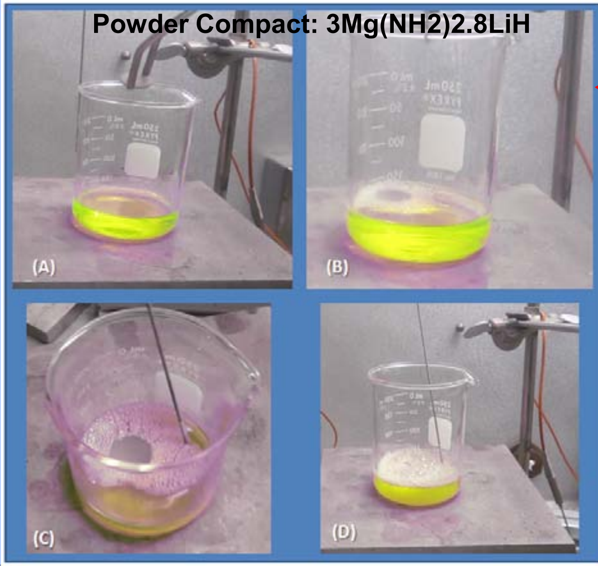
Figure 8: Hydrogen Desorption (wt %) vs. Time (hrs) for 10 Cycles



$NaAlH_4$ + 4 mole% $TiCl_3$

Overview of Risk Mitigation Tests (cont'd)

Figure 8: Powder and Powder Compact Contact Tests with Different Fluids (water, brine, windshield washing fluid, antifreeze, engine oil and thermo-oil)



0.5-gram wafer dropped into 50 ml engine coolant (antifreeze) – mild reaction with bubbles and liquid temperature rise of ≈1-2°C and no ignition.

Brine solution gradually dropped on a 0.5-gram heap of 3Mg(NH2)2.8LiH. First, gases evolved upon contact followed by ignition and fire.

Powder: 3Mg(NH2)2.8LiH

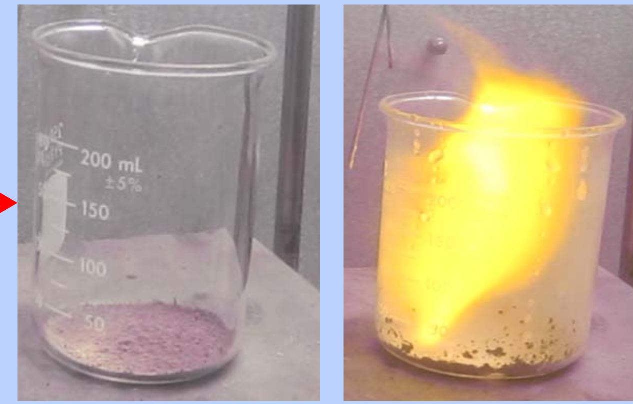
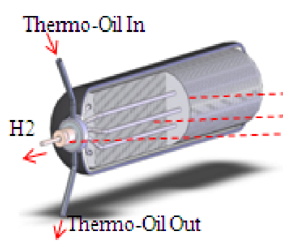
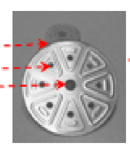


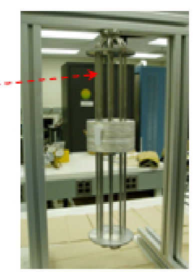
Figure 9: Localized Flame Impingement Test (UTRC in collaboration with SNL)



Prototype 2 Vessel



Heat exchanger (0.004" Al) fin geometry – total 80 fins



Prototype 2 heat exchanger assembly with consolidated fin stack (HX U-tubes are shown)

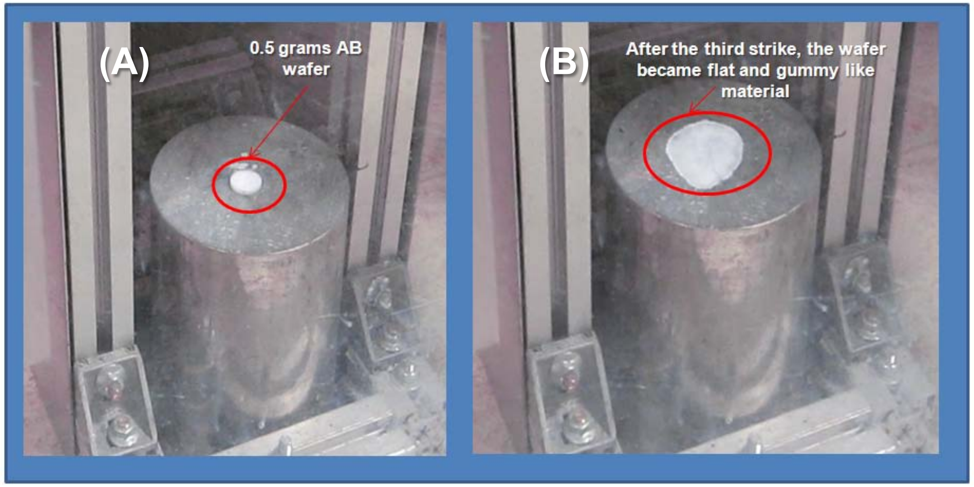
Completed heat exchanger / Stainless Steel liner assembly

Addition of carbon fiber wound composite

UTRC Prototype-2 Carbon Fiber Composite Vessel (1/8th scale) Containing 3.5 kg Sodium Alanate

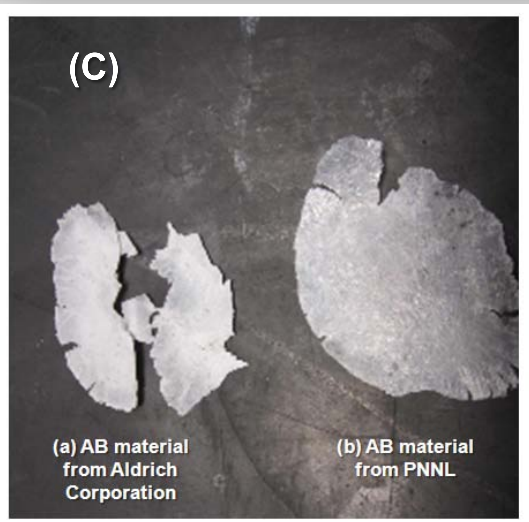
Solid Ammonia Borane Mechanical Impact Sensitivity Test

- *Solid AB powder from different sources: Aldrich Corporation and Aviabor*.*
- *Powder compaction at UTRC.*



<u>Test Observations</u>:

- Wafer flattened out as a result of the mechanical impact.
- Material didn't ignite – not sensitive to mechanical impact.

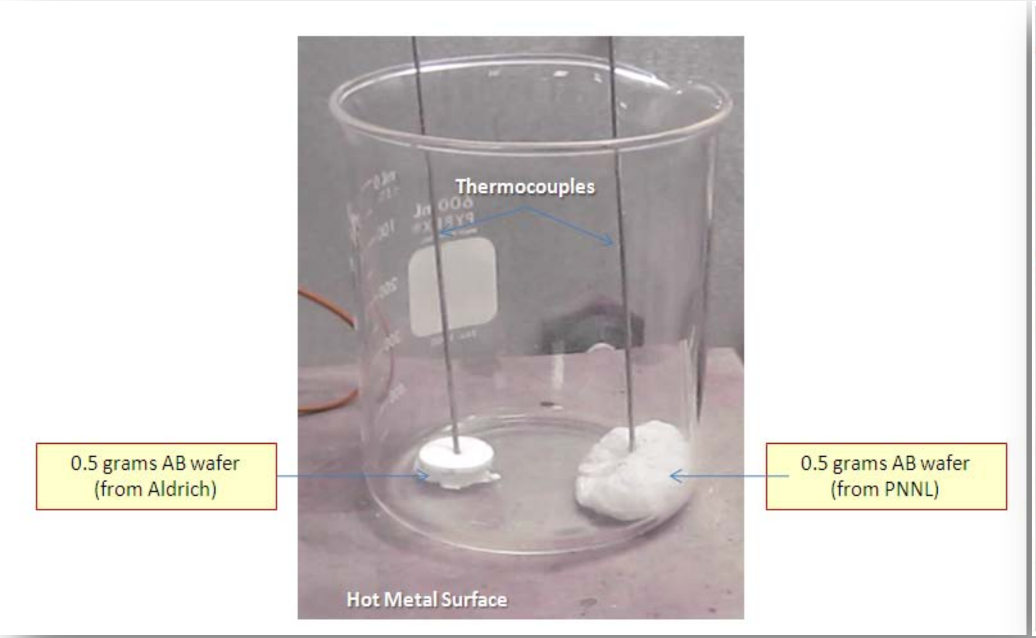


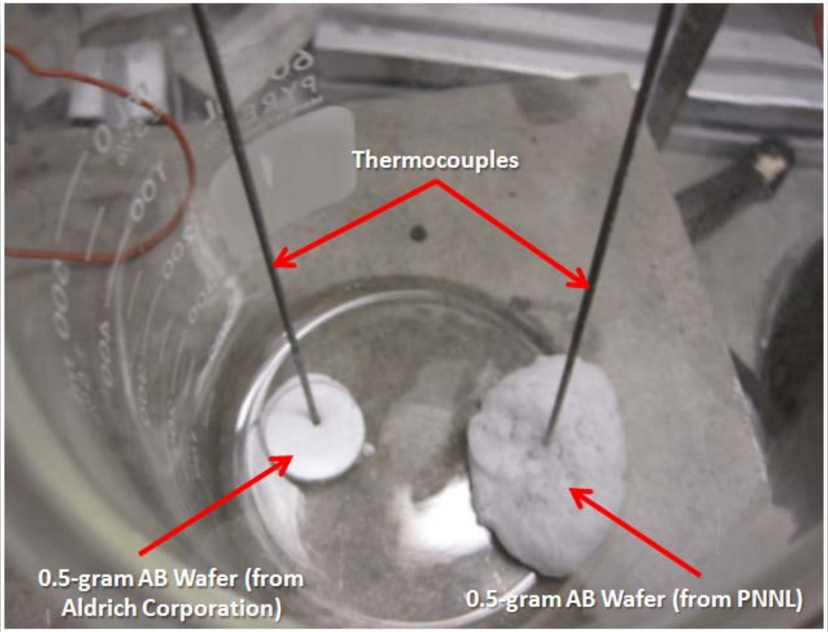
Mechanical Impact Test of a 0.5-gram Solid AB Wafer
Impact energy = 98 Joules

PNNL sample originally purchased from Aviabor.

Solid Ammonia Borane (AB): Hot Surface Contact Test

- *Solid AB powder from different sources: Aldrich Corporation and Aviabor.*
- *Powder compaction at UTRC.*





AB Powder Compact (0.5 grams wafers) in Contact with a Hot Metal Surface Maintained at ≈ 210.5^{o}F (the top surface of the wafer reached ≈ 181^{o}F)

<u>Test Observations</u>:

- As shown in Figs. 5(A) and (B), the two samples swelled out after about a 2 hours but didn't ignite.
- The swelling and foaming of the PNNL sample was more pronounced compared to the Aldrich sample. It is possible that the impurities present in the PNNL sample contributed to this observed phenomenon.

Solid Ammonia Borane (AB): XRD Analysis

- *Solid AB powder from PNNL / Aviabor.*
- *Powder compaction at UTRC.*

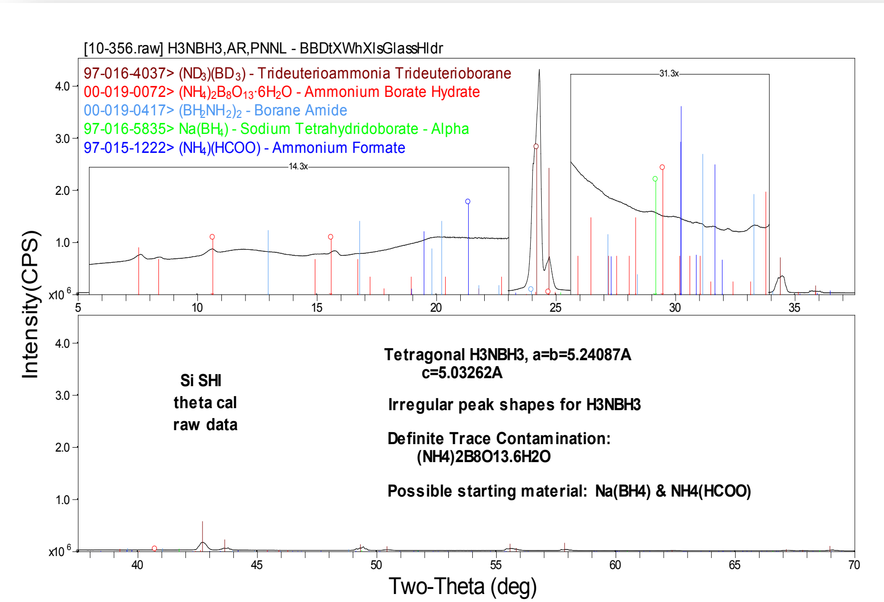


Fig. A: XRD of the As-Received AB Sample from PNNL.

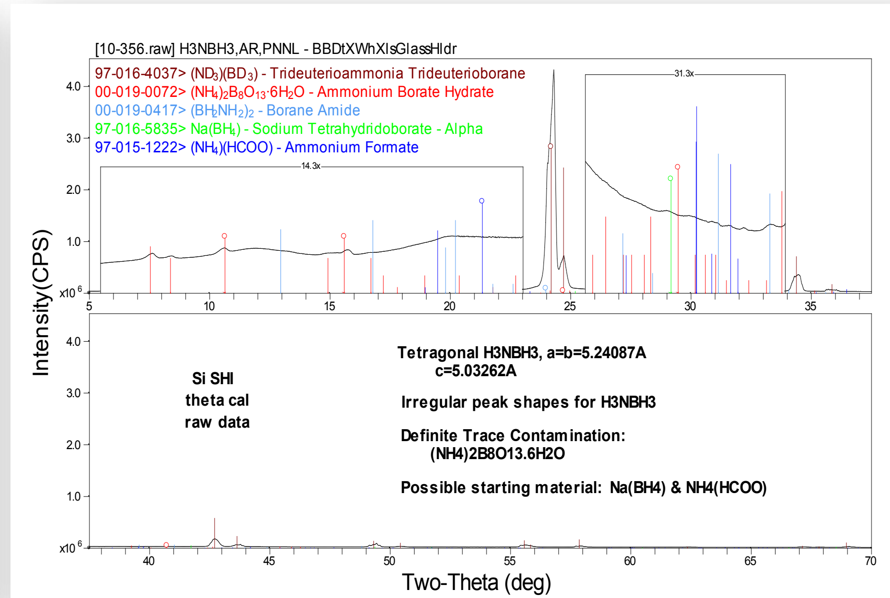


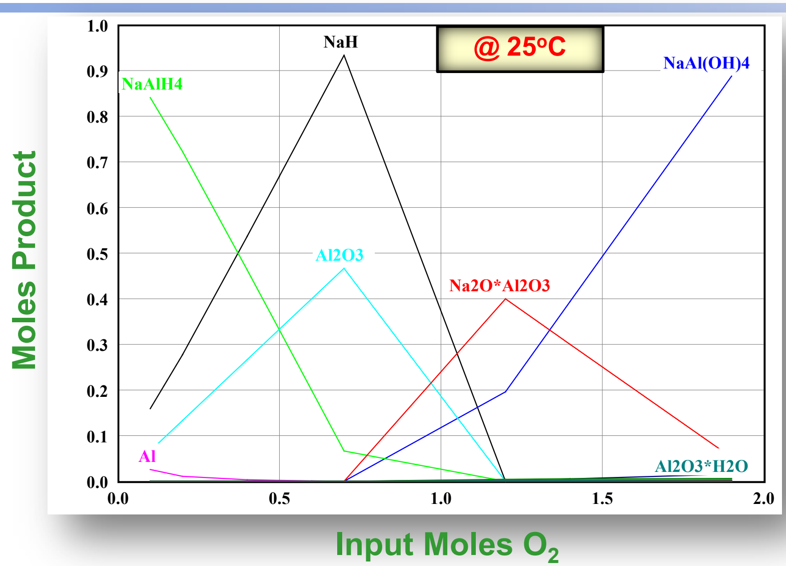
Fig. B: XRD of PNNL-Supplied Ammonia Borane Sample after the Mechanical Impact Test.

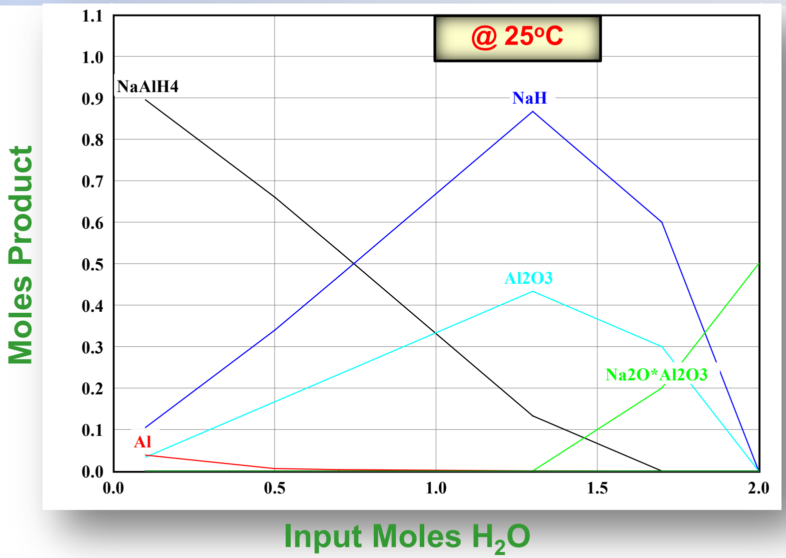
Test Observations:

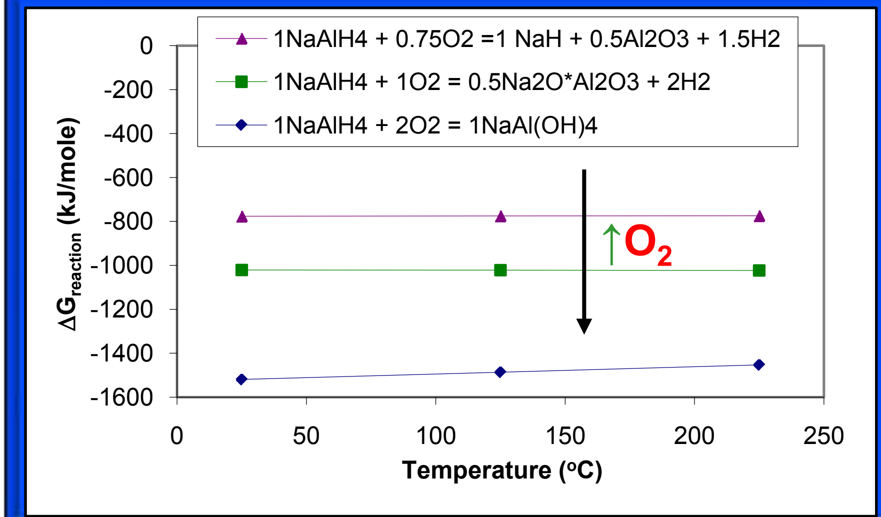
- X-ray diffraction conducted on the as-received AB sample that was received from the PNNL before the mechanical impact tests were conducted – Figure (A). As shown, the sample is tetragonal H3NBH3 with a low level contaminants.
- X-ray diffraction conducted on a portion of the AB powder compact sample after the mechanical impact test was completed to assess the level of impurities that might be present in PNNL-supplied AB – Figure (B).

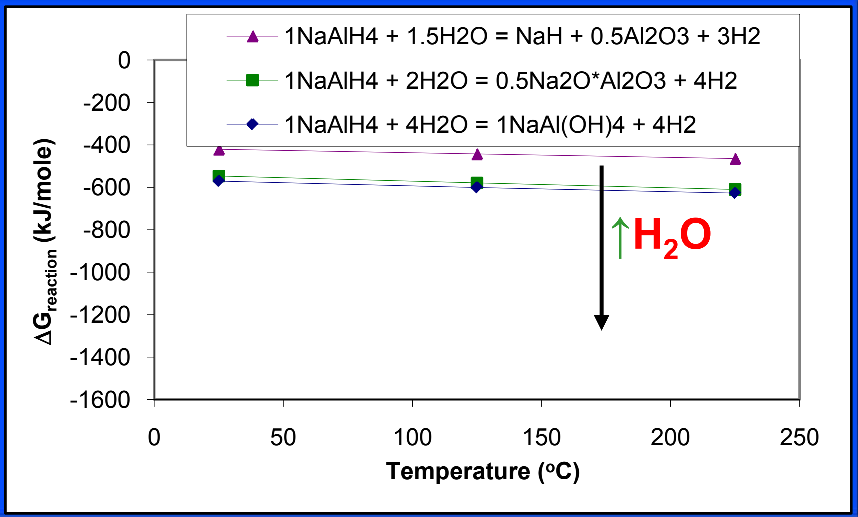
$NaAlH_4$ Oxidation/Hydration Products Vary with $[O_2/H_2O]$

Most Stable solid products of 1 mole $NaAlH_4$ with ↑ moles O_2 and H_2O at 25 ºC









With ↑ $O_2/H_2O:NaAlH_4$, surface reactions progressively form Al_2O_3, $Na_2O*Al_2O_3$, and $NaAl(OH)_4$.

Dust Cloud Combustion Characterization: Summary of Test Results

Parameter	**Hydrogen Storage Material**					
	Maxsorb (AX-21)	Charged AlH_3	Discharged AlH_3	($2LiBH_4$ + MgH_2)	Charged $NaAlH_4$	H_2 Gas*
$(\Delta P)_{MAX}$ Bar-g	8.0	3.7	10.3	9.9	11.9	7.9 @ 29 vol% H_2 in air
$(dP/dt)_{max}$ = R_{MAX}, bar/s	449	370	4082	1225	3202	5435 @ 29 vol% H_2 in air
K_{ST} bar-m/s	122	101	1,100	333	869	1477
MIE, mJ	Range 500 - 1000	< 10	< 10	< 9.2	< 7	0.02
MEC, g/m^3	80	30	125 - 250	30	140	4 vol% in air
T_C, ^oC	760	200	710	230	137.5	n/a

* *Hydrogen gas is used as a frame of reference*

Key Risk Insights from Dust Cloud Combustion Characterization Tests

Based on the results generated from combustion characterization tests for selected hydrogen storage materials (*compared to H2G as a frame of reference*), the following insights can be drawn:

1. **Discharged alane** has ΔP_{max}, ΔR_{max} and K_{ST} much greater than corresponding values of **charged alane**.

2. Relative ranking of dust cloud combustion severity as measured by $\mathbf{K_{ST}}$ index (bar-m/s):

H2G > Discharged AlH_3 > Charged $NaAlH_4$ > ($2LiBH_4$-MgH_2) > AX-21 > Charged AlH_3

3. Relative ranking of dust cloud minimum ignition energy (**MIE**):

AX-21 > Charged & Discharged AlH_3 > ($2LiBH_4$-MgH_2) > Charged $NaAlH_4$ > H2G

Other Safety-Related Properties

4. Relative ranking of **toxicity** of material or its decomposition products:

Solid NH_3BH_3 > H2G* > Maxsorb AX-21

* Compressed hydrogen gas (H2G) is considered to be an Asphyxiant by displacing O_2 in air

5. Relative ranking of material **reactivity in dry air**:

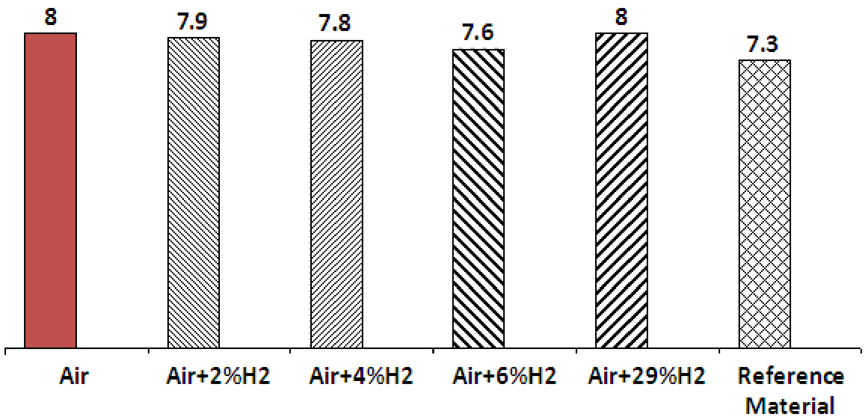
$NaAlH_4$ > Charged & Discharged AlH_3 > ($2LiBH_4$+MgH_2) > Solid NH_3BH_3

6. Relative ranking of material **reactivity in moist air**:

$NaAlH_4$ > Charged & Discharged AlH_3 > ($2LiBH_4$+MgH_2) > Solid NH_3BH_3

Maxsorb Activated Carbon Powder Combustion Characterization Tests

Maximum Explosion Pressure (P_{MAX}), bar-g

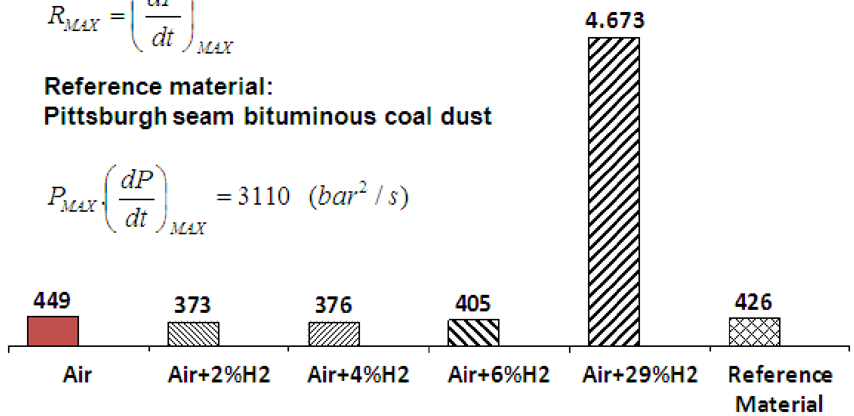


Maximum Rate of Pressure Rise (R_{MAX}), bar/s

$$R_{MAX} = \left(\frac{dP}{dt}\right)_{MAX}$$

Reference material:
Pittsburgh seam bituminous coal dust

$$P_{MAX} \cdot \left(\frac{dP}{dt}\right)_{MAX} = 3110 \quad (bar^2 / s)$$



Maximum Volume-Scaled Rate of Pressure Rise (K_{ST}), bar-m/s

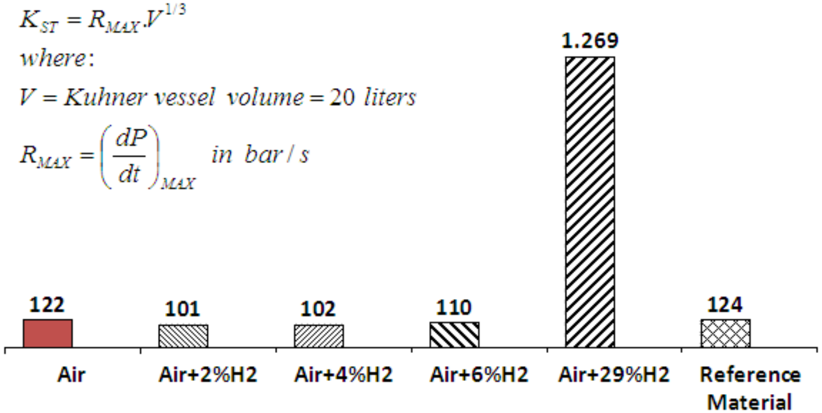
Explosion Severity Index (K_{ST}) :
Volume-scaled index expressed by a Cube Law

$$K_{ST} = R_{MAX} . V^{1/3}$$

where:

$$V = \text{Kuhner vessel volume} = 20 \text{ liters}$$

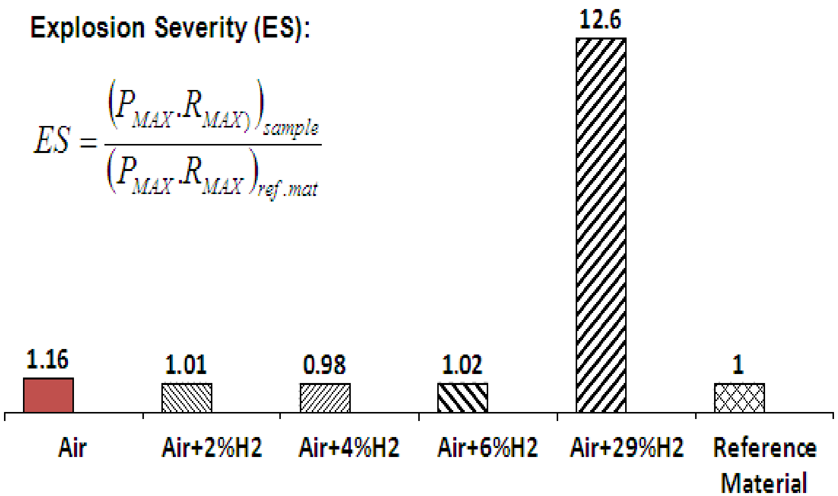
$$R_{MAX} = \left(\frac{dP}{dt}\right)_{MAX} \quad \text{in } bar/s$$



Explosion Severity (*ES*)

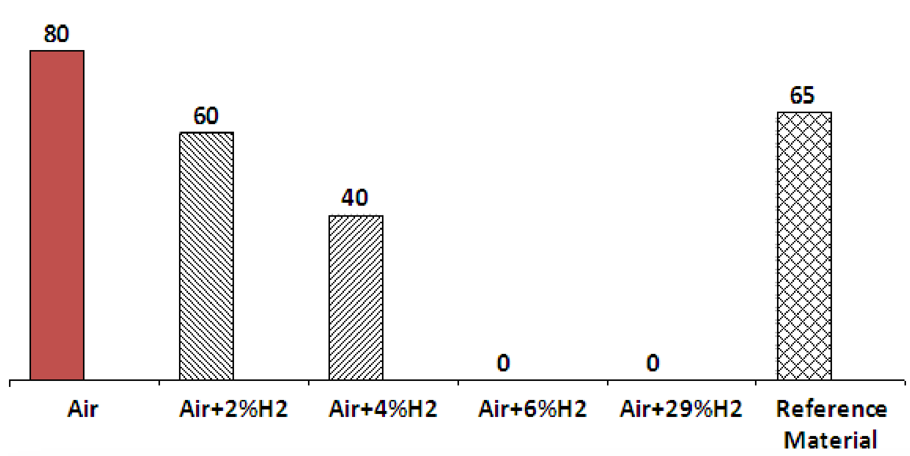
Explosion Severity (ES):

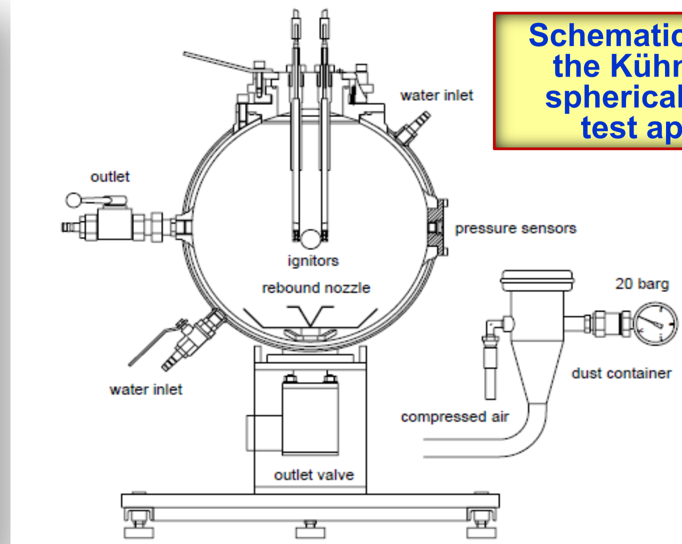
$$ES = \frac{(P_{MAX} . R_{MAX})_{sample}}{(P_{MAX} . R_{MAX})_{ref.mat}}$$



Maxsorb Activated Carbon Powder Combustion Characterization Tests

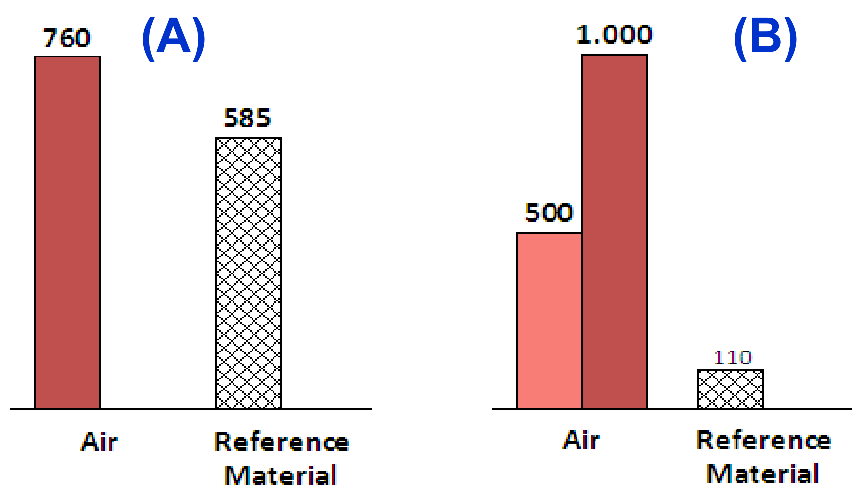
Minimum Explosible Concentration (MEC), g/m^3

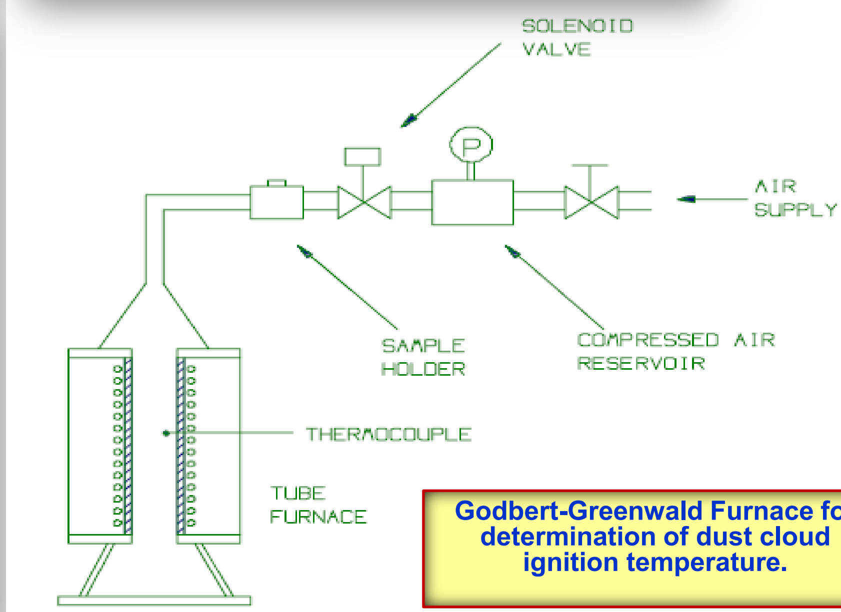




Schematic diagram of the Kühner 20-liter spherical explosion test apparatus.

(A) Minimum Ignition Temperature (T_C, °C)
(B) Minimum Ignition Energy (MIE, mJ)



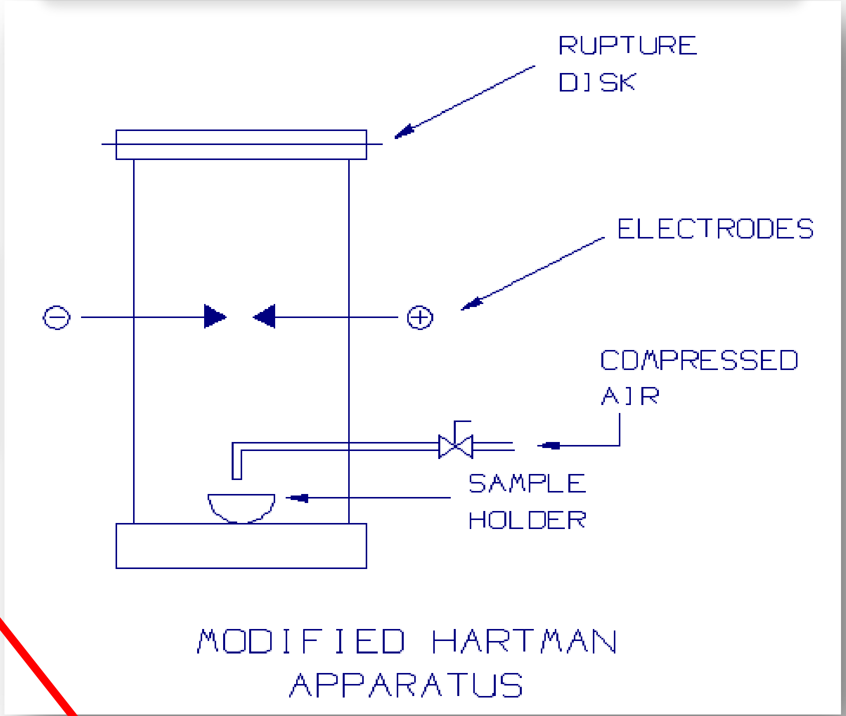


Godbert-Greenwald Furnace for determination of dust cloud ignition temperature.

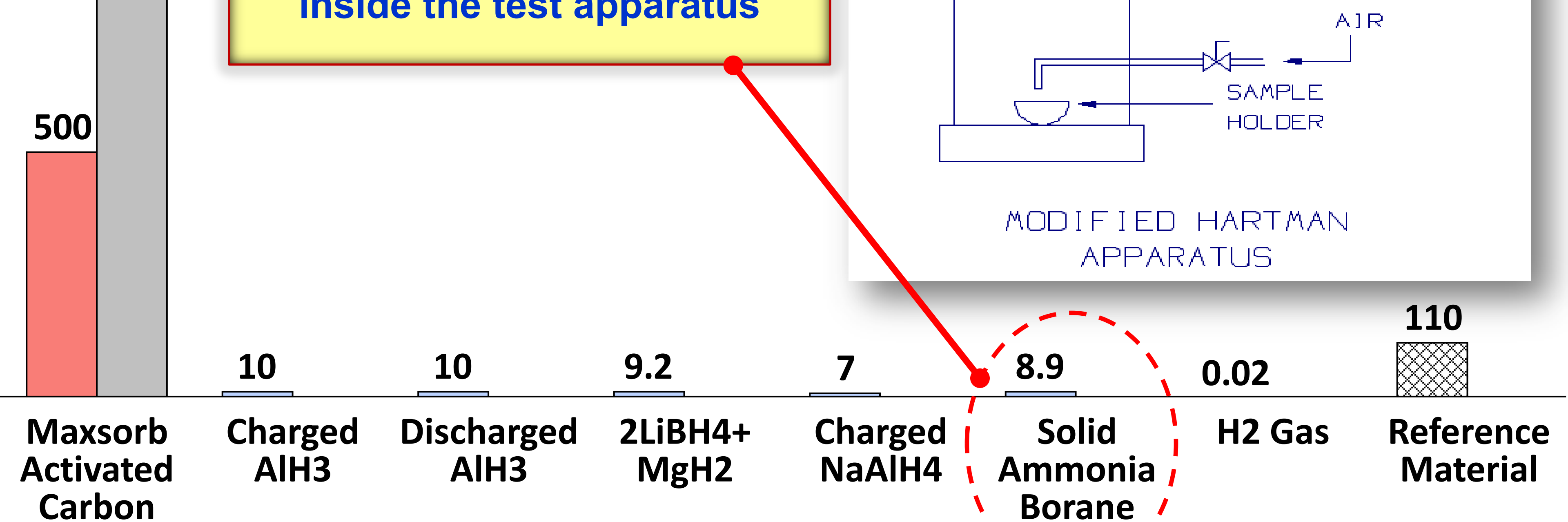
Minimum Ignition Energy (MIE in mJ) of Selected Metal Hydrides, Chemical Hydrides and Adsorbents

ASTM E-2019 reference material is Pittsburg seam coal.

Modified Hartmann apparatus for determining MIE (mJ)



Solid ammonia borane (NH_3BH_3) ignited violently inside the test apparatus



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Fast Depressurization Test Matrix

$NaAlH_4$ | NH_3BH_3 | $NaH+NaCl+Al+Ti_2O_3+C$ | $3Mg(NH_2)_2.8LiH$

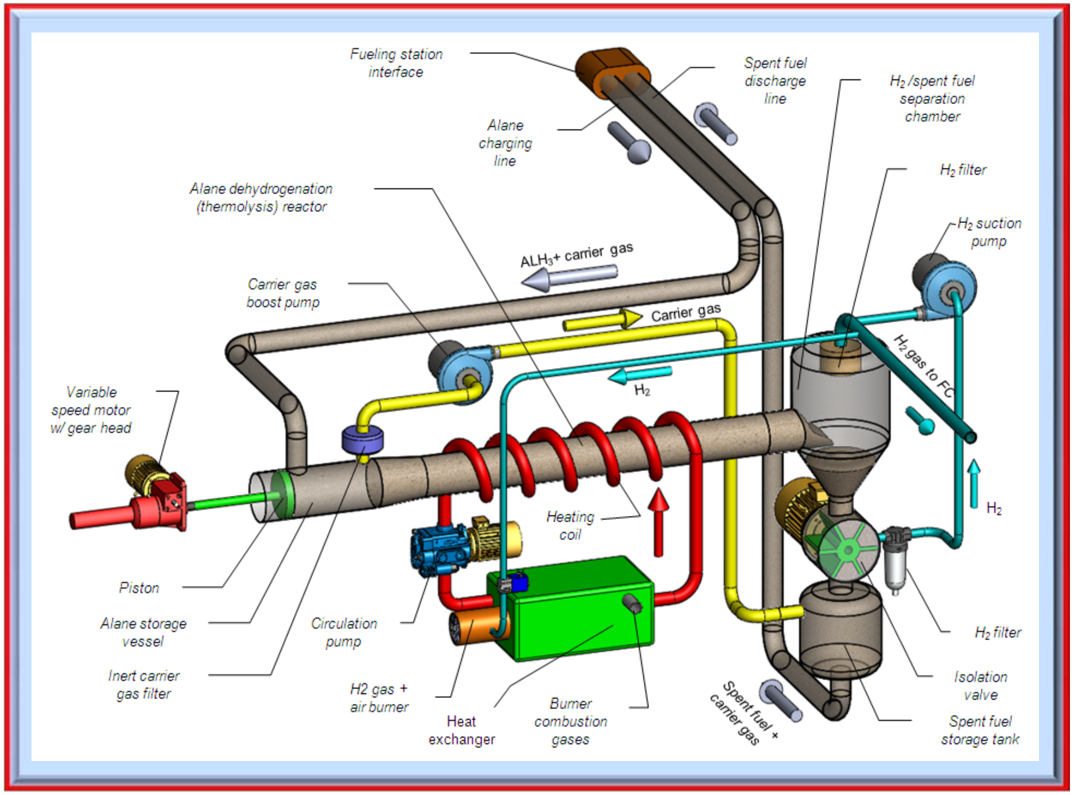
Depressurization from 100 atm to 10 atm in 45 msec.

Charged, Discharged, and # of Cycles	Powder Mass (gr)	Powder Compact (Wafer) Mass (gr)				
	30	0.5	1.0	1.5	4.0	6.0
As received (discharged)	16.5 wt% blown off / entrained	No fragmentation		No fragmentation		Fragmented, 66 wt% blown off / entrained
Cycled once (discharged)						Fragmented, 28 wt% blown off / entrained
Cycled once (charged)					No fragmentation	Fragmented, 1 1 wt% blown off/entrained
Cycled 5X (charged)			No fragmentation		No fragmentation	
Cycled 10X (charged)			Fragmented, no entrainment.			
Cycled 15X (discharged)			Fragmented, no entrainment.			

Preliminary observations from the fast depressurization / blowdown tests:

- The likelihood of fragmentation of the powder compact increases as the mass of the hydride increases.
- The likelihood of fragmentation of the powder compact increases as the number of H_2 absorption / desorption cycles increases.

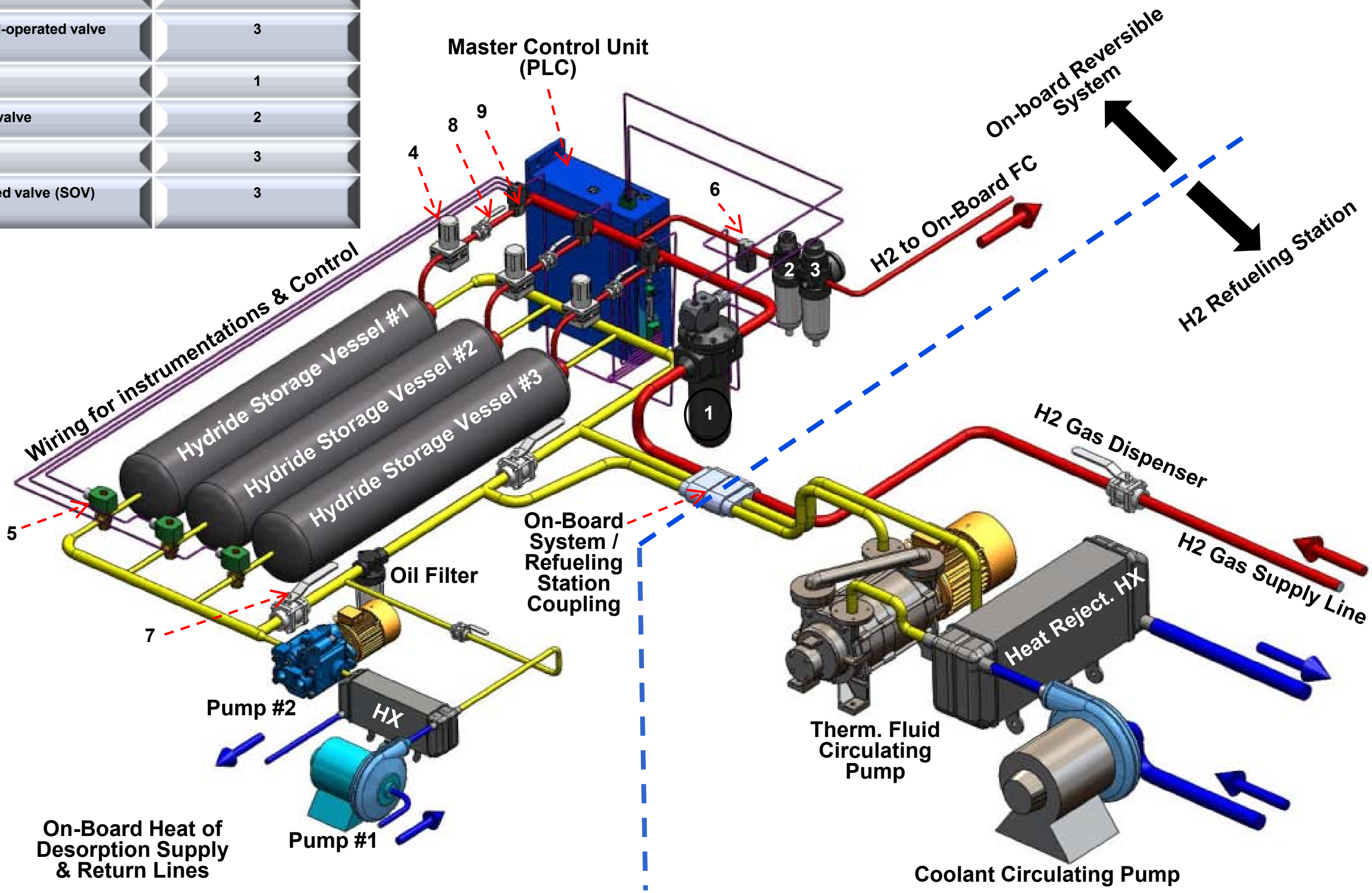
Critical Failure Mechanisms of UTRC Baseline Design of an Off-Board Regenerable Alane (AlH_3) System



Critical Failure Mechanisms	Failure Causes
1) Failure to transport the fresh AlH_3 powder through the system.	• Failure of the variable-speed motor to operate or jamming of the connected driving piston will lead to failure to deliver the fresh alane to the thermolysis reactor and, hence, failure to generate hydrogen gas to feed the on-board fuel cells.
2) Failure of thermal management of the on-board AlH_3 thermolysis reactor.	• Failure of the hydrogen burner or the pump that circulated the thermo-fluid that heats the thermolysis reactor. • Leakage of the thermo-fluid from the heating coil.
3) Accidental exposure of the spent fuel (discharged alane) to air leading to dust cloud explosion.	• Rupture in the pressure boundary of the spent fuel separation chamber or the spent fuel collection tank.

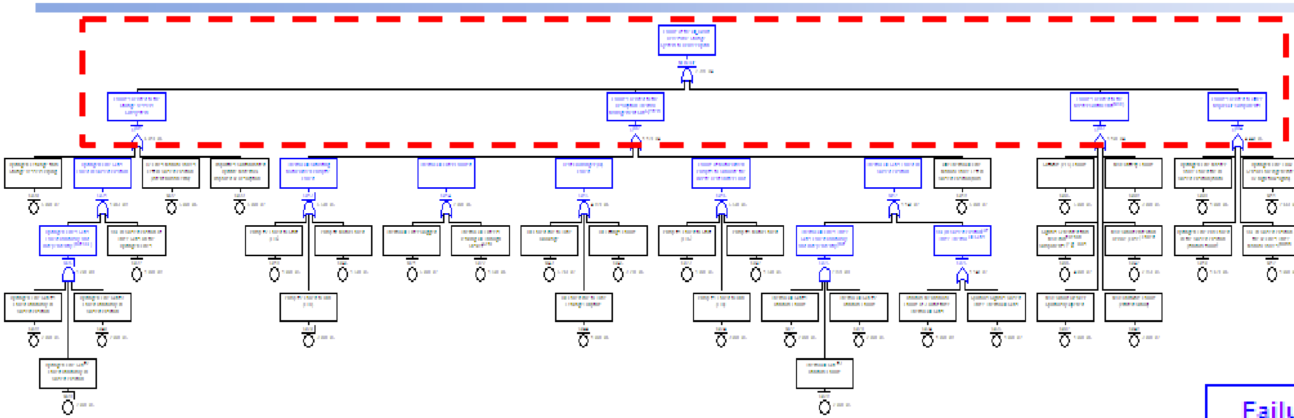
UTRC Baseline Design of an On-Board Reversible Storage System

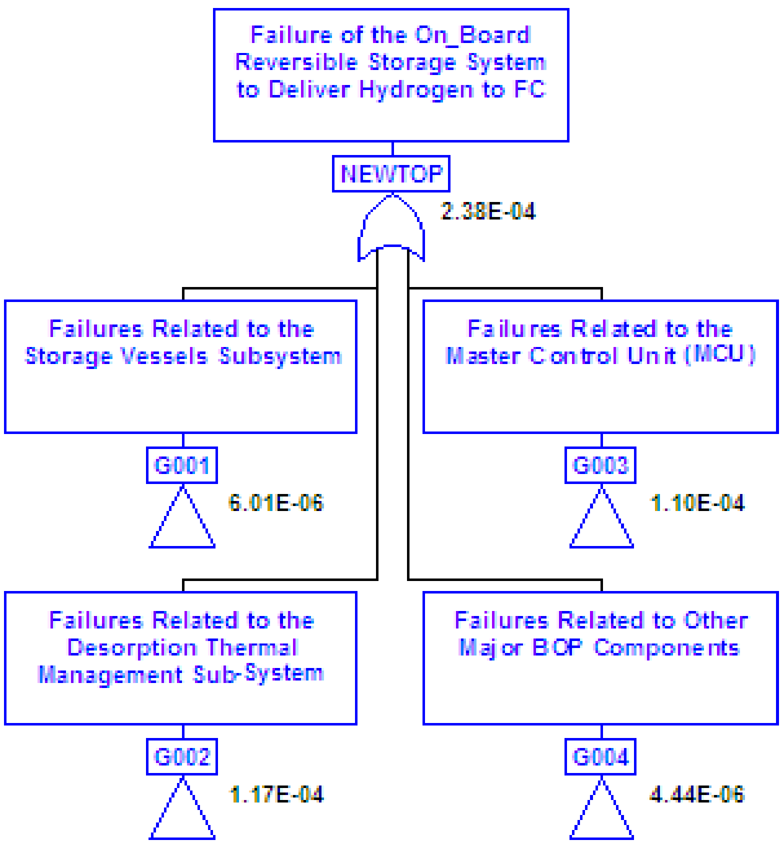
ID	Description	# of Components
1	Particulates filer & humidity sensor	1
2	H2 line master valve	1
3	H2 line pressure regulation valve (PRV)	1
4	H2 line pressure relief device (PRD)	3
5	Thermo-oil line solenoid-operated valve (SOV)	3
6	H2 line flow sensor	1
7	Thermo-oil line manual valve	2
8	H2 line manual valve	3
9	H2 line solenoid-operated valve (SOV)	3



United Technologies Research Center

On-Board Reversible Storage System Fault Tree (FT) Model





FT model quantification resulted in:

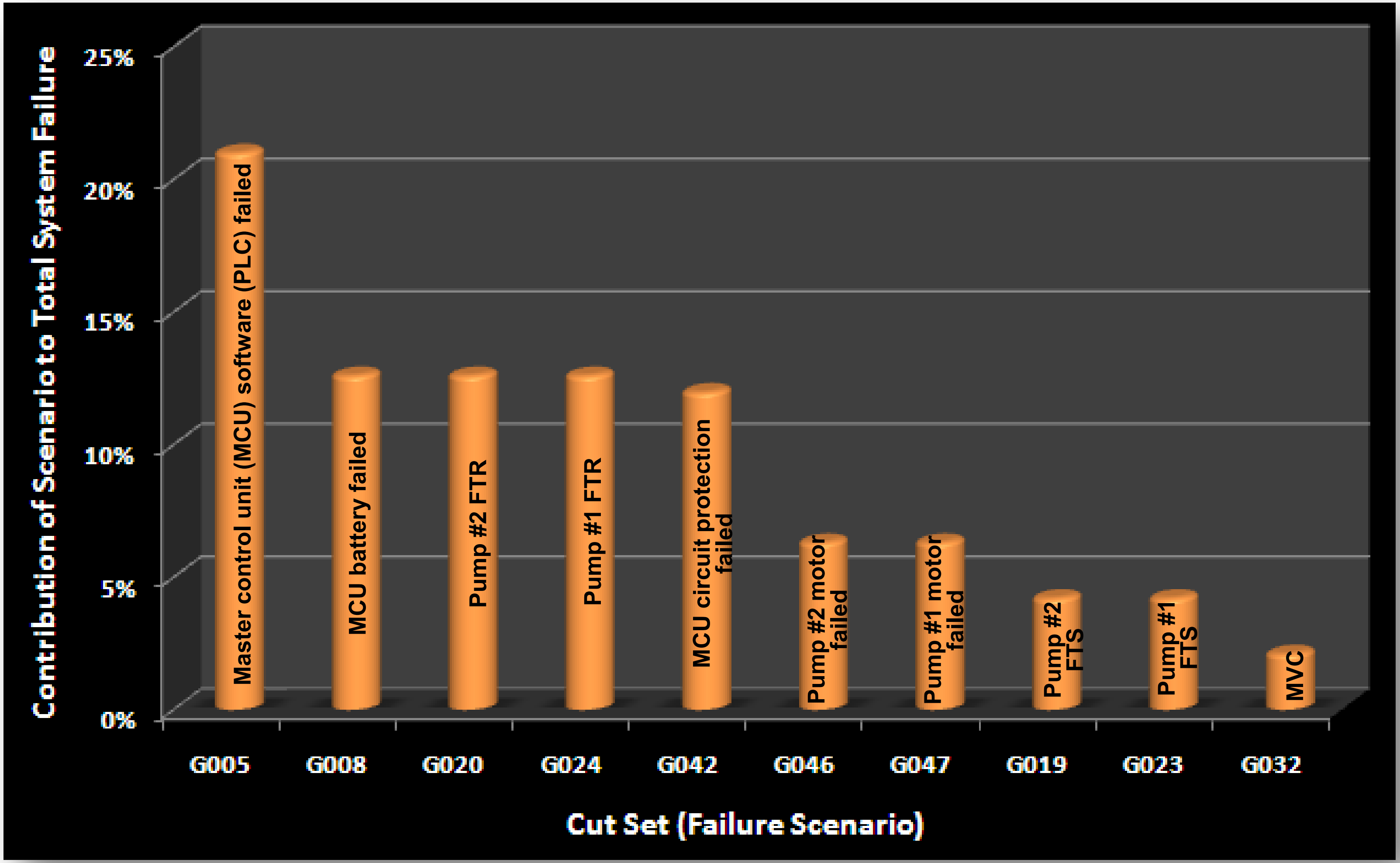
- Thirty mutually exclusive minimal cut sets (failure scenarios).
- Based on an assumed quantification truncation limit of < 1.0E-8, two cut sets were screened out.
- Twenty eight mutually exclusive minimal cut sets (failure scenarios) were above the truncation limit.

Probabilities shown are preliminary and based on input from the expert panel.

Mutually Exclusive Minimal Cut Sets (Failure Scenarios) with Importance Measures

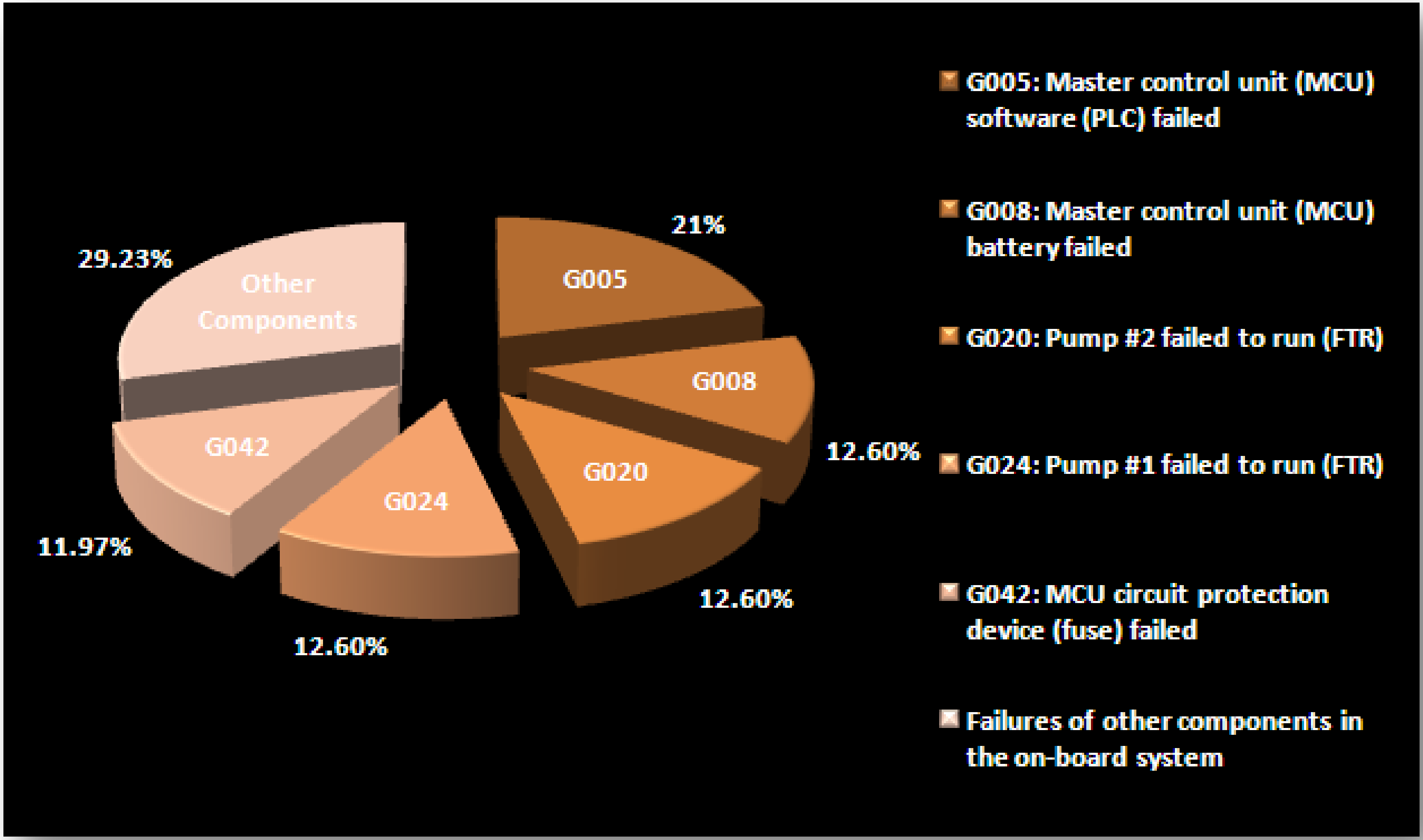
Minimal Cut Set	Description of Minimal Cut Set (Failure Scenario)	$(RRW)_{BE}$	$(FV)_{BE}$	$1 - (FV)_{BE} = 1 / (RRW)_{BE}$
G005	Master control unit (MCU) software (PLC) failed	1.2658	0.210	0.790
G008	Master control unit (MCU) battery failed	1.1441	0.126	0.874
G020	Pump #2 failed to run (FTR)	1.1441	0.126	0.874
G024	Pump #1 failed to run (FTR)	1.1441	0.126	0.874
G042	MCU circuit protection device (fuse) failed	1.1359	0.120	0.880
G046	Pump #2 motor failed	1.0672	0.063	0.937
G047	Pump #1 motor failed	1.0672	0.063	0.937
G019	Pump #2 failed to start (FTS)	1.0438	0.042	0.958
G023	Pump #1 failed to start (FTS)	1.0438	0.042	0.958
G032	H_2 lines manual valves left in closed (MVC) position (latent human error)	1.0214	0.021	0.979
G045	Heat exchanger (HX) fittings failure	1.0140	0.014	0.986
G010	H_2 line PRV failed in closed position (random failure)	1.0071	0.007	0.993

Top Ten Minimal Cut Sets (Failure Scenarios) Ranked Based on Contribution to Total On-Board Reversible System Failure



The top ten contributors to total system failure identify the best candidate components to reduce likelihood of failure of the on-board reversible system

On-Board Reversible System Reliability Improvement



About 70% reduction in system unreliability can be achieved by improving the reliability of the on-board master control unit (MCU) and the on-board thermal management circulating pumps.

Proposed Future Work

FY11

Task	Description
Task 1	• Establish a framework for incorporating risk mitigation into the event tree (ET) models that characterize the accident sequences for different initiating events (IE). • Establish a framework for consequence analysis of selected accident sequences as derived from QLRA and QRA.
Tasks 2 and 4	• Perform dust cloud combustion characterization tests for solid ammonia borane (AB) to determine: P_{max}, R_{max}, K_{st}, *MIE, MEC, and MIT* (T_c), respectively.
Task 4	• Continue risk mitigation experiments (mech. impact., submersion, hot surface contact, and fast depressurization) using other hydrides such as those supplied by SNL, SRNL and PNNL. • Complete the atomic and thermodynamic modeling of $NaAlH_4$ oxidation and hydration reactions. • Identify passivation and surface treatments that can be used to suppress the reactivity and sensitivity of some complex hydrides (such as $NaAlH_4$) to mechanical impact. Established treatments that will be investigated include: a) controlled surface oxidation/passivation, b) fluoridation, c) boronization, and d) solvent ligands for formation of organometallic complexes. • Experimentally Investigate the impact of fire retardants (inorganic and organic additives) on hydrides sensitivity to mechanical and reactivity
Task 5	• Complete the localized flame impingement test using UTRC Prototype-2 vessel. The test will be conducted at SRI and in collaboration with SNL.

Summary

Project Summary

Relevance: Contribute to quantifying the DOE On-Board Storage Safety Target: "*Meets or exceeds applicable standards*."

Approach:

- Evaluate reactivity of key H2 storage materials under development in the materials Centers of Excellence.
- Develop methods to reduce risks.

Technical Accomplishments and Progress:

- QRA: completed fault tree models for baseline designs of on-board reversible and off-board regenerable systems and subsystems.
- QLRA: identified critical failure mechanisms of baseline designs of on-board reversible and off-board regenerable systems.
- Risk mitigation tests (mech. Impact, hot surface contact, etc).
- Performed atomic and thermodynamic modeling for hydrides (e.g., $NaAlH_4$) oxidation and hydration reactions.
- Identified passivation and surface treatments that can be used to suppress the reactivity and sensitivity of some complex hydrides to mechanical impact.