Safe use of hydrogen as a promising energy carrier for light-duty vehicles

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Presentation's theme and topics

1) **Presentation's theme**

Relevant to two of WPI's Center for Global Public Safety's six main focus areas:
Fire | Water | Food | Emergency Response | **Transportation | Energy**

2) **Presentation topics**

- DOE 2025 technical targets for onboard hydrogen storage for light-duty vehicles (LDV)
- DOE/UTRC contract on hydrogen storage materials reactivity and safety

DOE 2025 technical targets for onboard hydrogen storage for (LDV)

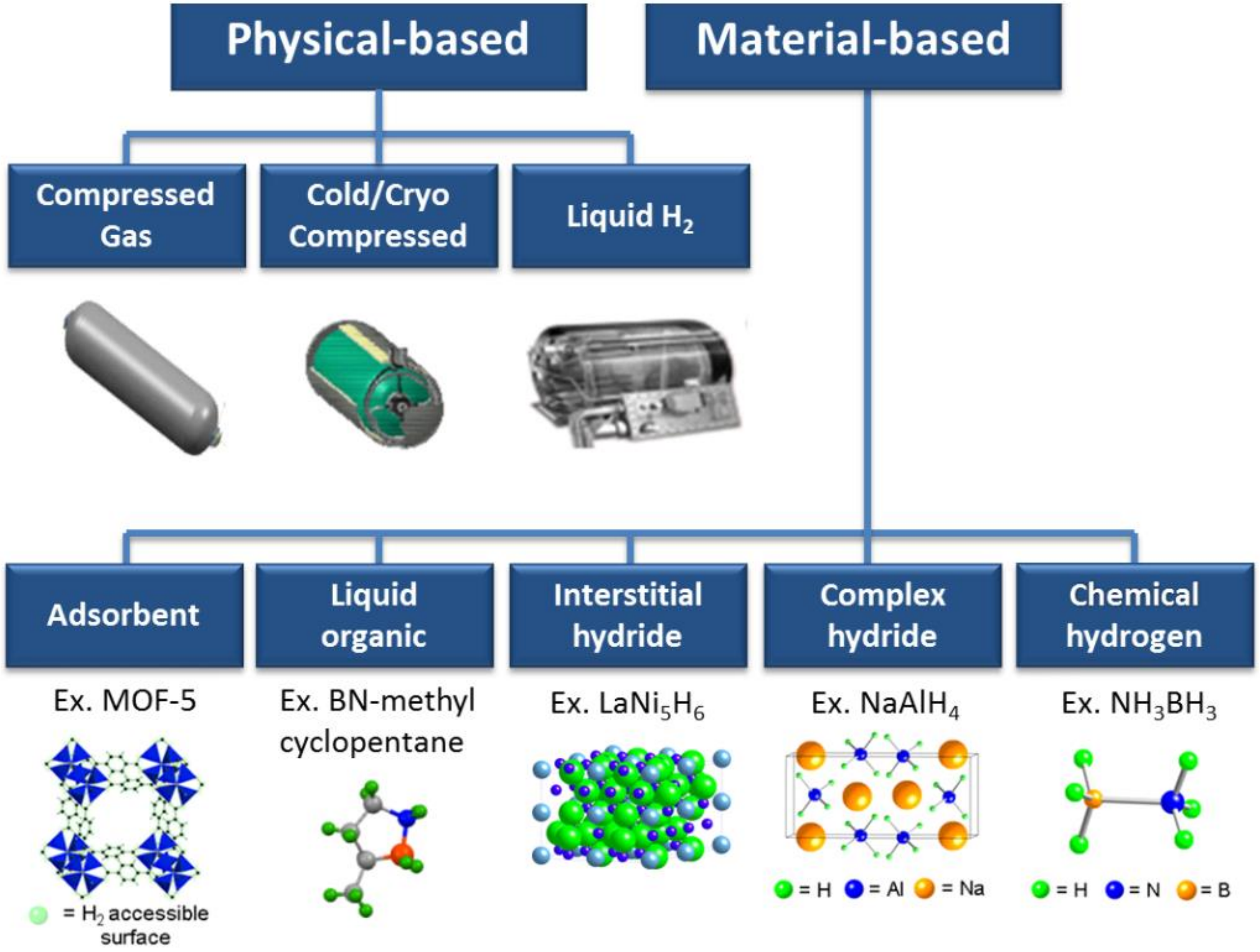
Nine parameters

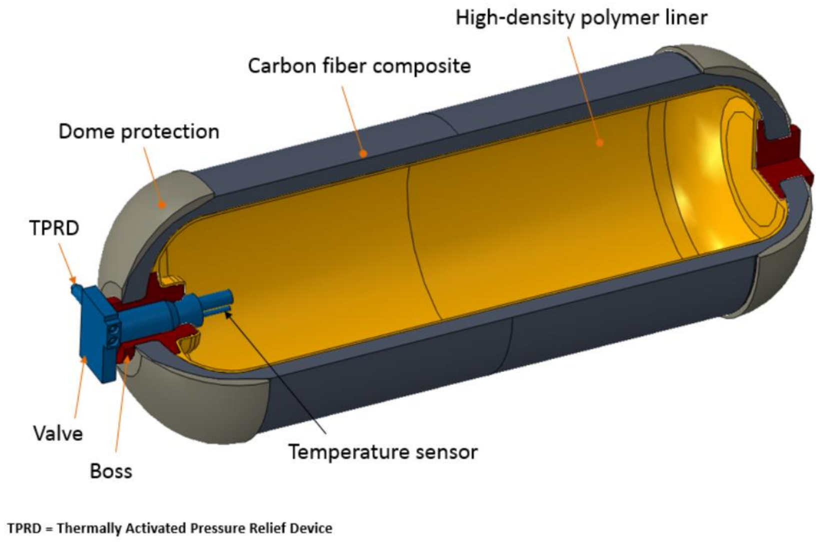
1) System Gravimetric Capacity: 0.055 kg H2/kg system*
2) System Volumetric Capacity: 0.040 kg H2/L system
3) Storage system cost: $300/kg H2
4) Fuel cost: $4/gge at pump
5) Durability/Operability: Operating and delivery temperature and pressure, efficiency, # cycles over life (1,500 cycles)
6) Charging/Discharging Rates: Fill time 3-5 minutes
7) Fuel Quality
8) Dormancy (in days)
9) Environmental Health and Safety: leakage/ permeation, toxicity, and **safety**

** System refers to the on-board H2 storage system including balance of system (not just the storage tank).*

Source: https://www.energy.gov/eere/fuelcells/doe-technical-targets-onboard-hydrogen-storage-light-duty-vehicles

Different ways to store hydrogen for on-board light-duty vehicles

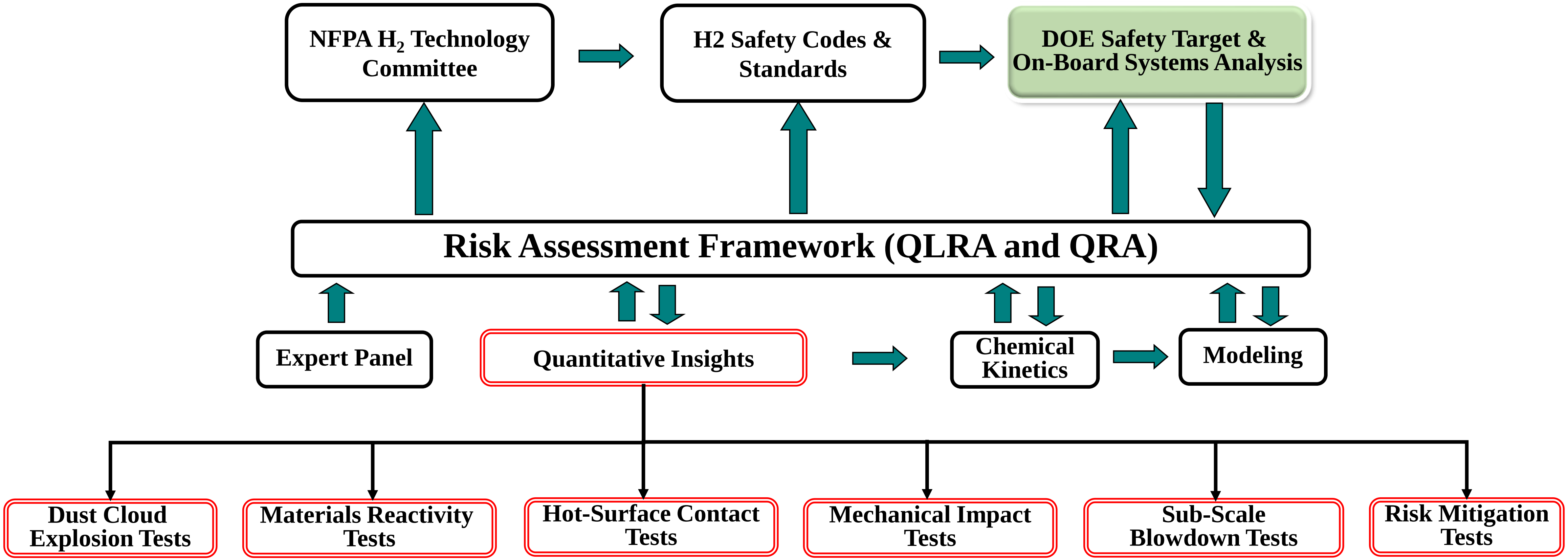




- Physical storage either a gas or a liquid.
- Gaseous storage at 350–700 bar [5,000–10,000 psi] tank pressure.
- Liquid storage at 1 bar & 20ºK or cryogenic storage at 700 bar & 228ºK.
- Material storage: adsorption or absorption.

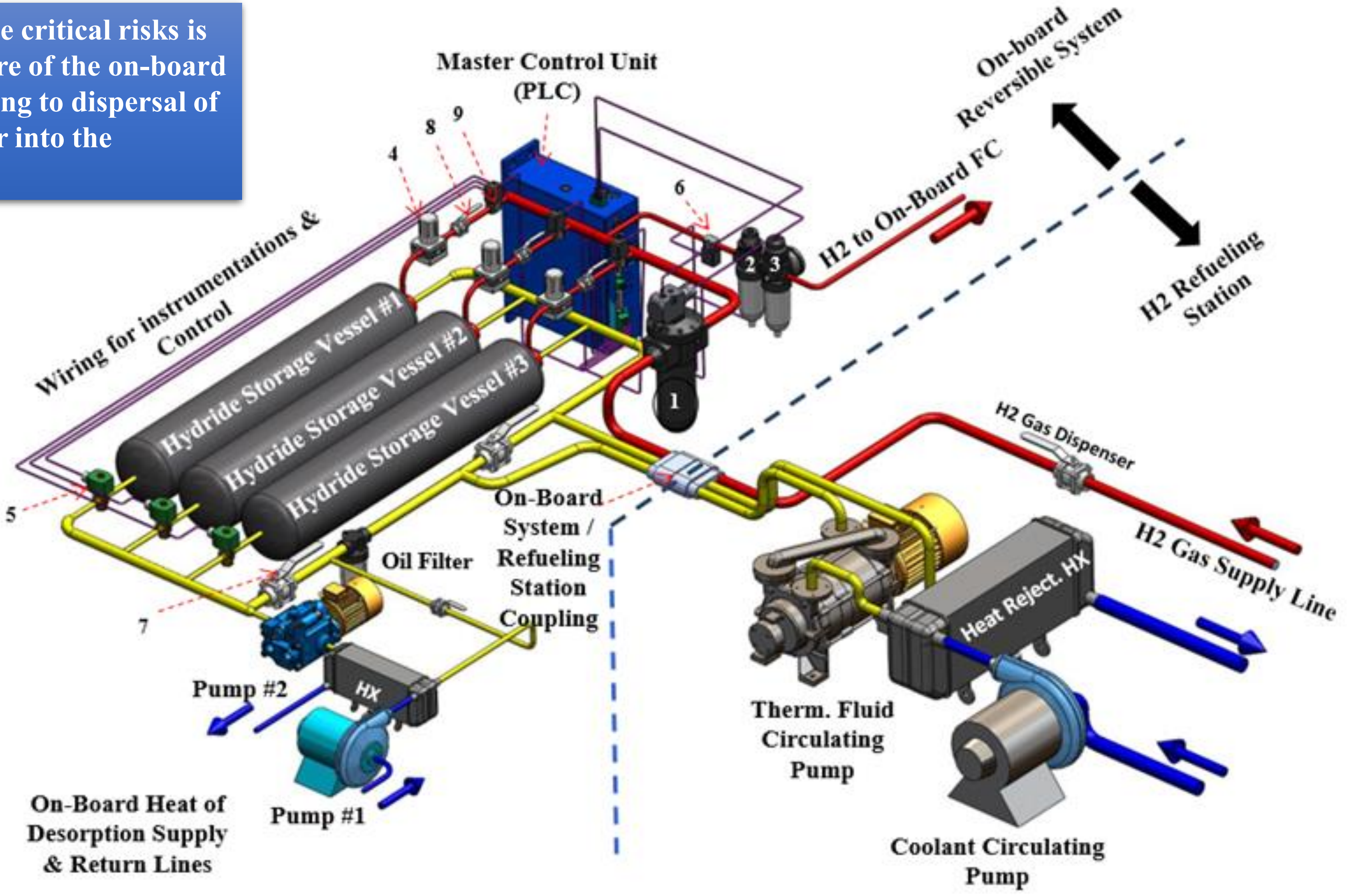
Sources:
https://www.energy.gov/eere/fuelcells/hydrogen-storage
https://www.energy.gov/eere/fuelcells/physical-hydrogen-storage

DOE/UTRC: solid-state hydrogen storage materials safety & reactivity project

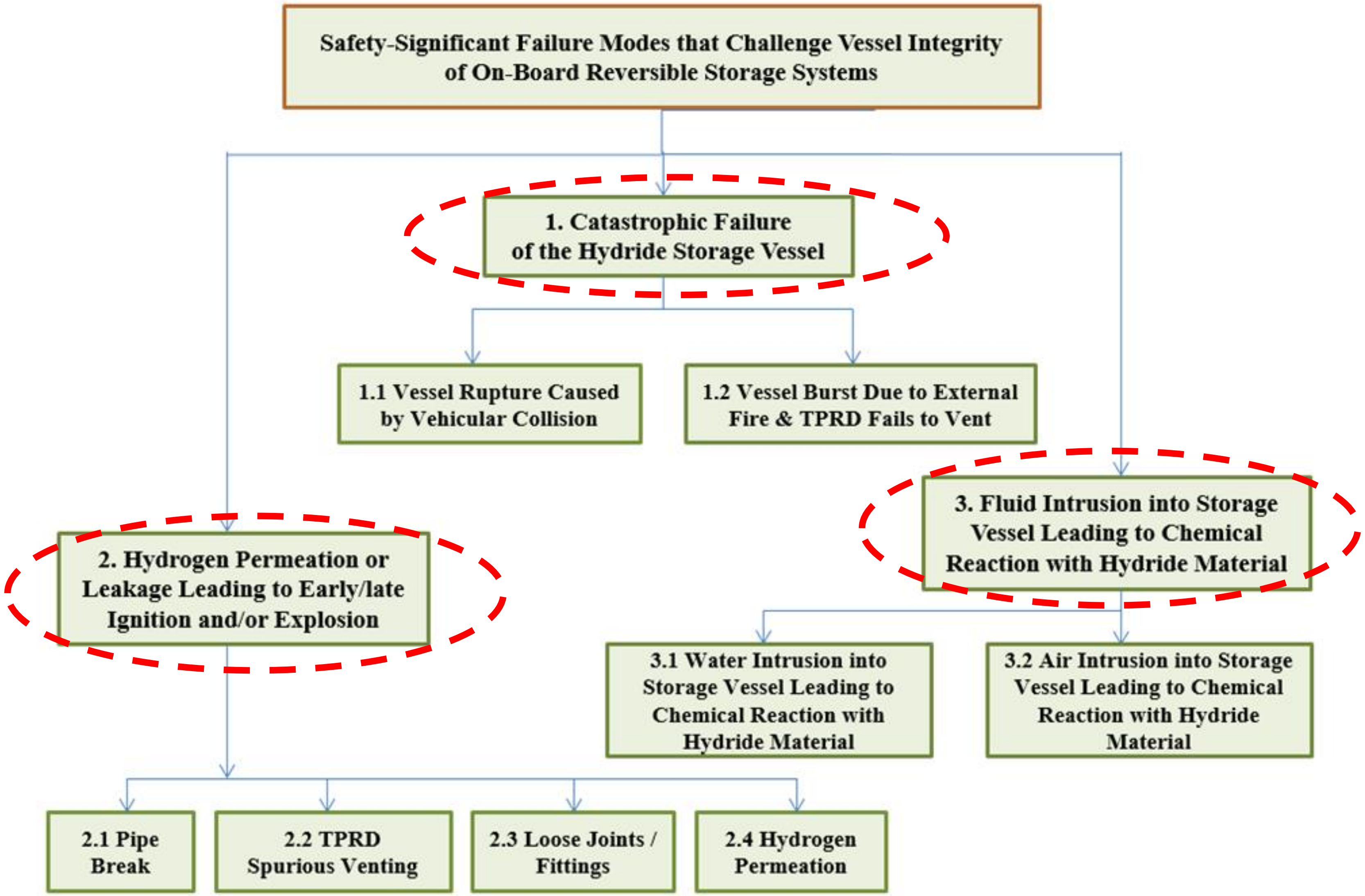


Baseline design of an on-board reversible hydrogen storage system (Khalil, 2011)

d-FMEA: one of the critical risks is catastrophic rupture of the on-board storage vessel leading to dispersal of the hydride powder into the atmosphere.



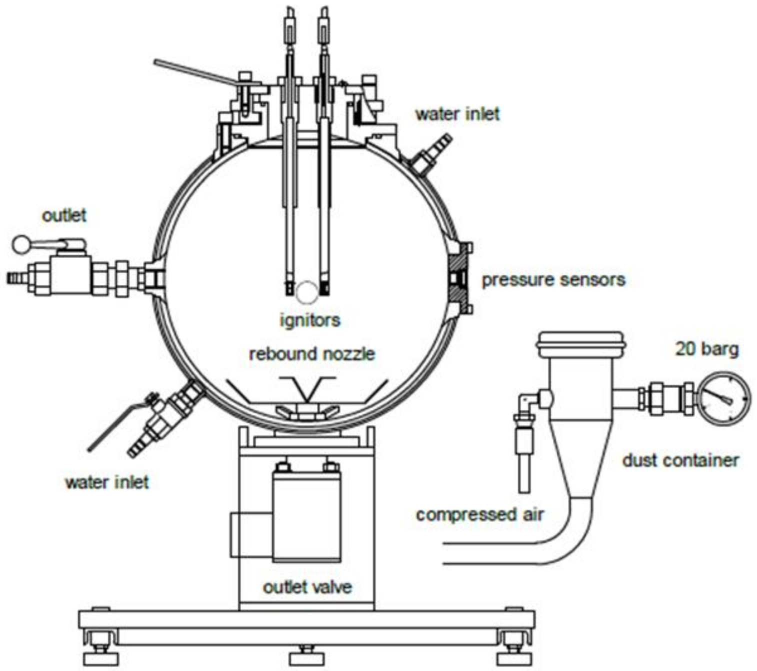
Safety-significant failure modes of on-board reversible storage vessels



On-Board Hydride Storage Vessel

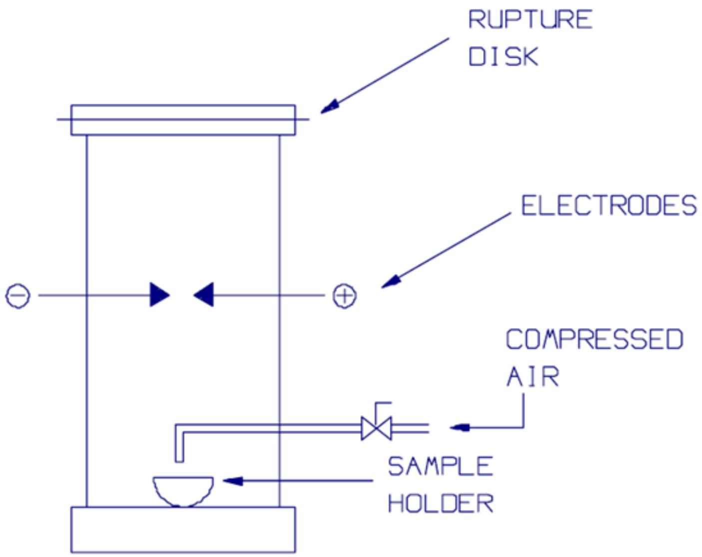
- Is the most safety-critical component in the system, and represents system **vulnerability to single-point failure** should the vessel fails catastrophically.
- High-severity consequences are associated with accident sequences that lead to catastrophic vessel failure (either rupture as a result of a vehicular collision or bust by overpressurization given an external fire in conjunction with failure of the thermally-activated pressure relief device (TPRD) to vent the vessel as design.

Dust cloud explosion characterization tests – ASTM standards



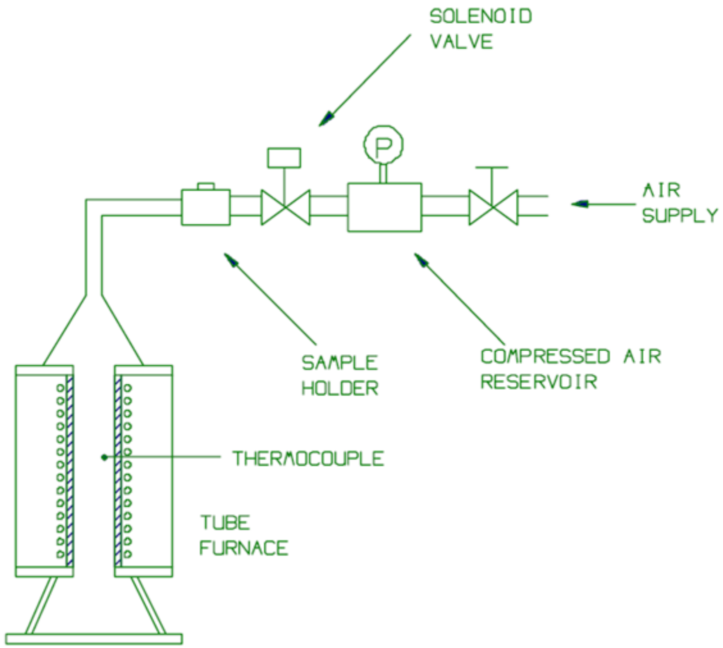
Schematic diagram of the Kühner 20-liter spherical explosion test apparatus

Dust Cloud Characterization Parameters	Test Method
• Maximum explosion pressure (P_{MAX}) • Maximum rate of pressure rise (ΔR_{MAX})	ASTM E-1226
Minimum explosible concentration (MEC) of combustible dust.	ASTM E-1515



Modified Hartmann apparatus used for determining minimum ignition energy (MIE).

Minimum ignition energy (MIE) of a dust cloud in air.	ASTM E-2019



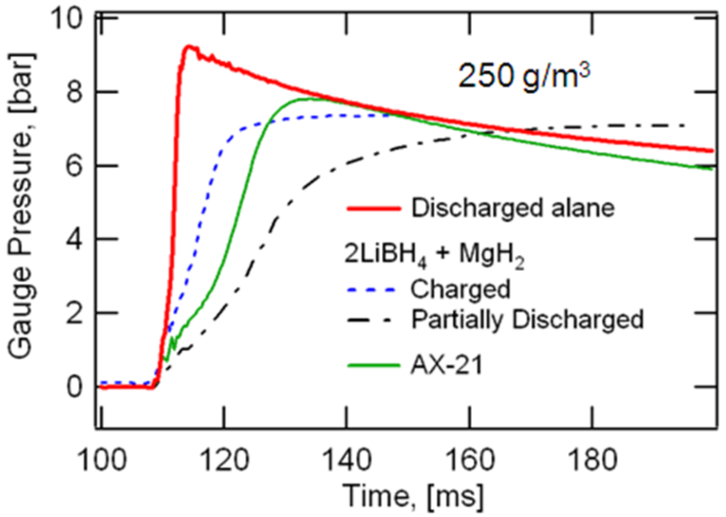
Godbert-Greenwald furnace for determination of dust cloud minimum ignition temperature.

Minimum ignition temperature (TC) of dust clouds.	ASTM E-1491

Dust cloud explosion characterization results

Table 6 - Dust Cloud Combustion Characterizations of Solid-State Hydrogen Storage Materials.

Dust Cloud Combustion Characterization Parameter	Solid-State Hydrogen Storage Materials (Complex Metal Hydrides, Chemical Hydrides, and Adsorbents)						Benchmarks	
	Maxsorb (AX-21)	Charged AlH_3	Discharged AlH_3	$2LiBH_4$ + MgH_2	Charged $NaAlH_4$	NH_3BH_3	Pittsburgh Seam Coal (1)	H_2 Gas (2)
ΔP_{MAX}, bar-g	8.0	3.7	10.3	9.9	11.9	18.4	7.3	7.9 (3)
$(dP/dt)_{MAX}$ = R_{MAX}, bar/s	449	370	4,082	1,225	3,202	2,840	426	5,435 (3)
MIE (4), mJ	Range 500 - 1,000	< 10	< 10	< 9.2	< 7.0	< 8.9	110	0.02
MEC (5), g/m³	80	30	125-250	30	140	< 20	65	4 vol% H_2 in air
T_C (6), °C	760	200	710	230	137.5	n/a	585	n/a
Hazard Class	St-1	St-1	St-3	St-3	St-3	St-3	St-1	
Explosion Severity (ES)	1.16	0.44	13.5	3.9	12.3	16.54	1.0	13.8
K_{ST} (8), bar-m/s	122	101	1,100	333	869	771	116	1,477
Combustible Dust Classification	Class-II	Footnote (7)	Class-II	Class-II	Class-II	Class-II	Class-II	n/a



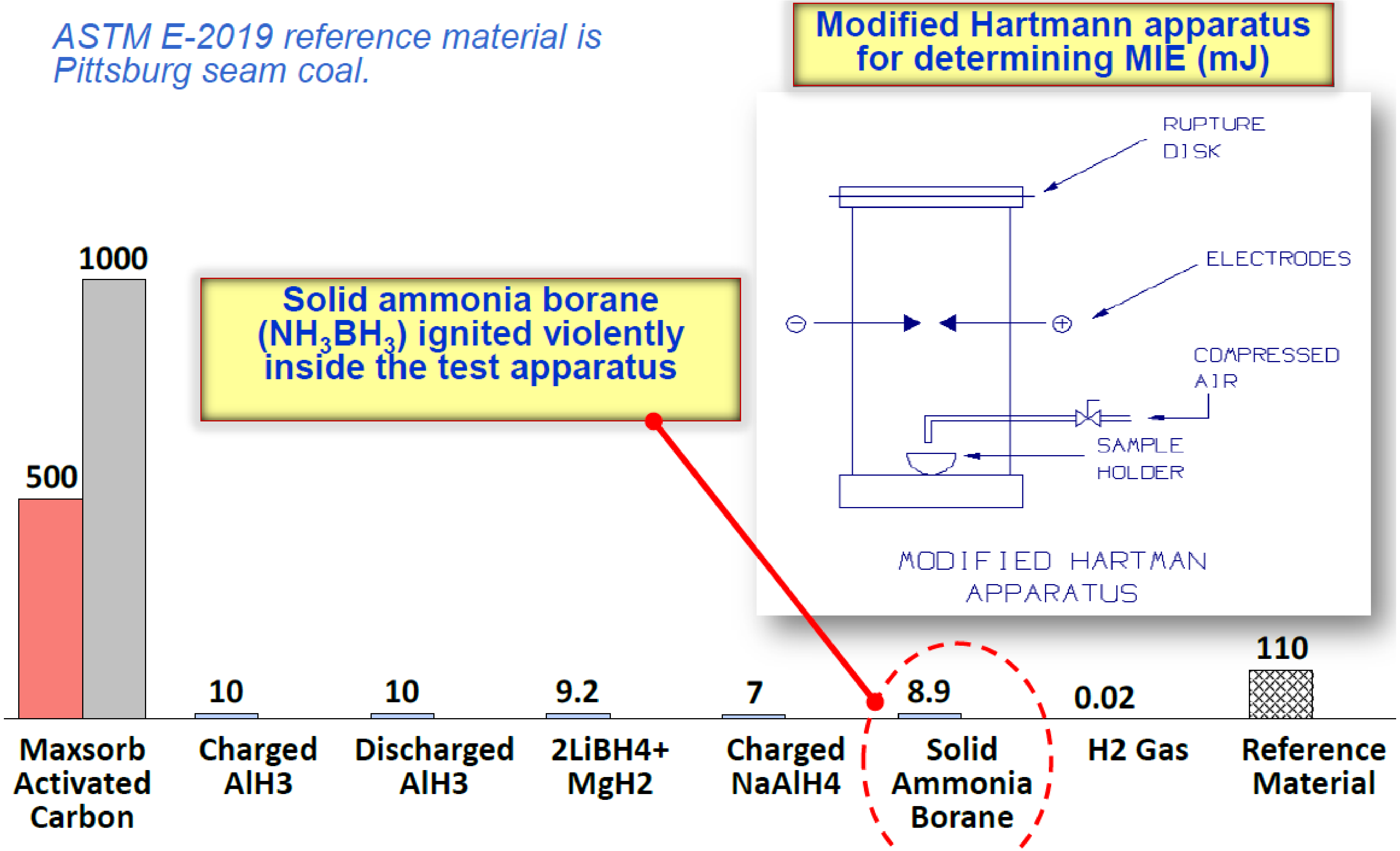
Pressure profiles of candidate storage materials tested per ASTM E1226

(1) ASTM reference material for dust cloud characterization.

(2) Added for comparison only.

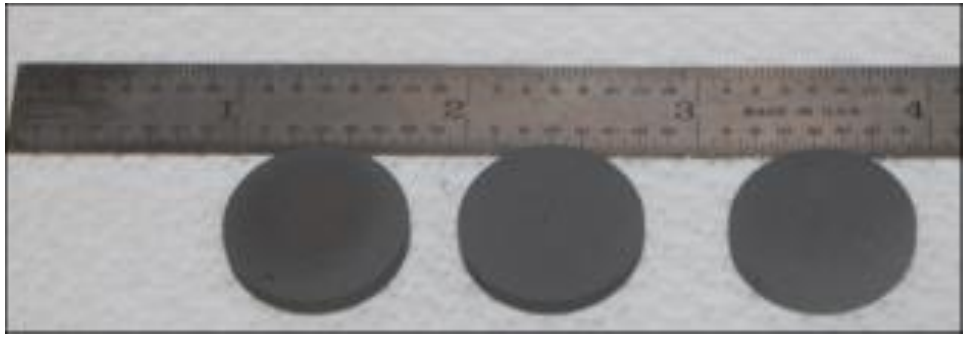
(3) At 29 vol% H_2 in air.

Minimum ignition energy (MIE, mJ) of selected metal hydrides, chemical hydrides and adsorbents



Pyrophoric hydride powder & effect of powder compaction

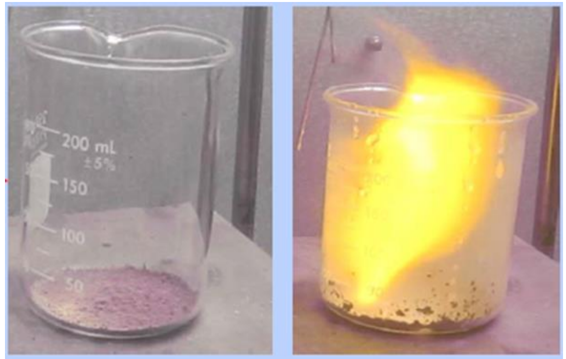
Sodium alanate ($NaAlH_4$) Pyrophoricity.



Sodium alanate ($NaAlH_4$) powder compaction.

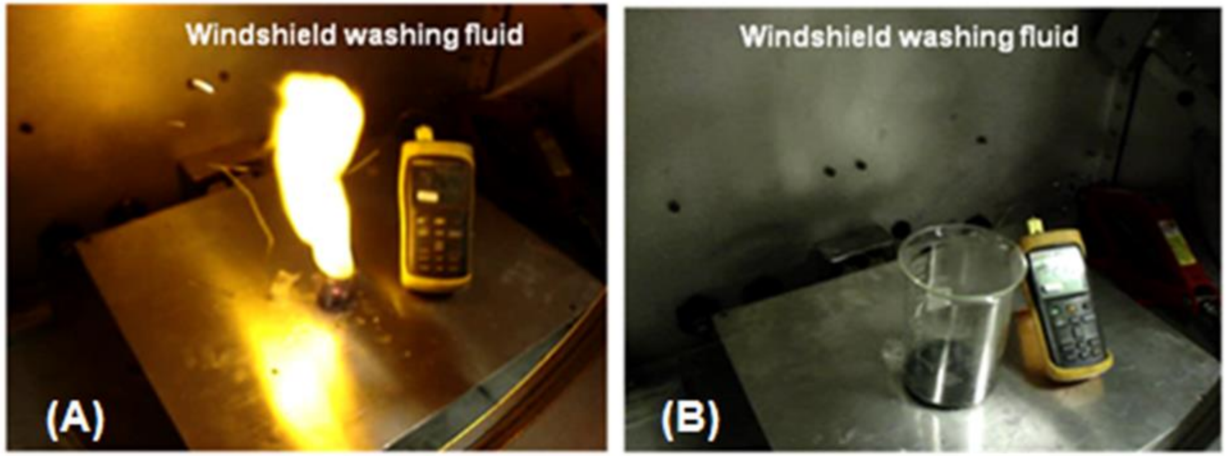
Materials' reactivity tests: liquid drop test

- Liquids examined: water, salt solution (brine), windshield washing fluid, engine oil, and engine coolant (antifreeze).
- These liquids assumed to come in contact with hydride powder during postulated accident scenarios involving LD-FCV.



Powder: 3Mg(NH2)2.8LiH

- Brine solution gradually dropped on a 0.5-gram heap of this hydride powder.
- First, gases evolved upon contact followed by ignition and fire.



Reactivity of $NaAlH_4$ as loose powder (A) and as powder compact (B) when it comes in contact with windshield washing fluid.

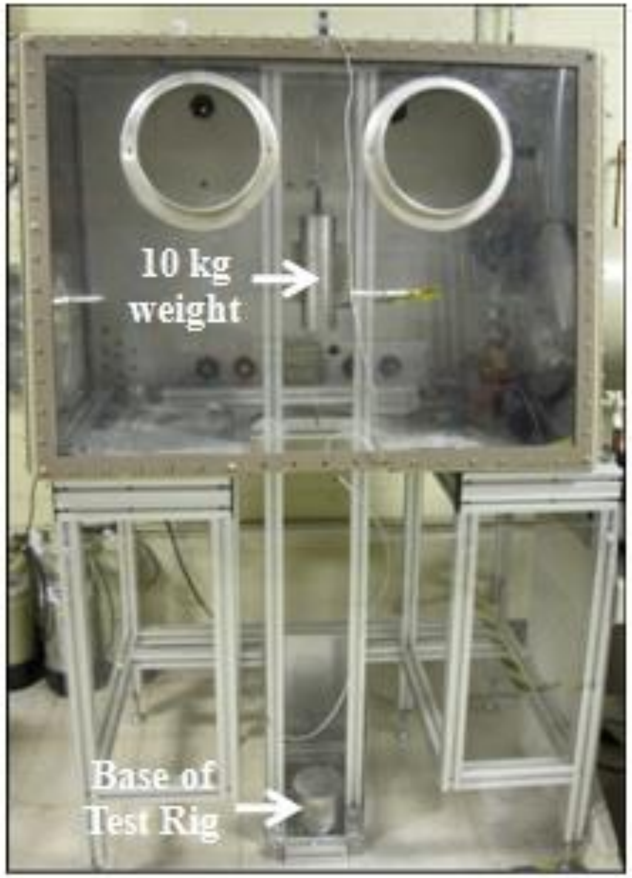
NaAlH4 powder reacts violently with water with ignition of evolved gases.

Key insights

- *Powder compaction can suppress hydride/liquid reactivity and, thus, preventing subsequent ignition of the evolved reaction gases.*

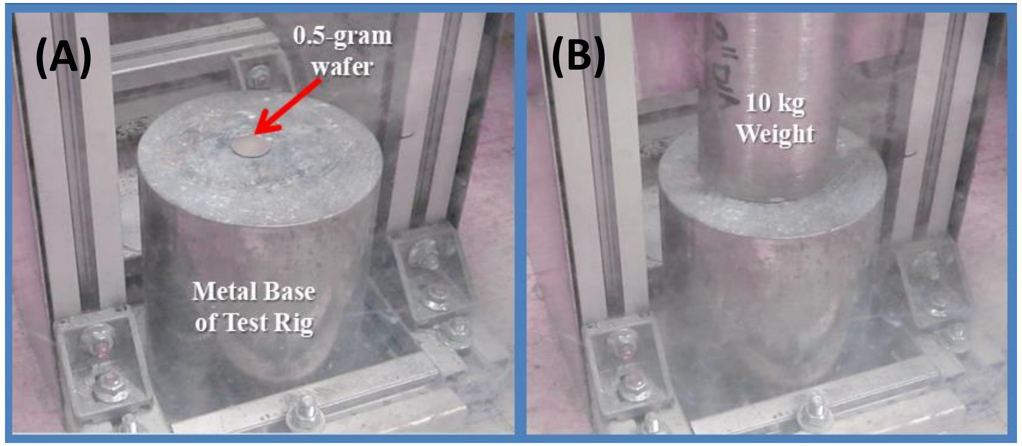
- *This experimental observation could be attributed to the fact that hydride powder compaction reduces available surface area that contacts the liquid.*

Mechanical impact tests: hydride powder compacts (wafers)



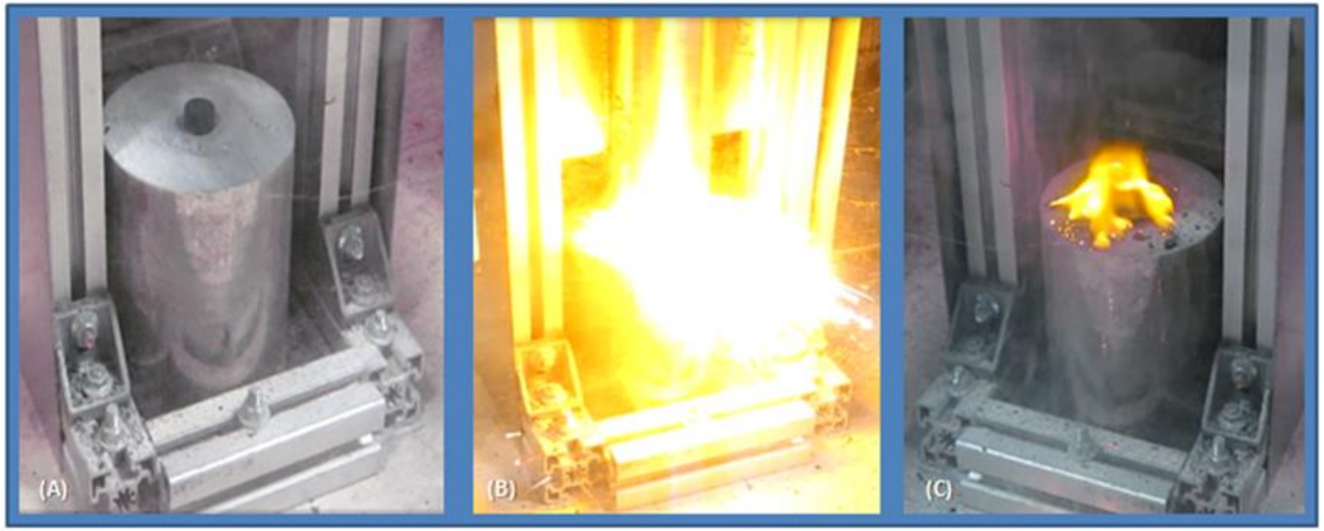
Mechanical impact test rig

$$Free-\ fall\ mechanical\ impact\ energy = m.g.h = (10\,kg).(9.8\,m/s^2).(0.5\,m)$$
$$= 49\ Joules\ OR\ 98\ Joules\,(for\ h = 1\,m)$$



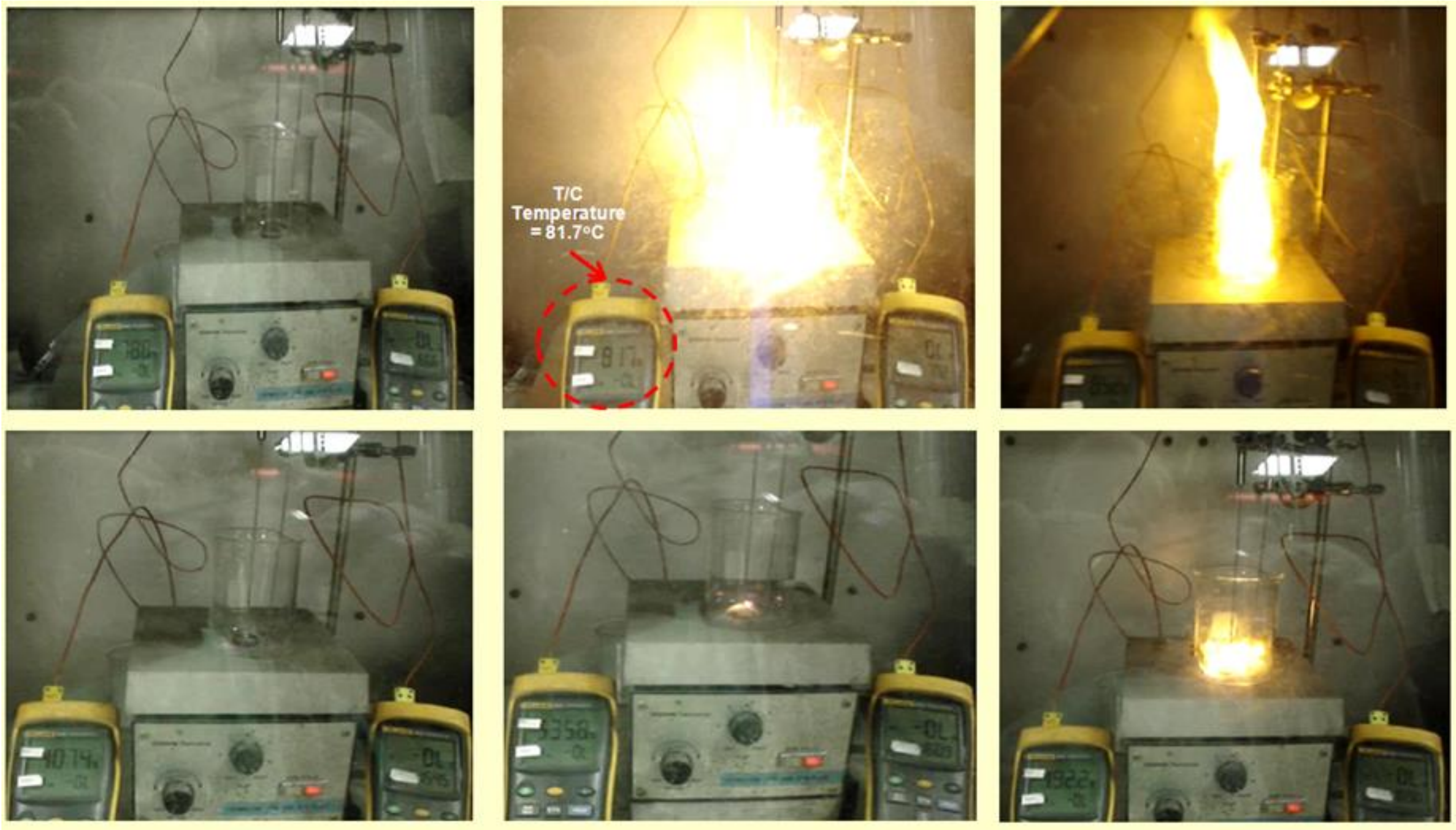
(A) 0.5 gram wafer of hydride material sitting on the metal base of the test rig.

(B) 10 kg weight after free fall and landing on the surface of the metal base in the test rig.

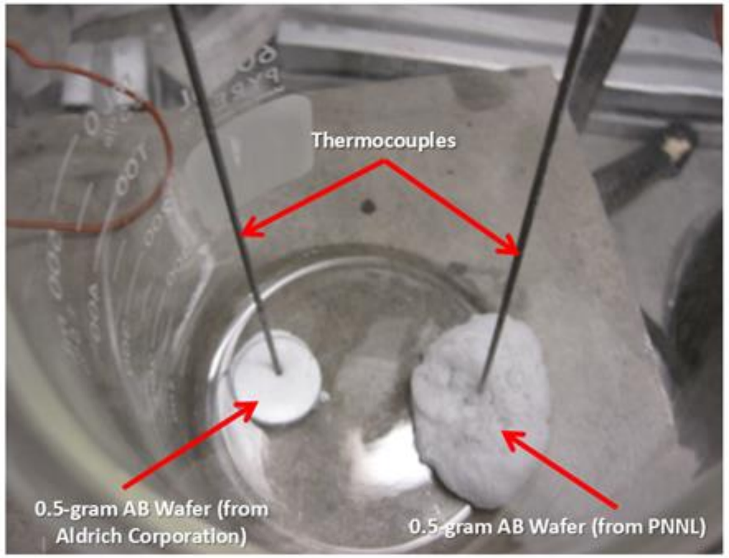


A 4-gram $NaAlH_4$ wafer ignited upon first impact (free fall height = 1 m).

Material – hot surface contact



Contact of $NaAlH_4$ powder compact with a hot metal surface (Khalil, 2011b)



Hot surface contact test for ammonia borane (AB) material (AB powder obtained from Aldrich and PNNL) – Khalil (2011d).

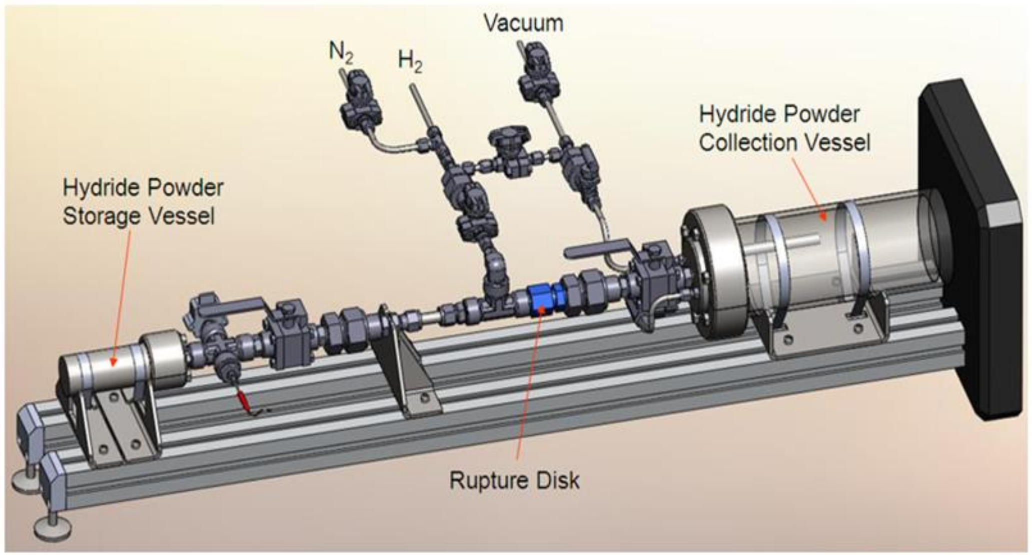
Fast depressurization test – mimicking catastrophic vessel breach

- The key components of the test rig: hydride powder storage vessel, rupture disk, hydrogen gas supply line, nitrogen purge line, vacuum line and the hydride powder collection vessel.

- The results showed that depressurization from 100 bars to 10 bars was completed in about 50 msec.

- Results of tests with $NaAlH_4$ powder showed ≈ 16.5% probability that some of the initial powder mass (30 grams) can be entrained to the collection vessel as a result of the blowdown.

- Other tests were conducted using powder compacts (including $NaAlH_4$, BH_3NH_3 and $3Mg(NH_2)_2.8LiH$) instead of the loose powder.



Fast depressurization (blowdown) test rig to mimic rupture of the hydride storage vessel (Khalil, 2010b, 2011a, 2011b).

- The results showed that mass of powder compact directly correlates with the likelihood of loss of wafer's structural integrity (fragmentation) as a result of the fast depressurization from about 100 bars.

- These experimental observations can be interpreted as follows: by increasing the mass of powder compact, the population of pores pressurized with the nitrogen gas also increases. Thus depressurization effect on wafers with larger mass has more severe effect on wafer's structural integrity compared to wafers with smaller mass.

- The test parameters that have been considered include: mass of the powder compact (1-g, 2-g, 4-g and 6-g wafers) and number of charging/discharging cycles of the hydride material before testing (namely, as pressed and after , 1 cycle, 5 cycles, 10 cycles and 15 cycles).

Collaborative R&D by Hydrogen Storage Engineering Center Excellence (HSECoE)

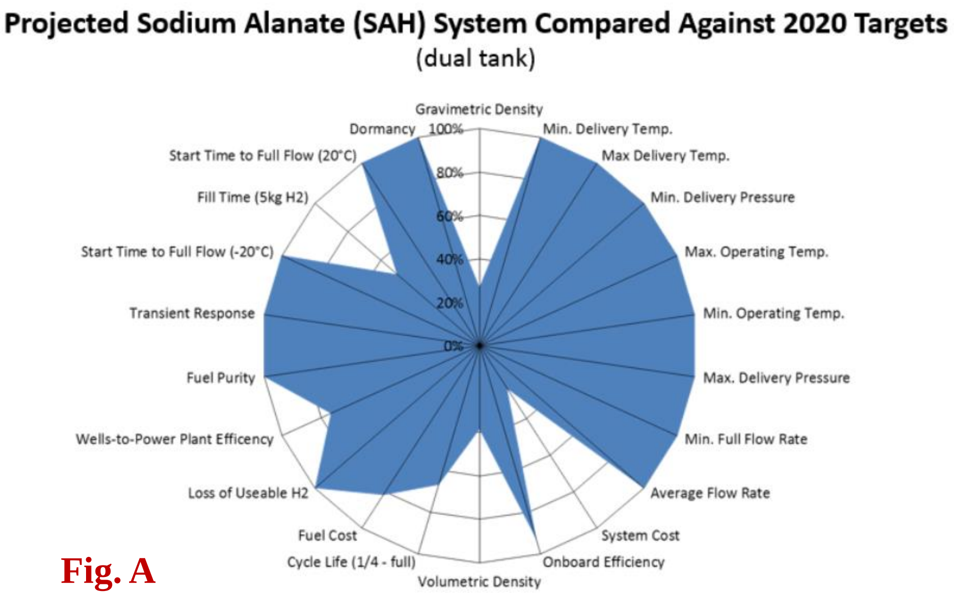


Fig. A

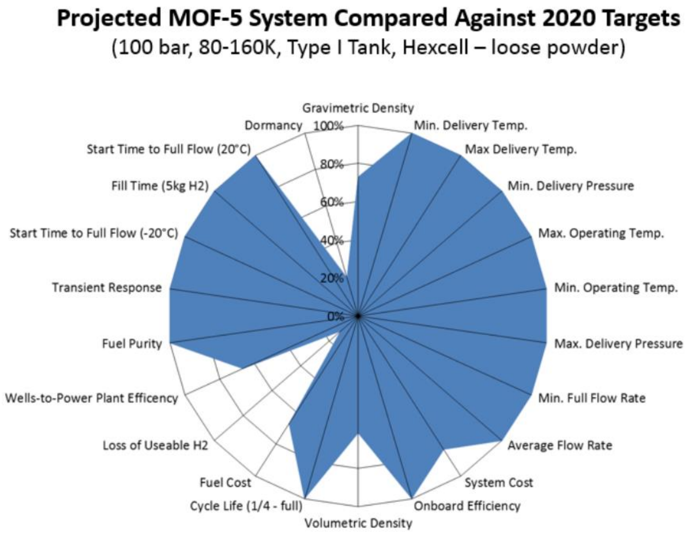


Fig. C

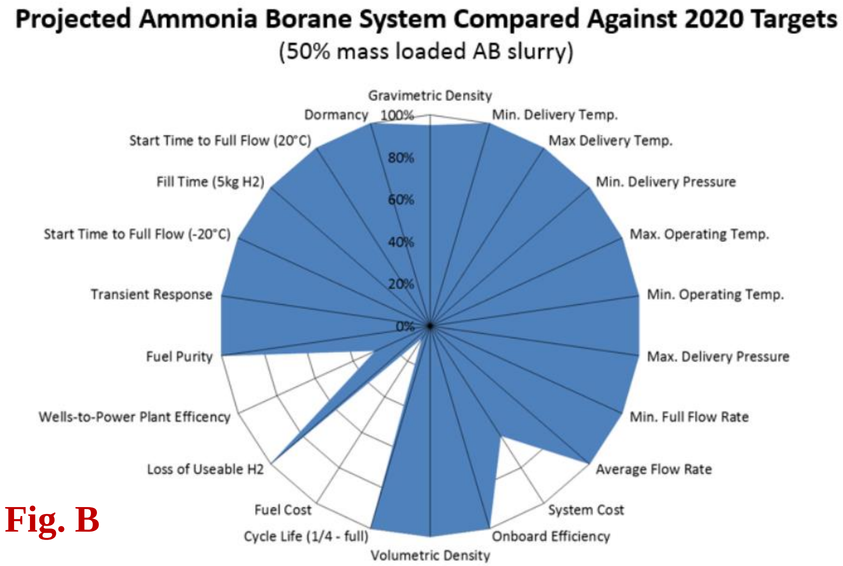


Fig. B

Fig. A: Example of an on-board reversible metal hydride-based system.

Fig. B: Example of an off-board Chemical Hydrogen Storage system.

Fig. C: Example of an on-board reversible adsorbent system.

https://www.energy.gov/eere/fuelcells/hydrogen-storage-engineering-center-excellence