Session storage
State of the Art and Gaps in hydrogen storage in material systems

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HySafe research priorities Workshop,
Washington, 11-12/12/2014

European Commission

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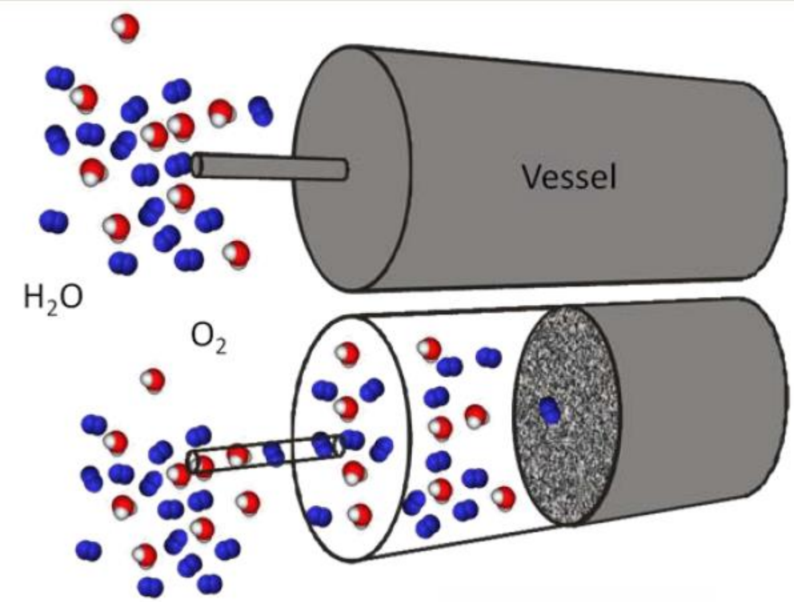
Things to be discussed

Is (safety of) hydrogen-storage material an issue?
State of the Art & Gaps at material level
State of the Art & Gaps at system level

Not discussed:
toxicology



Source SANDIA

From the previous Report (2013)

Metal hydrides exhibit high potential to meet the US DOE system targets for automotive hydrogen storage.

The hydrogen release is of moderate speed due to the fact that it is endothermal and is controlled by diffusion.

The hazards will rise, in presence of unpassivated light metals . A destruction of the storage containers might be expected generating a highly pyrophoric cloud in hydrogen.

Related knowledge gap

Investigation of accident/crash situation including hydride storage facilities.

Is solid-state storage still considered a viable solution?

For FCH JU no technologies with TRL ≥ 3.
It is not probable that hydrides will have a market chance for on-board storage
Fundamental research on hydrides is not in general a guarantee for safer storage.

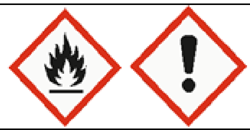
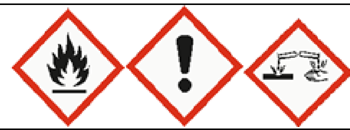
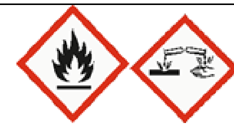
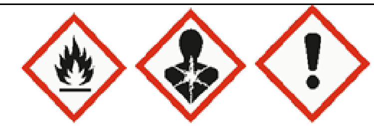
Classic storage materials now investigated for chemical compression and purification
The technology is still considered promising for stationary applications

What's going in Europe ? FCH JU projects

Project	Application	Output	Base materials
BOR4STORE	On-board storage	**FC-integrated Prototype**	**$LiBH_4$**
EDEN	Stationary, coupled to RES	**FC-integrated Prototype** tested in real condition	**MgH_2**
SSH2S	On-board storage	**FC-integrated Prototype** tested in real condition	**Li-imide $LiBH_4$**
HyPER	Aviation, Portable power	**FC-integrated Prototype** tested in real condition	**MgH_2 hydride-hydroxides**

Material Safety Data Sheets (MSDS)

An example of the information contained:

	MgH2	LiH	H_2LiN	LaNi5
2. Hazard identification				
				
2.1 Classification Regulation (EC) No 1272/2008	Substances, which in contact with water, emit flammable gases (Category 1) Skin irritation (Category 2) Eye irritation (Category 2)	Substances, which in contact with water, emit flammable gases (Category 1) Acute toxicity, Oral (Category 3) Skin corrosion (Category 1B)	Substances, which in contact with water, emit flammable gases (Category 2) Skin corrosion (Category 1B)	Pyrophoric solids (Category 1) Substances, which in contact with water, emit flammable gases (Category 1) Skin irritation (Category 2) Eye irritation (Category 2) Respiratory sensitization (Category 1) Skin sensitization (Category 1) Carcinogenicity (Category 2) Specific target organ toxicity - single exposure (Category 3) Specific target organ toxicity - repeated exposure (Category 1) Chronic aquatic toxicity (Category 3)

Very important in labs. Not enough for designers

UN Recommendations: Transport of Dangerous Goods

Classification

Almost all hydrogen storage materials fall in the UN-RTDG Class 4 material category which consists in "***flammable solids; substances liable to spontaneous combustion; substances which, in contact with water, emit flammable gases***".

Example of Testing requirements for class 4:

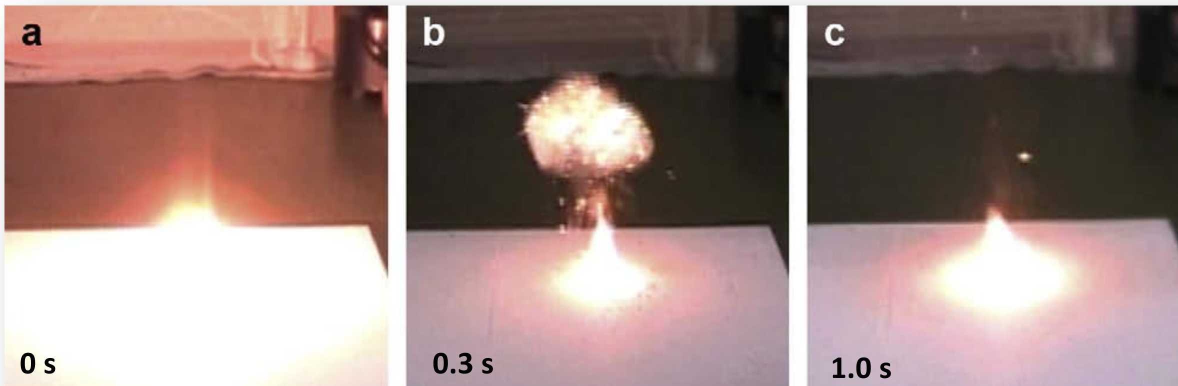
- Burning Rate Test (Class 4.1),
- Pyrophoricity Test (Class 4.2)
- Water-reactivity Test (Class 4.3).

Also of interest, tests for "explosives" in Class 1:

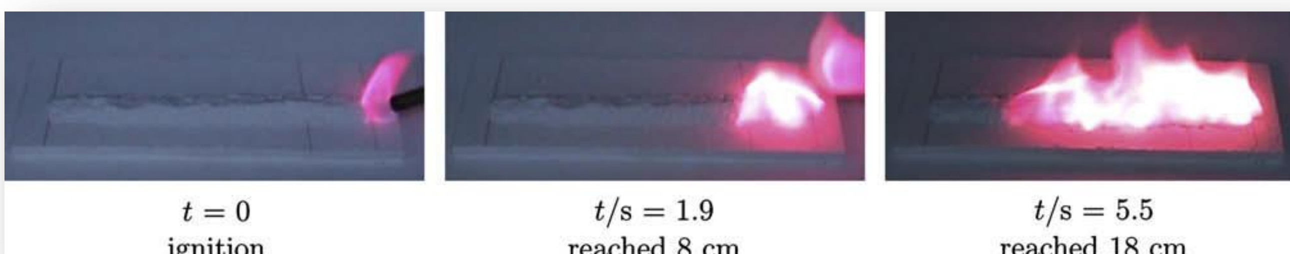
- Explosibility test
- Explosibility and auto-ignition temperature of dust cloud,
- Minimum concentration,
- Minimum ignition energy,
- Explosion characteristics
- Eruption test.

Behaviour of storage materials under accidental conditions

Example of testing



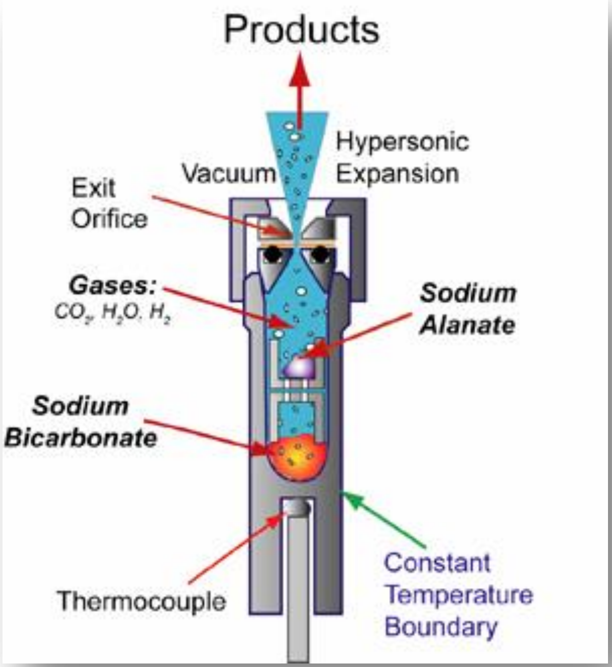
Pyrophoricity test for $NaAlH_4$ ($0.02TiCl_3$), consisting in dropping water on a certain quantity of material.



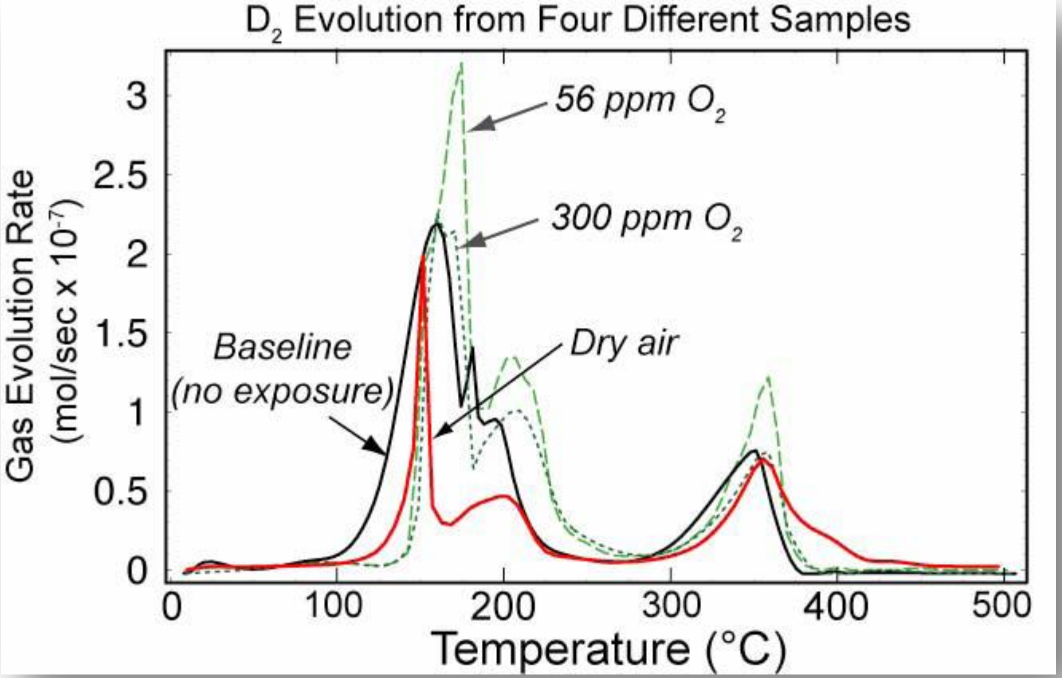
Burning rate test for $LiBH_4 + 2LiNH_2$

H. Tanaka,et al. , International Journal of Hydrogen Energy, 34 (2009) Pages 3210-3218

Reactivity of $NaAlH_4$ with O_2, H_2O, and CO_2



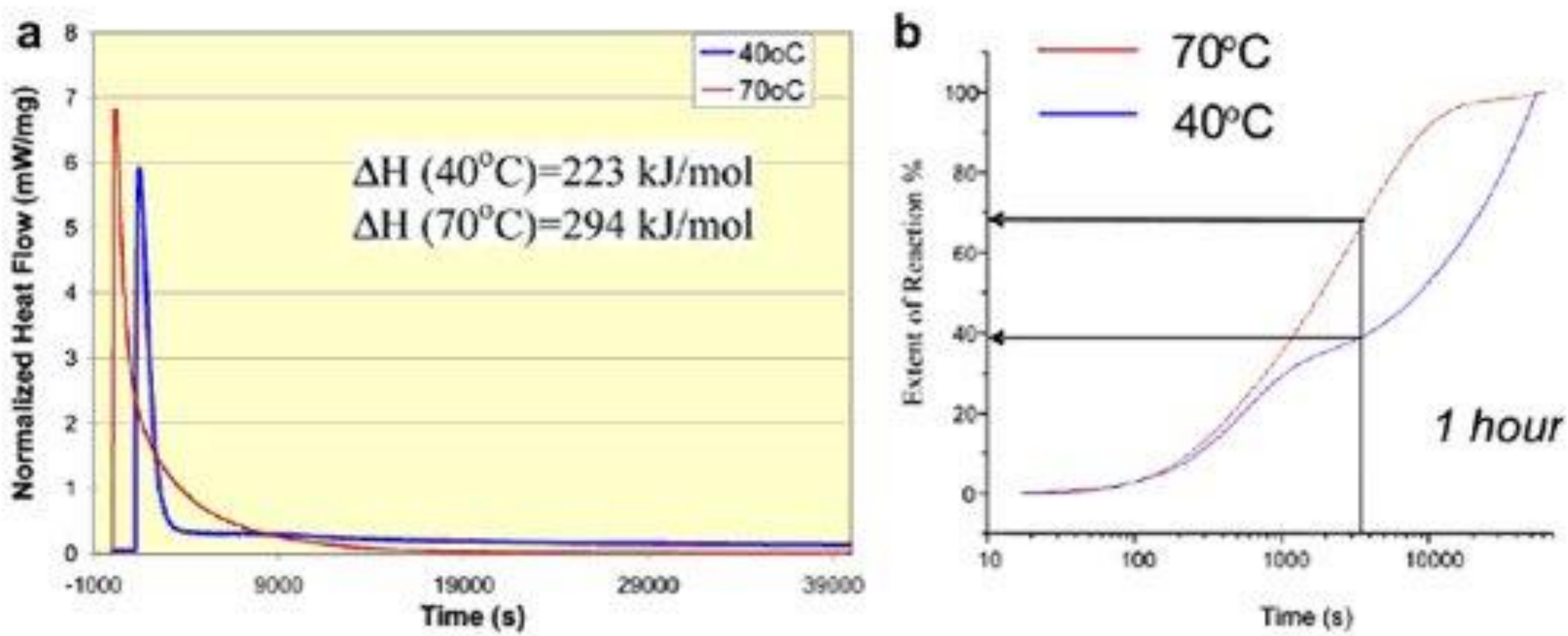
Simultaneous Thermogravimetric Modulated Beam Mass Spectrometer (STMBMS)



The gas evolution rate of D2 from samples of NaAlD4 that have been exposed to various levels of oxygen

SANDIA report SAND2007-4960

Reaction energies

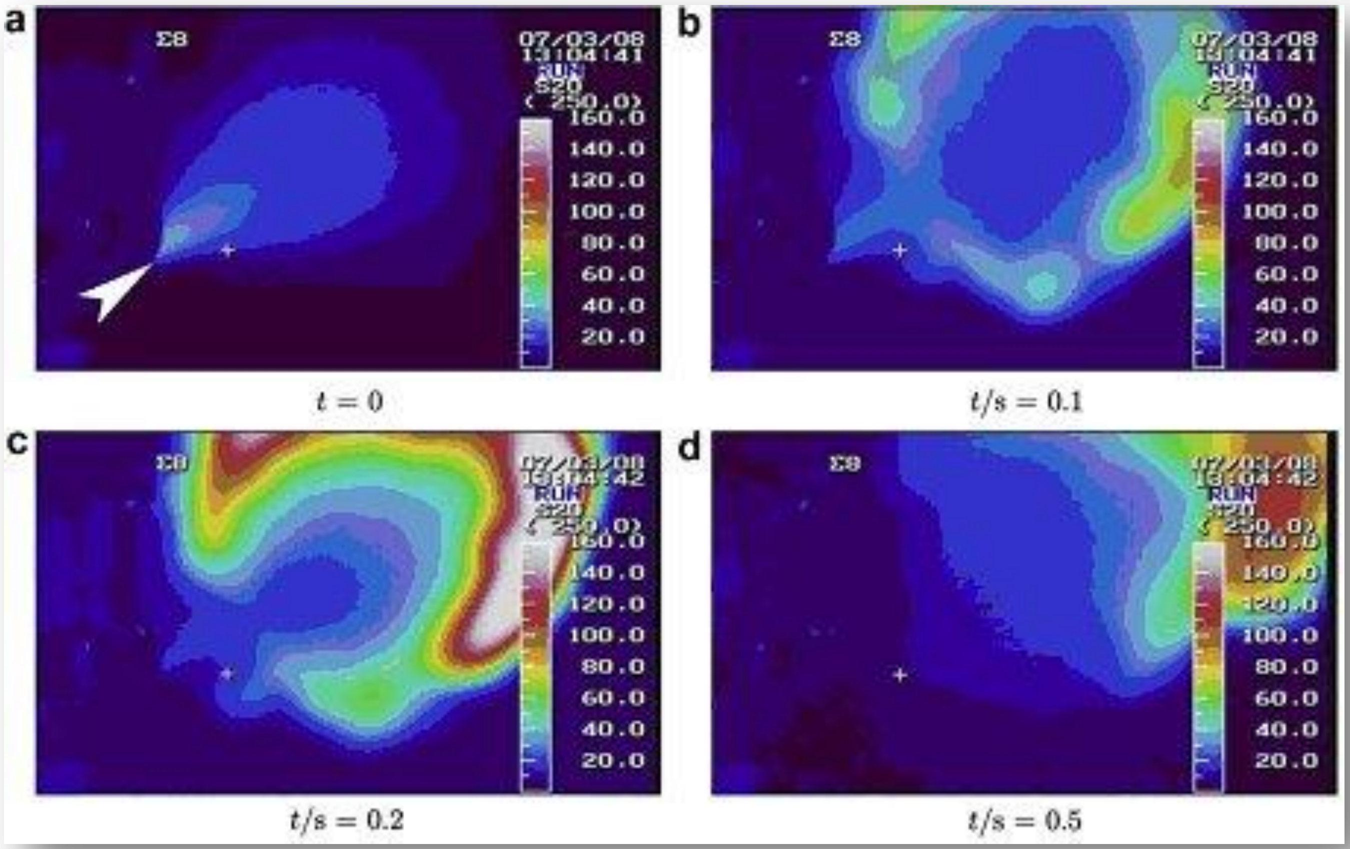


Heat flow from neutral water hydrolysis of $2LiBH_4{\cdot}MgH_2$ at 40°C and 70°C and

reaction progress as a function of time determined from the integrated calorimetric signal

C.W. James et al, ICHS2011

Eruption test of $NaAlH_4$



IR thermograms from the eruption test for $NaAlH_4(0.02TiCl_3)$. Colour temperature scale is in centigrades.

Tanaka et al., IJHE 34 (2009)

Conclusions at material level

The scientific works published up to now have contributed to one or more of the following research lines:

- The qualification of the chemical reactions during the environmental exposure, for example by means of the UN tests used for the classifications of the materials in various hazard classes.
- The quantification of the chemical processes by measuring reactivity properties such as energy release, temperature and pressure values to understand the fundamentals of contamination.
- The prediction of chemical reactions and hazards for a number of accidental scenarios to extend the process predictive capability to the application scale.
- The development of heat and mass transfer models.
- The modelling of reactions and their effects by computational methods.

Behaviour of solid-state storage tanks under accidental conditions

The RCS framework: a Swiss cheese

ISO 16111: Transportable gas storage devices in reversible metal hydrides

Not good for transport: only 150 l t max 25 MPa, not for fixed fuel-storage on-board hydrogen fuelled vehicles

Useful however as starting point for some tests:

- overpressure and fire protection (including temperature-activated pressure release device),
- shut-off valves and particulate confinement.
- actively cooled assemblies.

An update: in 2015 the ISO TC197 started the WG25 for an update of IS 16111

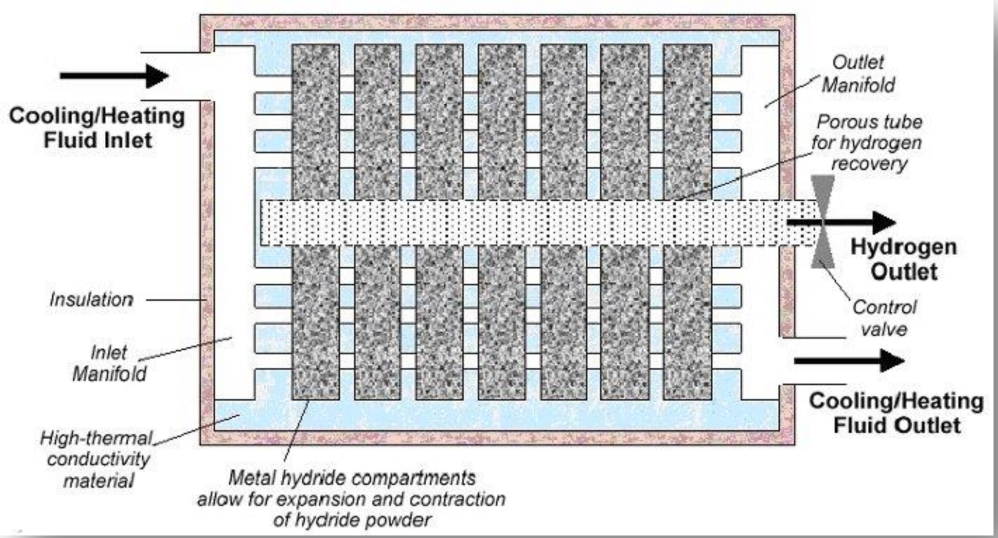
Additional ISO standards exists for hydrogen structural metals interactions.

A FIRST FMEA approach (project STORTHY)

- Hydrogen permeation or leakage leading to early or late ignition or explosion, caused for example by i) Pipe break, ii) TPRD spurious venting, iii) loose joints or fittings, iv) hydrogen permeation or diffusion.

- Catastrophic failure of the hydrogen storage vessel, caused for example by
  i) vehicular collision
  ii) burst due to external fire and TPRD failure to vent.

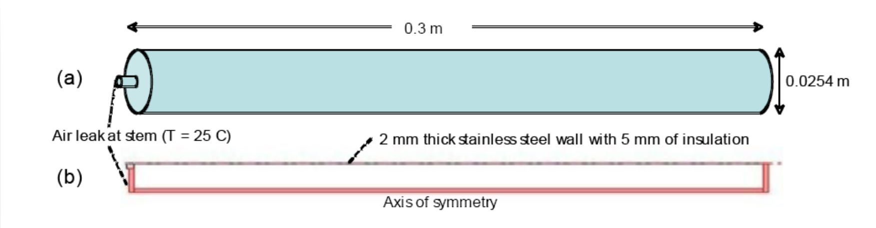
- Fluid intrusion into storage vessel leading to chemical reaction with hydrogen storage material, which includes water and/or air intrusion



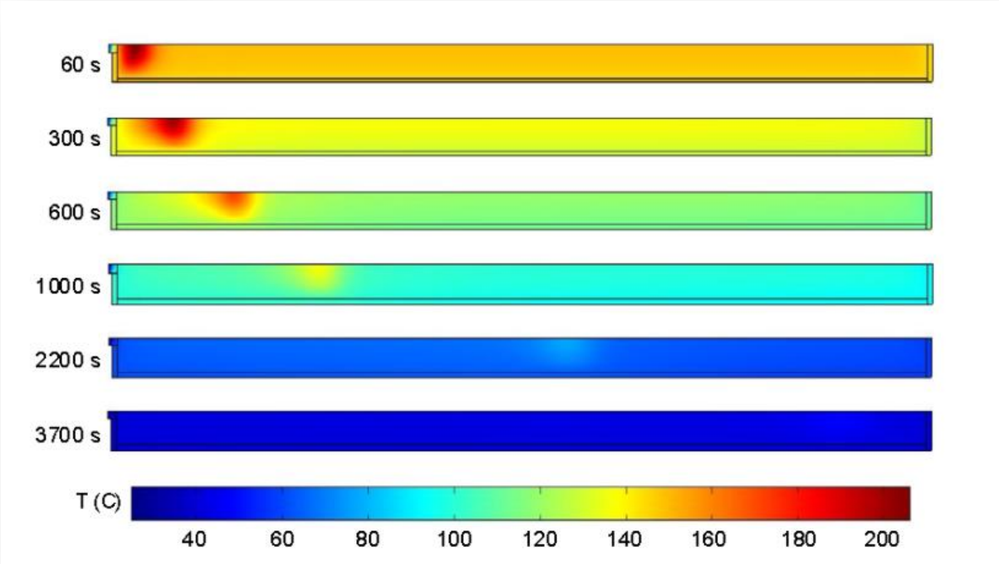
STORHY, subproject SAR, Deliverable DSA9

What if air get into the storage?

Modelling of a breach-in-tank scenario for an AlH_3 tubular tank



80% porous bed
a reaction front propagating through the system for one hour

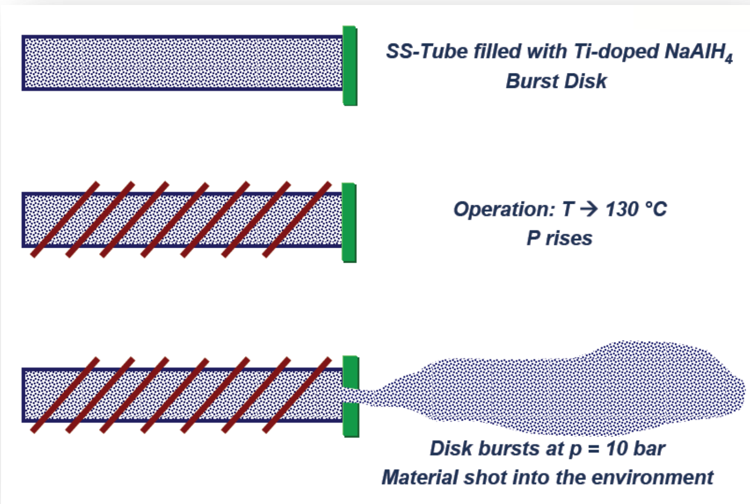


The conclusions suggest that this accidental scenario does not represent the worst case.

Dedrick et al. ICHS2009

What if air get into the storage

Experimental emission of $NaAlH_4$ nano powder



Principle of the KIT experiments

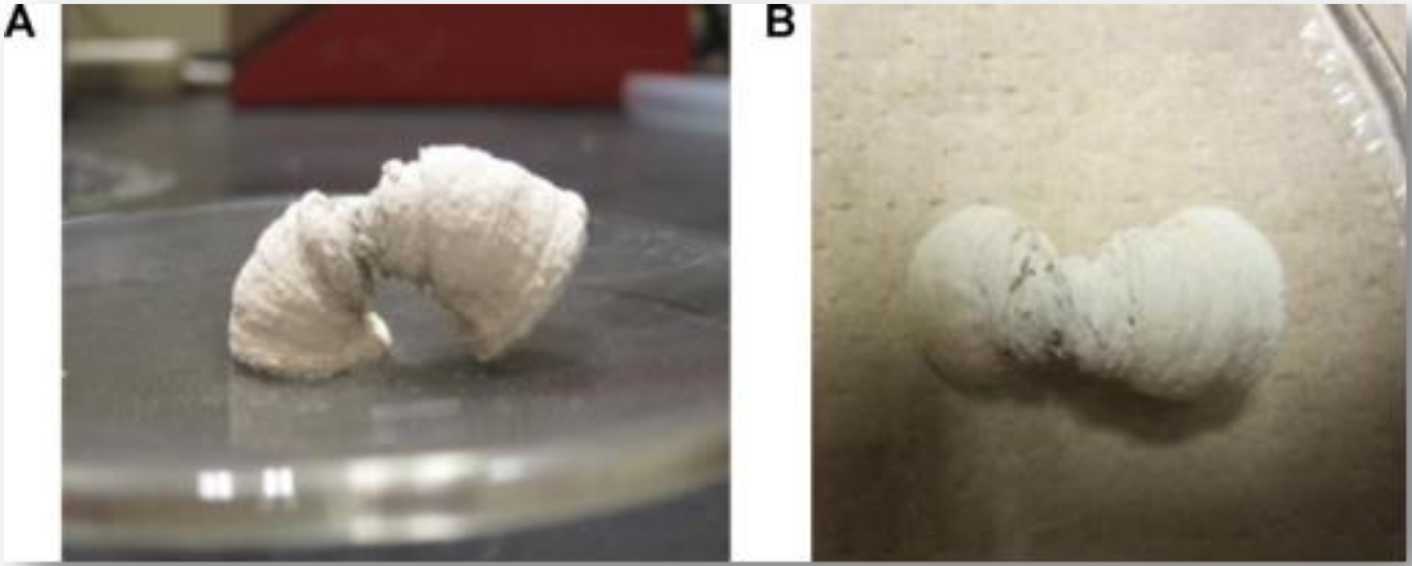
Powder expulsion cloud without external source of ignition

In all investigated cases, the **reaction speed in the powder–gas mixture is slower than in the case of the deflagration of pure hydrogen,** despite the fact that the energy content of the pure H_2 experiments is lower than in the H_2/powder mixture.

Lohstroh et al., doi:10.1016/j.ijhydene.2009.01.030

Reducing hazard by compacting

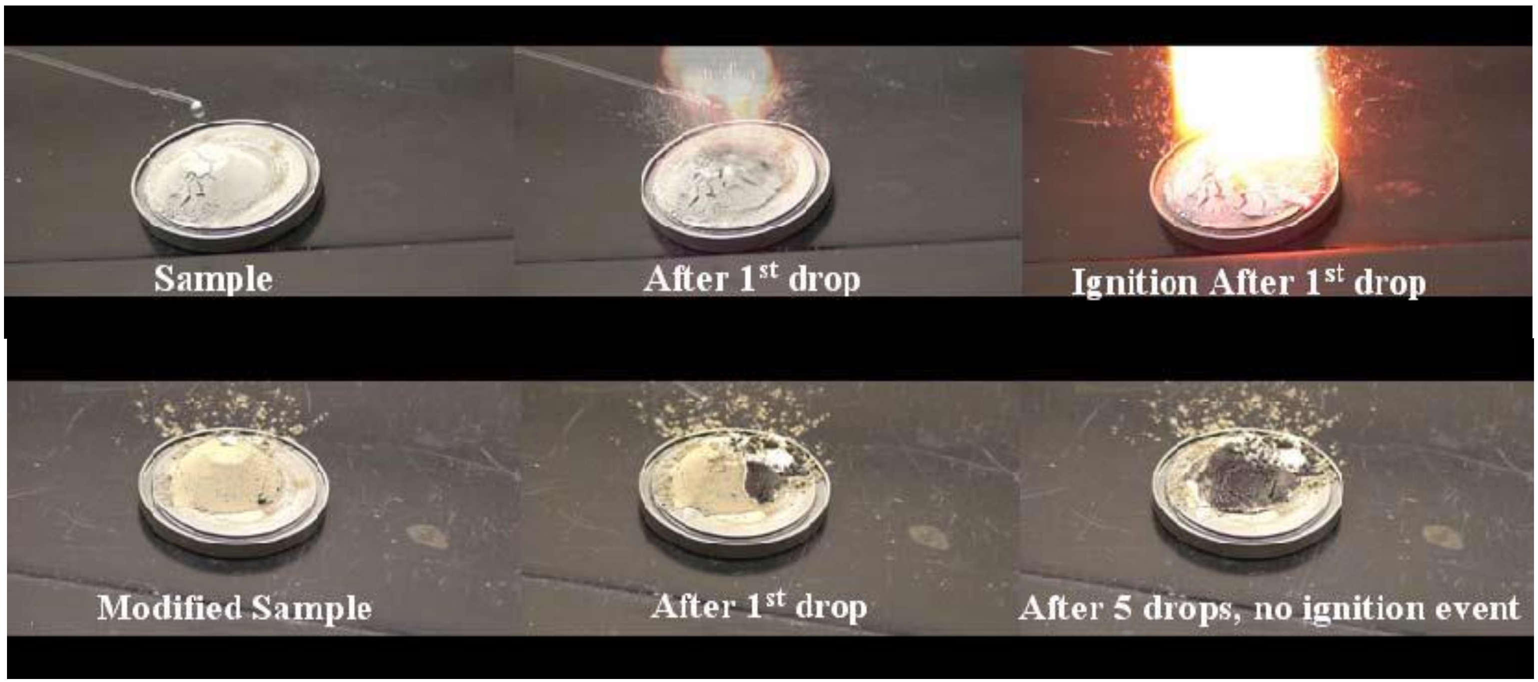
The trick here is to reduce exposure to air and its contaminants, without jeopardising the hydrogen loading and releasing kinetics



NaAlH4 wafer after 72 h of exposure to ambient air: (A) side-view and (B) top view.
Volume variation indicating slow reaction without sudden energy release

Khalil, Process Safety and Environmental Protection, 2013

Reducing hazard by additives



Water Drop Test for $8LiH \cdot 3Mg(NH_2)_2$
Top: pure material sample
Bottom: sample with flame retardant material

Cortes-Concepcion et al., ICHS2011

Conclusions

- Exposure of hydrogen storage **materials** to air and water causes in general first one or more material-liquid and/or material-gas reactions, followed by hydrogen release and possible hydrogen ignition.
- In the case of a de-hydrogenated material, presence of hydrogen is reduced, but the reactivity of the powder could by higher than in the fully hydrogenated case.
- In **storage tanks**, hydrogen is also present in gaseous form, so that hydrogen ignition can take place before or in parallel with material reactions, accelerating or even triggering them.
- In general, the hydrogen ignition and its consequences (detonation, deflagration) represent higher hazards than material-gas or material-liquid reactions (this however is not always true: for example in the case of desorbed material containing pure aluminium powder).

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Gaps

R&D gaps

Models and experiments produced so far are considerable, but not enough to calculate quantitative risks related to full scale tanks under accidental conditions.

This is mainly because:

- ☞ Complexity of the system (gas and powder, multiple reaction paths in parallel)
- ☞ Quantitative and time-dependent reaction data scarce. Strong focus on few material systems.
- ☞ No data from real accidental conditions with the required material quantities.

In addition, end-of-life aspects should be also considered:

- ☞ Disposal guidelines missing

RCS gaps

Each project developing a prototype has to learn how and perform a safety analysis and obtain license.

- ☞ There is a need for filling the gaps and for harmonisation of solutions.