RISK MANAGEMENT IN A CONTAINERIZED METAL HYDRIDE STORAGE SYSTEM

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September 19-21, 2023

International Conference on Hydrogen Safety – Québec City, Canada

0. BACKGROUND AND CONTEXT

HyCARE Project (2019-2023):

- Funded by Clean Hydrogen Partnership, successor of FCH 2 JU.
- Demonstrator installed at ENGIE Lab CRIGEN facilities in France in Paris metropolitan area
- Hydrogen is absorbed and released by metallic hydrides in a reversible reaction
- Several safety risk assessments have been performed during design

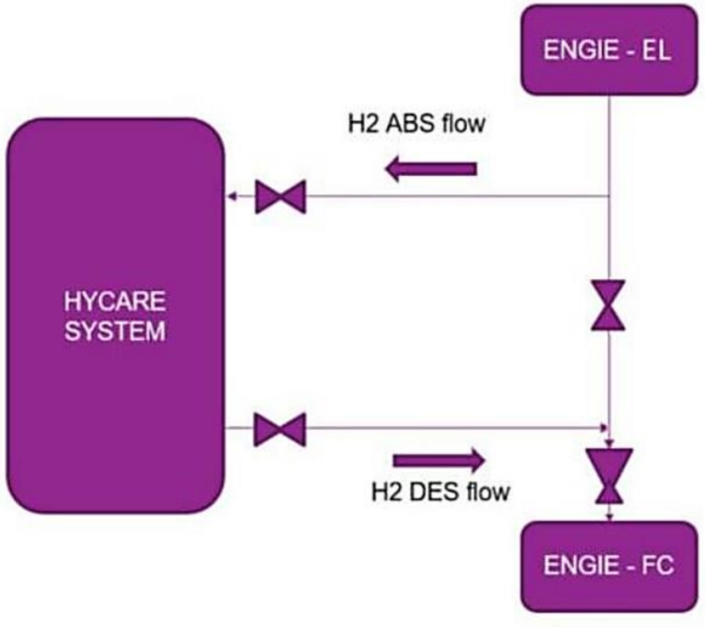
Metal hydride (MH) hydrogen storage systems help to:

- Decrease the footprint and cost of hydrogen storage
- Reduce storage pressures

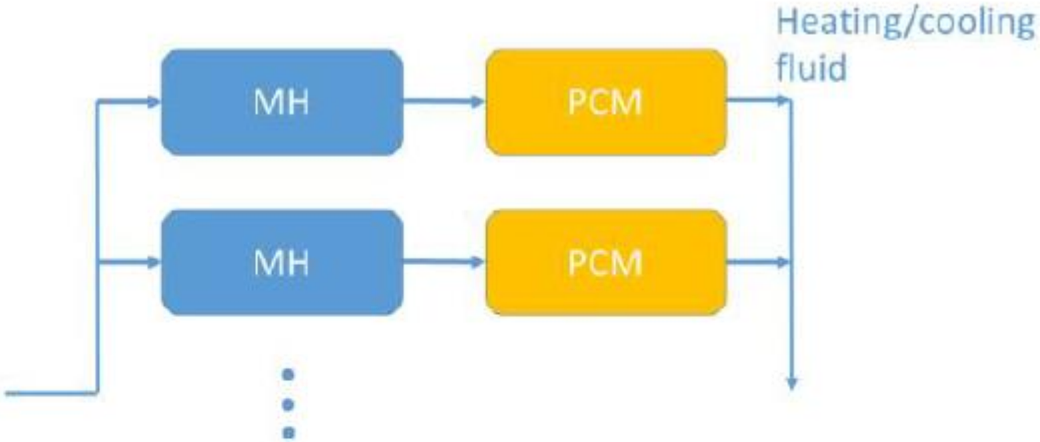
Some safety challenges of hydrogen storage:

- Reducing safety separation distances while keeping storage capacities
- Dealing with hydrogen leaks, particularly indoors

1.1 HyCARE DEMONSTRATOR DESCRIPTION - OPERATION



Hydrogen circuit scheme



Thermal fluid circuit scheme

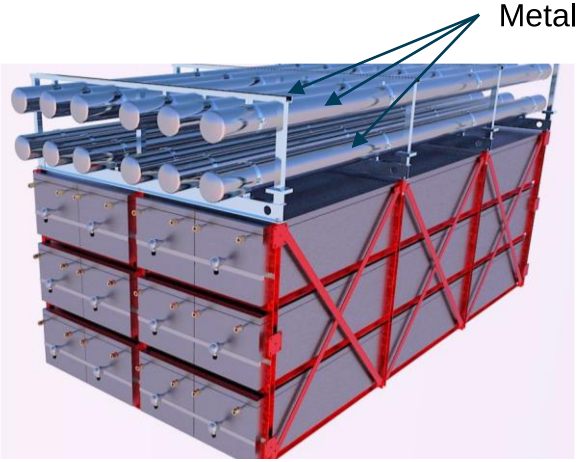
Absorption (exothermic)	→	**Heat sinks in PCM**
Desorption (endothermic)	→	**Heat is extracted from PCM**

1.2 HyCARE DEMONSTRATOR DESCRIPTION - EQUIPMENT

Reduced footprint

40 kg

Storage capacity in 20 feet container

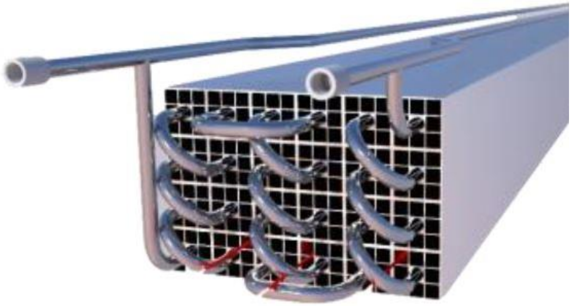


Metal Hydride (MH) storage tanks

Hydrogen storage based on pelletized Metal Hydride

12 MH tanks

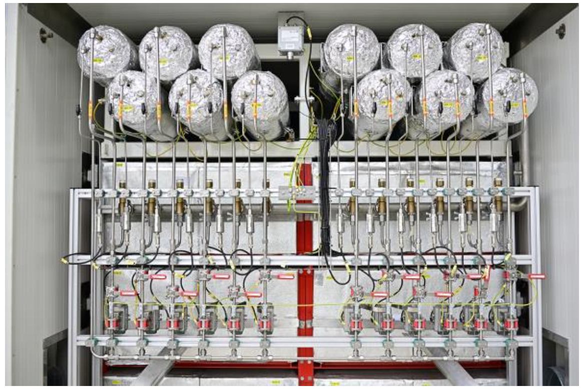
TiFe alloy as H2 carrier



Heat storage through Phase Change Material (PCM)

12 PCM tanks

Heat exchange via Water-glycol thermal fluid vector



Integration with upstream and downstream system without compression

30 bar

Storage pressure

2. SOLID-STATE CARRIER STORAGE RELATED RISKS

Solid phase risks (Metal Hydride)

- Oxidation in contact with oxygen or water (e.g. accidental air/water ingress in the tanks) → Exothermic
- Hydride expansion during absorption → Potential damage to the tank's hull

Inherently safe design mitigation in HyCARE:

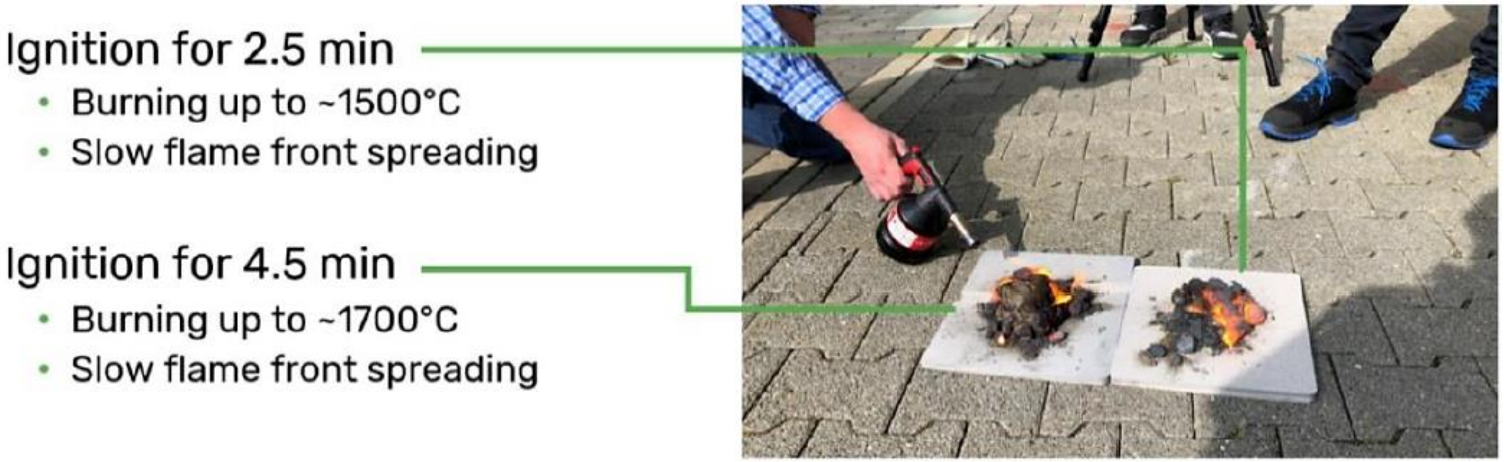
The storage tanks host MH pellets installed in a configuration of expandable discs avoiding damage and major safey risks in case of contamination with water or air

MH submerged in water:

→ ~ 6 mL of H_2 (gas) released per cm^3 of MH

MH in air at ambient conditions:

→ The MH cooled down slowly



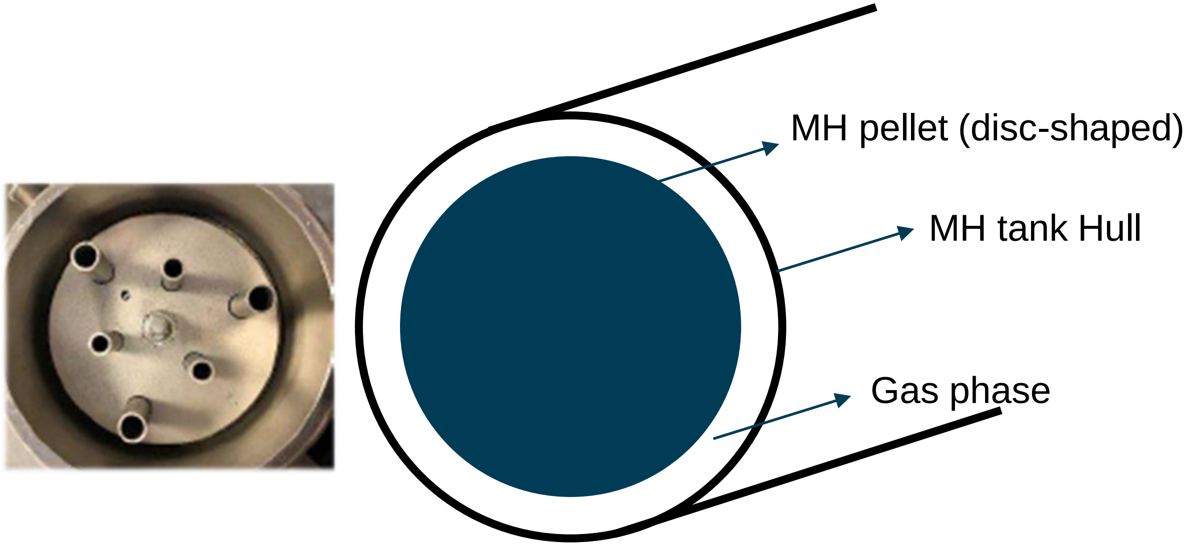
Ignition for 2.5 min
- Burning up to ~1500°C
- Slow flame front spreading

Ignition for 4.5 min
- Burning up to ~1700°C
- Slow flame front spreading

Pellets' structure allows natural passivation of the active surface, preventing a rapid runaway oxidation of the MH even at extreme conditions

2. SOLID-STATE CARRIER STORAGE RELATED RISKS

Gaseous phase risks (Hydrogen gas)



MH tank cross-section

- Exothermic absorption reaction in MH → Pressure increase in the gas phase upon charging can be steeper than expected
- Main classical Hydrogen accidental scenarios identified in HyCARE project preliminary risk assessment in case of leak:
  - Jet fire in case of immediate ignition
  - Flash fire in case of late ignition
  - Unconfined Vapour Cloud Explosion in case of late ignition outdoors with some congestion
  - Confined Vapour Cloud Explosion in case of late ignition indoors (inside container)

Inherently safe design mitigation in HyCARE:

Volume of the gas phase is limited. Only ~ 30% of the internal tank volume occupied by free hydrogen gas and pressure is low compared to simple pressure storage vessels.

In case of leakage, hydrogen leaves the MH tank with self-limiting speed, leading to a lower rate of hydrogen emission than e.g. from a pressure vessel of the same internal volume at an identical pressure.

3. HyCARE SAFETY RISK ANALYSIS

HAZOP methodology was used for the identification of safety risks during the detail design of HyCARE demonstrator.

The most critical scenarios identified were:

- Unconfined explosion due to hydrogen release caused by:
  - Pipe rupture
  - Sampling valve remaining open
  - Relief through leakage into the thermal fluid loop
  - Misdirected flow of hydrogen to other areas (e.g. contamination of argon)
- Internal explosion inside MH-tanks with potential escalation caused by:
  - Air ingress in the system due to human error, mixing with hydrogen and explosion if ignited
  - Insufficient flow of argon causing air ingress, mixing and explosion if ignited
- Confined explosion in container due to hydrogen release inside the container caused by:
  - Instrumentation failure and temperature decrease producing hydrogen leakage
  - Exceeding hydrogen loop design pressure
- Asphyxiation or anoxia (oxygen deficient atmosphere) caused by argon (flushing fluid) or nitrogen (for pneumatic control of the valves) leakage and accumulation in container.

4. CONSEQUENCE ASSESSMENT

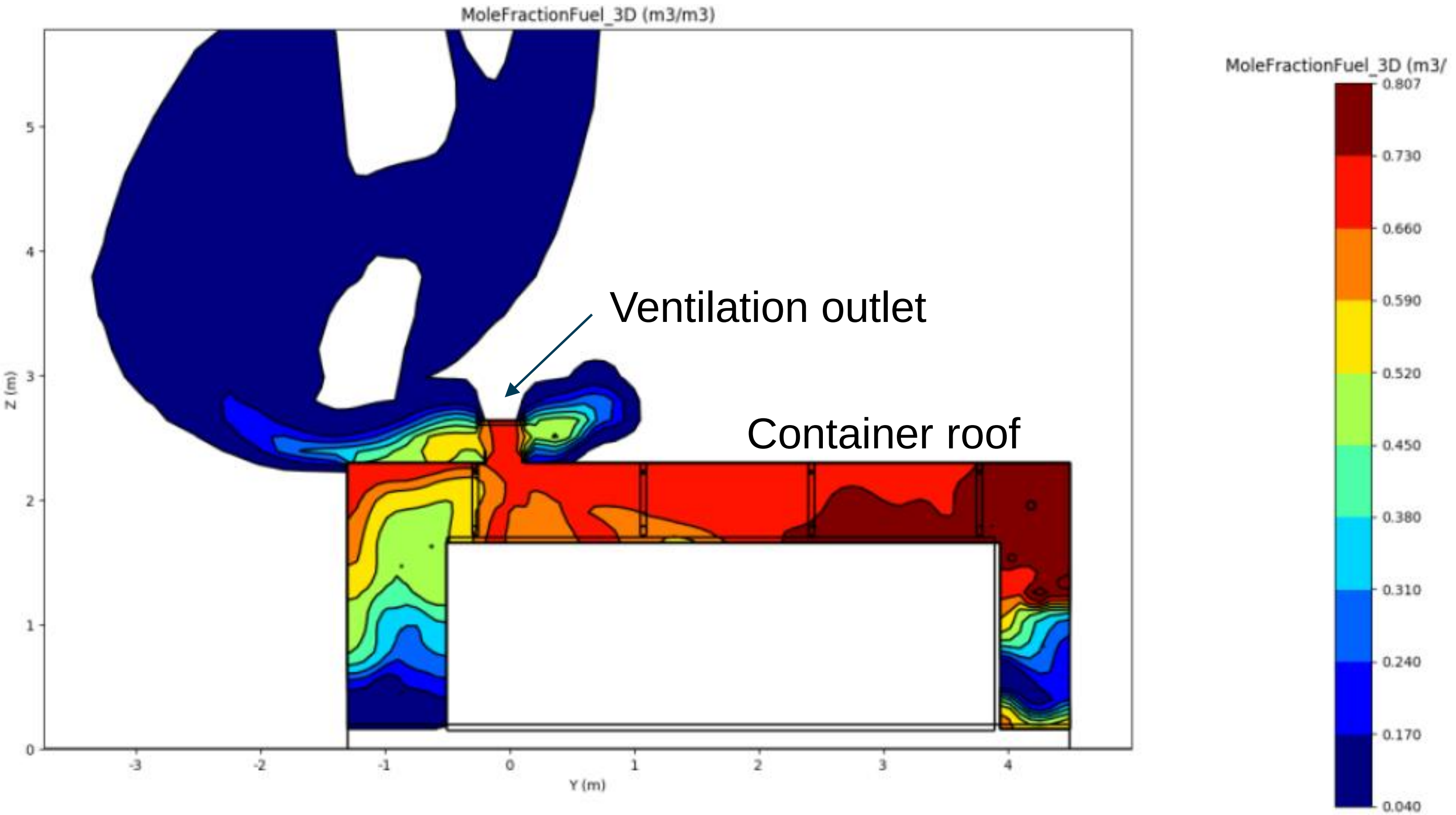
REF.	Scenario description	Method
1-u	**Pipe rupture on H2 supply (outdoor)** **UVCE**	PHAST-Multi- Energy
1-jf	**Pipe rupture on H2 supply (outdoor)** **Jet fire**	PHAST
1-ff	**Pipe rupture on H2 supply (outdoor)** **Flash fire**	PHAST
2-u	**H2 relief through damage to TFV loop (water glycol loop). Release by safety valve.** **UVCE**	PHAST-Multi- Energy
2-jf	**H2 relief through damage to TFV loop (water glycol loop). Release by safety valve.** **Jet fire**	PHAST
2-ff	**H2 relief through damage to TFV loop (water glycol loop). Release by safety valve.** **Flash fire**	PHAST
3	**Explosion inside MH- tanks with escalation (air presence in the tanks & ignition of H2-air mixture with escalated loss of containment and VCE in container)** **Internal explosion + Confined explosion in container**	Brode + Dispersion CFD and Multi-Energy
4	**Confined explosion in container**	FLACS CFD

4. CONSEQUENCE ASSESSMENT – CFD ANALYSIS – DISPERSION

½" Full bore rupture

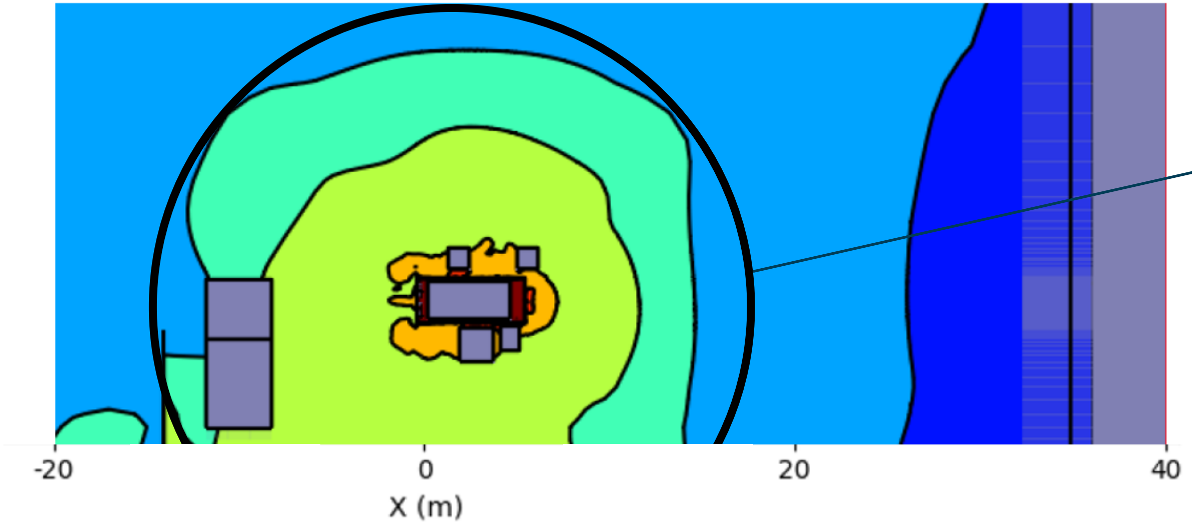
0.14 kg/s H2 leak

2560 m3/h ventilation rate

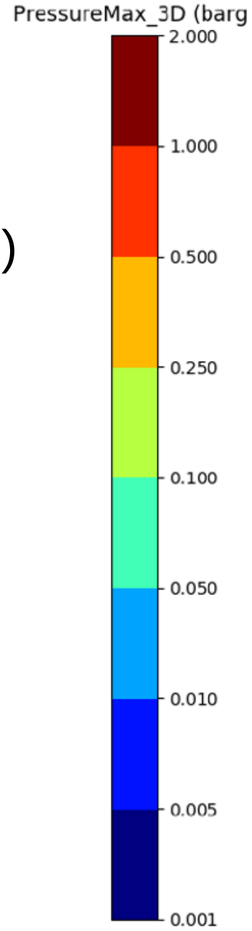


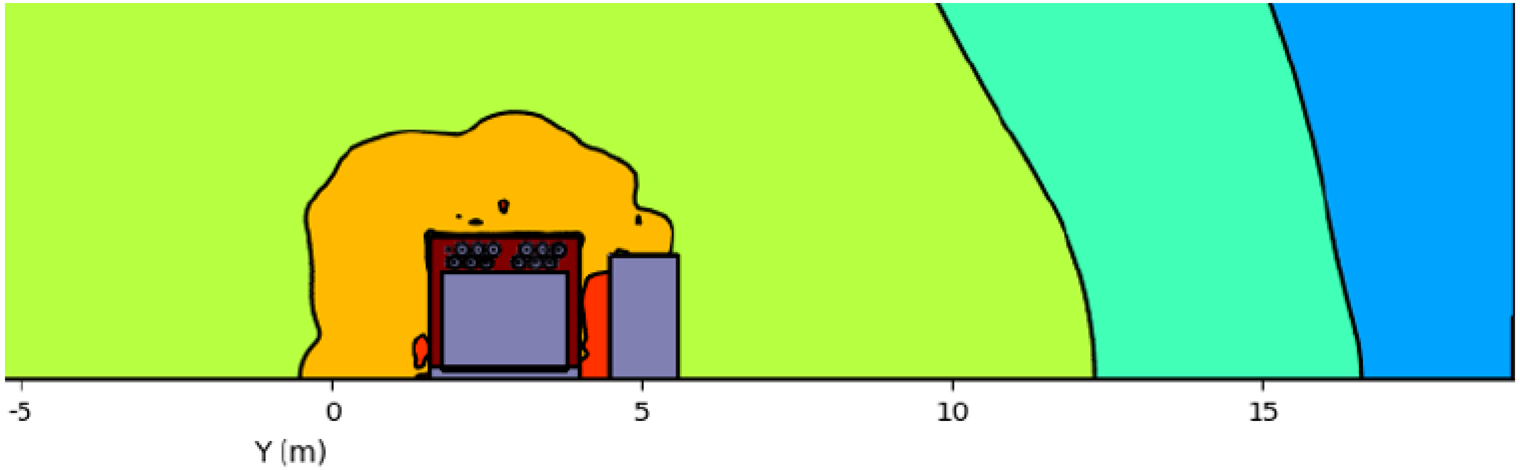
Container cross section presenting flammable gas concentration contour plots for Full bore rupture and ventilation of 2560 m3/h

4. CONSEQUENCE ASSESSMENT – CFD ANALYSIS – EXPLOSION



50 mbar
Irreversible effects for
people (French regulations)





5. PREVENTION AND MITIGATION STRATEGIES

Some of the most relevant safeguards from original design or raised during the risk and consequence analysis :

- Design of **pellets** and tank tubes to compensate activation growth of MH
- **Protection of the inlet and outlet hydrogen piping** from external mechanical damage (e.g. vehicles)
- Control of ignition sources through **Hazardous Area Classification** (**ATEX zoning)**
- **Self-closing connectors** at sampling points as well as manual valves for double isolation
- **Check valves** to prevent back flow between systems at different composition
- **Safety Interlocks**
- **Pressure Safety Valves**
- **Dedicated inert utility gases** for purging and pneumatically-powered instrumentation
- **Specific procedures were HAZOPed**, namely activation of MH tank and long storage period
- **Mechanical ventilation upon hydrogen detection** at 25% of the lower flammable limit
- **Fire and hydrogen detection** inside the container triggering the system ESD
- **Cables attached to the doors** and ground in order to limit the projection of the doors in case of VCE inside the container
- **Layout** of facilities considering results from consequence modelling

6. CONCLUSIONS

- Hydrogen storage in metal hydride has both **specific and shared risks with conventional pressure storage**
- **Inherently safe design** strategies are possible through adequate selection of the metal hydride form (pellet) and disposition in the tank (considering metal hydride expansion)
- A preliminary (**HAZID**) and a detailed (**HAZOP**) risk assessment were performed for the HyCARE demonstrator
- **Consequence modelling** of potentially hazardous scenarios allowed identifying the potential effect distances
- **Explosion scenarios** were identified as more critical (larger effect distances than jet fire and flash fire effects).
- The CFD analysis simulating an explosion in the container resulted in distances of **18 m to 50 mbar overpressure** threshold (irreversible effects for people).
- **Safety prevention and mitigation barriers** were implemented from the early stages, starting with inherently safe design of the metal hydride and coherently integrating safeguards, some of which are widespread in conventional hydrogen
  - Selection of material adapted to hydrogen and design conditions
  - Safety Instrumented Systems, Pressure Safety Valves and venting system
  - Mechanical ventilation
  - Hazardous Area Classification and control of ignition sources
  - Fire and Gas detection and strategy

THANK YOU FOR YOUR ATTENTION

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Acknowledgement:

This work is funded under the Clean Hydrogen Partnership, successor of FCH 2 JU, answering to the call H2020-JTI-FCH-2018-1. Grant agreement ID: 826352. Partners acknowledged in this work: University Of Turin, GKN Sinter Metals Engineering GMBH, ENGIE Lab CRIGEN, Tecnodelta s.r.l., Stühff Maschinen- und Anlagenbau GmbH, Fondazione Bruno Kessler, Helmholtz-Zentrum hereon GmbH, Centre National de la Recherche Scientifique, Institutt for Energiteknikk, Environment Park S.p.A.