

## Research Priorities Workshop on Hydrogen Safety

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## JRC CONFERENCE AND WORKSHOP REPORTS

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## Executive Summary

This report discusses the results of IA-HySafe Research Priority Workshop for Hydrogen Safety held in Petten, The Netherlands in September 2016. During the workshop the participants were asked to identify the state-of-the-art, current research directions and gaps that needs addressing to ensure safe deployment of hydrogen technologies in a commercial setting. This was done in each of the topical areas highlighted during the workshop. These topical areas were:

- 1 Industrial programs
- 2 Integrated computational tools
- 3 Accident Physics – Gas phase
- 4 Accident Physics – Liquid phase
- 5 Applications
- 6 Hydrogen Storage
- 7 Materials
- 8 General Aspects of Safety

These topics were a growth from previous workshops. Also new issues needing consideration as we continue to deploy hydrogen technologies into the commercial environment were introduced. After the workshop the participants and other members of IA-HySafe were asked to rank the importance of these topics in the frame of an online survey. The following priorities have been derived from the summaries related to the topical areas provided by the chairs of those topical areas and from the results of the survey.

The first set of priorities deals with the accident physics and material issues which are the indispensable basis for improved risk assessment and management methodologies and for safer applications in general.

With respect to hydrogen in its gaseous phase, premixed combustion is given highest priority for further investigation. Modeling of flame acceleration, Deflagration to Detonation Transition (DDT) and associated pressure effects for large scale applications with obstacles and interaction with mitigation techniques, in particular venting and water sprays, need further work. With regard to non-premixed combustion, and with lower priority, validation data for radiation properties of large scale fire balls and jet fires should be investigated.

Regarding the liquid hydrogen behaviour a number of knowledge gaps still exist, validated models are lacking for all accident phenomena. Validated models for multiphase releases (choked flow/jets) and accumulations in particular in congested areas indoors and outdoors have highest priority. Second priority is attributed to pool spreading and fires as well as potential for BLEVE and fire resistance of cryo-containers. Although some efforts and little progress in the dispersion modelling could be made with few large scale experiments performed by HSL, these experiments also generated new open questions in particular the multiphase characteristics of the pool fire and spontaneous ignition.

In general for both, hydrogen in its gaseous and liquid phase, realistic boundary conditions (congestion and confinement) as well as the ignition physics are highlighted.

Setting up and filling a database of fatigue data for the most relevant pressure vessel materials have been given highest priority in the Materials topic. Highly correlated is the need for better understanding the influence of pressure, purity and temperature on these data and to agree on suitable qualification metrics and test strategies. For polymers appropriate models for lifetime prediction under realistic conditions, standard test protocols and selection criteria have been prioritized on a similar high level.

With respect to Risk Assessment considerable progress can be achieved with the QRA Tool HyRAM. As the QRA Tools topic had been prioritized strongly in the previous workshop (Washington 2014) several related activities have been initiated or enforced worldwide. However, highest maturity is achieved with the US DOE supported HyRAM

tool. For all of these tools frequency data and suitable models for accounting for mitigation measures are lacking, representing the highest priorities in this topic. In general, validation concepts have to be developed for these tools. Possibly some results of the FCH-JU Project SUSANA for the validation of CFD codes for risk assessment could be transferred.

The different applications add special technical aspects to the general physics prioritized above. For public supply infrastructure, i.e. hydrogen fueling stations the expected scaling up and efficiency requirements of the fueling services implies increasing usage of LH<sub>2</sub>. Therefore most relevant scenarios include LH<sub>2</sub> related phenomena (like safe transfer of LH<sub>2</sub> from trucks to the stations), but also general fire, pressure vessel ruptures and explosions of premixed systems including direct and missile effects at the HFS.<sup>1</sup> First priority is to account for cascading effects, presence or accident initiation with conventional fuels (multi-fuel stations) and the complex and partially confined real geometries in the applied risk assessment. Appropriate models for mitigation concepts should eliminate unnecessary over-conservatisms and avoid raising unjustified safety concerns in the public. Obviously, the HFS topic also links to the material issues. In particular the welding processes for steels suitable for high pressure, high purity application deserve further attention.

For the hydrogen vehicles in particular accidental scenarios in confined or partially confined environment, like tunnel, garages, and repair shops or at fueling stations, have been given highest priority. These scenarios include the critical issue of safe strategies for first and second responders and concepts for mitigating catastrophic pressure vessel ruptures. With the onboard storage representing the most critical component of a hydrogen vehicle this topic is highly correlated with general safety topics of hydrogen storage. There improved protection against fire or thermal excursions has highest priority. This ranking is supported by the required upgrade of the GTR n°13 where definition of more realistic car fires (heat flux measurements and testing) is required to standardize the corresponding testing appropriately. Structural health monitoring has 2nd priority in the Storage topic. Also, closely related to the Materials issues, the modeling of ageing and thermal degradation with a special focus on liner stability and permeability has 3rd priority.

Most of the open issues of the Power-to-Hydrogen (P2H) application are material related. Compared to the other applications, this application has matured considerably. Safety relevant parameters of hydrogen/natural gas blends have been evaluated or are just on the way to be published. However, support for international harmonized standardization is required for transnational solutions and for demonstration of a harmonized common knowledge. To this end collection of field data is considered the most important action. Although not treated explicitly in the workshop and questionnaire, high temperature and pressure electrolysis will involve new safety issues, which should be addressed appropriately.

Hydrogen aerospace and aviation applications are mainly applying LH<sub>2</sub> for gravitational performance reasons. Therefore these applications refer to the same gaps in the basic understanding and in the modeling capabilities as introduced above for the general LH<sub>2</sub> related accident physics.

Hydrogen sensors are currently and successfully being deployed to assure safety. Nevertheless, there are still critical gaps with regard to sensor technology. Most urgently needed is appropriate guidance on selection and placement of sensors for the different applications.

Besides mitigation concepts risk management is addressed by appropriate education and training. First responders training for tunnel and garage scenarios and guidance for second responders dealing with pre-damaged high pressure equipment have been highlighted. However, providing specially tailored state-of-the-art educational and

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<sup>1</sup> Note: Explosion used in this report refers to any combustion process that results in significant overpressure.

training material for all involved stakeholders is a continuous task, which supports adequate risk perception and acceptance of hydrogen technology and helps achieving an excellent safety culture.

# 1 Introduction

The Research Priority Workshop on Hydrogen Safety is organized every even year, Petten in September 2016 following the workshops held in Washington (2014), Berlin (2012), and Petten (2009). The International Association for Hydrogen Safety IA-HySafe organizes this meeting in the framework of its Research Committee activities in cooperation with the Joint Research Center (JRC) and the US Department of Energy (DOE).

The main focus of the workshop is to identify and prioritize existing knowledge gaps. The gaps were addressed from the standpoint of scientific knowledge - including experimental, theoretical and numerical capabilities - and collected the opinions of industry.

The outcome of this exercise is intended to help coordinate research, guide research directions and supply funding agencies with a list of prioritized work topics. Building on the foundations of previous workshops, it aims at providing an incremental update on the state-of-the-art and knowledge gaps. This process avoids re-addressing already filled gaps, and helps to demonstrate progress. The workshop aims also at preparing and introducing the relevant topics of the International Conference on Hydrogen Safety which is organized every odd year. The output of this workshop was presented at the ICHS2017 in September 2017.

For preparing the workshop a panel of experts and chairs was selected by the organizers. The selected participants covered their respective areas of competence and their contributions were put together by the different chairs.

During the workshop, the chair of each topical session provided an executive summary, aggregating and coordinating the contributions of the relevant experts. Each panelist, through their contribution, was invited to answer the following questions:

1. What has been done in the last three to four years (progress)?
2. What is planned for near term research direction (working topics)?
3. What are the needs / gaps that need to be filled by future research (new directions)?

The respective presentations of the chairs are accessible from the IA-HySafe website<sup>2</sup>. The current report collects the chairs' contributions, which in turn reflect the contributions of the participants. The chairs played a key role in summarizing and harmonizing the contributions and the comments from participants and other experts received before and during the workshop. In the following, the contributions from the chairs are presented according to the sessions order held during the workshop.

This report is the main product of the Research Priority Workshop and follows earlier reports<sup>3</sup> produced after previous workshops.

Annex I collects the results of a prioritization exercise carried out after the workshop. Experts were asked to rank topics related to hydrogen safety. The outcome of an on-line survey on topics prioritization is presented in the Annex.

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<sup>2</sup> <https://www.hysafe.info/activities/research-priorities-workshops/rpw2016-agenda-and-presentations/>  
(Registration might be required).

<sup>3</sup> Berlin (2012) <https://publications.europa.eu/en/publication-detail/-/publication/5acc2c57-56b9-40f1-8dd5-9f097bbc1584>

Washington (2014) <https://www.hysafe.info/activities/research-priorities-workshops/research-priorities-workshop-2014-washington/>

Petten (2009) <http://publications.jrc.ec.europa.eu/repository/handle/JRC58011>

## **2 Industrial<sup>4</sup> Programs**

Chair: M. Steen (EC-JRC) - Participants and contributors: Mirela Atanasiu (FCH2-JU), Tetsufumi Ikeda (HySUT), Nha Nguyen (DOT), Chris San Marchi (SNL)

### **2.1 HySUT - Japan Introduction and Stage Setting**

Tetsufumi Ikeda gave an overview of the HySUT (The Association of Hydrogen Supply and Utilization Technology-Japan) activities and goals. In particular, the new HySUT roadmap targets for Fuel Cell Vehicles (FCV) and Hydrogen Fueling Stations (HFS) were given: 40,000 units by 2020, growing to 800,000 by 2030 for FCVs, and 160 HFSs by 2020 in the major metropolitan areas, with the addition of another 100 small scale HFSs, also by 2020.

Ongoing activities on hydrogen quality control in HFS, hydrogen fueling protocols and hydrogen metering technologies with the aim of developing JISs (Japan Industrial Standard), were presented.

The development of a Reliability Database containing not only negative (accidents and incidents), but also positive occurrences such as successful operation time, was presented.

### **2.2 H2FIRST – U.S.A.**

Chris San Marchi gave an overview on US activities. The special focus on development and validation of fueling protocols was covered. It was mentioned that in the US, currently it is responsibility of the OEMs to assess HFS' compliance against their requirements. Reference components in a HFS are monitored by H2FIRST, but the focus is mainly on costs rather than safety. It was mentioned that due to reluctance from industry to finance HFSs deployment, the state of California established funding programs to deploy the first 100 stations. The situation for HFSs in the North-East is different, since financial contribution from industry is playing a key role there. However, government funding from the states will still be required to deploy HFS in sufficient numbers to enable successful deployment of FCEV's.

### **2.3 FCH2-JU – Europe**

Mirela Atanasiu gave an overview on the structure of FCH2-JU, its role within the European Energy Union strategy, its budget and its activities. This was followed by a summary on projects related to hydrogen safety financed by the Joint Undertaking.

### **2.4 GTR n°13 – International**

Nha Nguyen presented the activities of UNECE's Global Technical Regulation No.13 (Hydrogen and fuel cell vehicles). The working group consists of governmental participants from China, European Union, Korea, Canada, United States and India, industry participants from standards developing organizations, automobile and component manufacturers. Contracting Parties are obligated to start an adoption process of GTR No.13 into their national regulations. The three main FCEV's parts considered by GTR 13 are:

- The high pressure fuel container system
- Fuel system at vehicle level: in-use and post-crash hydrogen leakage limits
- Electrical integrity of high voltage system: in-use and post-crash

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<sup>4</sup> Remark: In fact the title of this session misleading; initially it was planned that industry partners present their programs. In the further planning of the workshop it became obvious that rather publicly funded programs and international overarching activities should be highlighted in the beginning of the workshop. The actual activities of the industry are included in the technical sessions.

Some tests and the requirements for each group were presented.

Currently GTR 13 has been adopted by EU (transposed GTR into UN-ECE), Japan and Korea. The US is currently preparing a notice of proposed rulemaking (NPRM), which is expected in 2017. A 'phase 2' for GTR is expected to start soon and should touch material compatibility, stress rupture, electric safety, improved test procedures and the potential scope for revision to include other vehicle classes.

## **2.5 Gaps and Next Steps**

In further discussions high priority was given to upgrading the GTR n°13 with regard to

- Realistic car fires (heat flux measurements and testing)
- Update of existing requirements and test procedures in GTR 13
- Mechanical performance of polymer liners and effect of high and low temperature excursions (softening temperature, ductile properties and permeability loss).

### 3 Integrated Computational Tools

Chair: Andrei V. Tchouvelev (AVT) - Participants and contributors: Katrina Groth (SNL), Dmitriy Makarov (UU), Frank Markert (DTU) and Thomas Jordan (KIT)

#### 3.1 Introduction and Stage Setting

Topical research areas directly relevant to Integrated Computational Tools were highly ranked at the Research Priorities Workshop (RPW) in 2014 shown in Table 3.1.

Table. 3.1: Ranking of research areas from the RPW2014 report

Topic Number	Topic	% of Votes Received
1	QRA Tools	23%
2	Reduced Model Tools	15%
3	Indoor	13%
4	Unintended Release – Liquid	11%
5	Unintended Release – Gas	8%
6	Storage	8%
7	Integration Platforms	7%
8	Hydrogen Safety Training	7%
9	Materials Compatibility / Sensors	7%
10	Application	2%

Within the Topic “Tools and resources for QRA” the user-friendly industry-focused tools received the highest ranking as well as shown in Table 3.2 below.

Table 3.2: Ranking within “QRA Tools” from the RPW2014 report.

Topic Number	Topic	Number of Votes	% of Votes Received
1.1	User-friendly, industry-focused software tools to enable risk-informed decision making	21	22%
1.2	Guidance on the use of risk insights in decision making	17	18%
1.6	Validated probability models and consequence scenarios including: overpressure, cryo-release, barrier walls, and detonation/ignition probability	16	17%
1.4	Comprehensive incident databases and guidelines for estimating the probability of events	14	15%
1.7	Development of static and dynamical QRA systems to facilitate reproducible risk assessments for a variety of scenarios	13	14%
1.3	Hydrogen-specific data for updating probability models	11	11%
1.5	Statistics on initiation data	4	4%

As shown in Table 3.1, reduced model tools were recognized as a significant need to address a technical gap in hydrogen safety R&D activities worldwide (15%). This represents a direct link to the QRA Tools, wherein such tools will be implemented. Sub-ranking with the reduced model tools is shown on Table 3.3.

Table 3.3: Ranking within "Reduced Model Tools" from the RPW2014 report.

Topic Number	Topic	Number of Votes	% of Votes Received
2.2	Model of barrier wall effects on flame and overpressure behavior	22	22%
2.7	Collect tools published in peer reviewed journals and develop/support an online tool for hydrogen safety research & engineering	20	20%
2.1	Cryogenic release behavior prediction	16	16%
2.3	Validated two-zone notional nozzle model and notional nozzle model for non-circular orifice	11	11%
2.4	Integration of tools to provide a systematic approach	10	10%
2.5	Deflagration overpressure prediction	10	10%
2.8	Transient models	10	10%

To better understand the context and purpose of Integrated Computational Tools, the following definition has been proposed.

**Integrated Computational Tools** for hydrogen safety – a suite of **engineering** probabilistic and / or physical effects (consequence) validated models integrated into a user-friendly interface allowing the user to input user-specific information and boundary conditions and capable of generating risk and / or hazard assessment data within reasonably short time (seconds to minutes).

The words "integrated" and "engineering" are key and is highlighted to differentiate these tools from more sophisticated ones such as Computational Fluid Dynamics (CFD) that normally requires hours to days to get a result on a specific hazard scenario.



## 3.2 Risk Assessment Tools

### 3.2.1 Quantitative Risk Assessment Tools

This topic was presented by Dr. Katrina Groth from Sandia National Labs, USA, who leads this international effort within IEA HIA Task 37. Figure 3.1 below illustrates how Quantitative Risk Assessment (QRA) has been enabling hydrogen infrastructure deployment with US within the past 12 years.

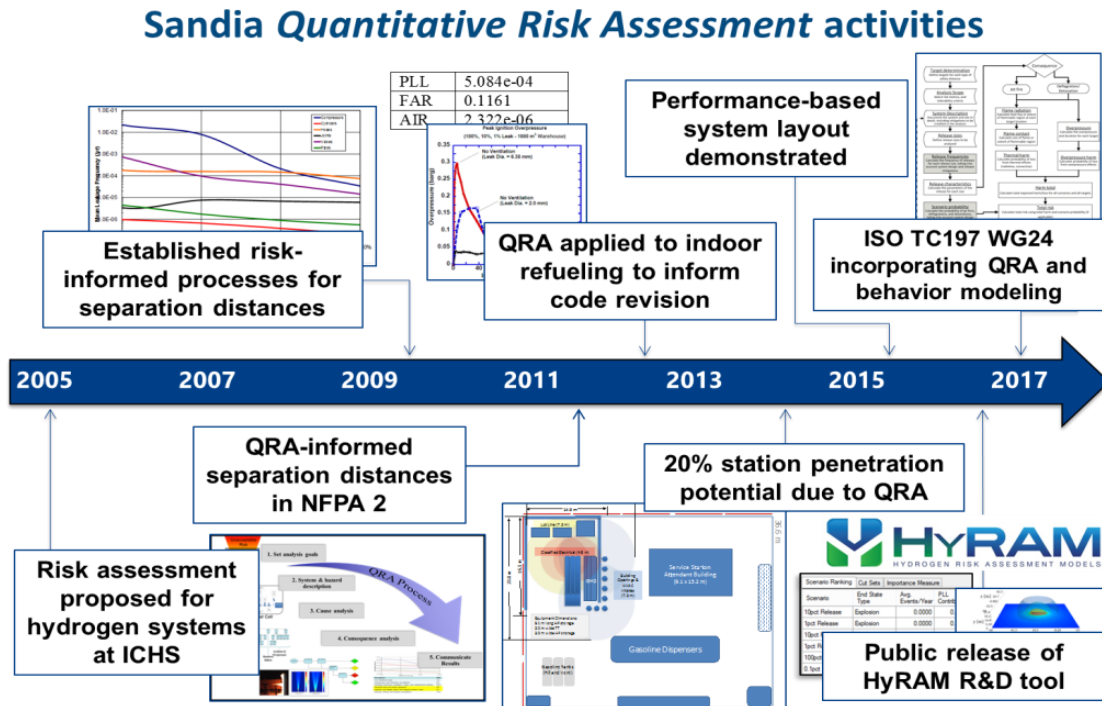


Fig. 3.1: Sandia QRA activities since 2005.

In 2014 Sandia developed the HyRAM (Hydrogen Risk Assessment Models) tool [1-3], which fits perfectly the above definition of an integrated computational tool. HyRAM is a comprehensive methodology and accompanying software toolkit for assessing the safety of hydrogen fueling and storage infrastructure via Quantitative Risk Assessment (QRA). HyRAM incorporates integrated consequence analysis (discussed in this section) and/or stand-alone use of deterministic consequence models (discussed further in section 4.3). The HyRAM software toolkit provides a consistent, documented methodology for QRA with validated integrated reduced-order physical models for use in hydrogen systems. HyRAM also contains probabilistic data and models that have been vetted by the international hydrogen research community. HyRAM is intended to facilitate evidence-based decision-making to support codes and standards development and performance based compliance.

HyRAM is a model integration platform for comprehensive QRA, providing a unified language and architecture for models and data relevant to hydrogen safety. The development of a unified software framework also facilitates completeness and usability: experts from across the international hydrogen safety research community can contribute validated models from their domain of expertise, and the hydrogen industry benefits from a "one-stop-shop" for those models.

HyRAM core functionality includes:

- Documented Quantitative risk assessment (QRA) methodology
- Generic data for gaseous hydrogen (GH<sub>2</sub>) systems: component leak frequencies, ignition probability; modifiable by users

- Fast-running, experimentally validated models of gaseous hydrogen physical effects for consequence modeling
- Release characteristics (plumes, accumulation)
- Flame properties (jet fires, deflagration within enclosures)
- Probabilistic models for human harm from thermal and overpressure hazards

HyRAM key features are:

- GUI and Mathematics Middleware
- Documented approach, models, algorithms
- Fast running on a personal computer: to accommodate rapid iteration
- Flexible and expandable framework; supported by active R&D

The HyRAM QRA methodology follows the general QRA approach. The HyRAM toolkit contains two user-interfaces – one that allows stand-alone implementation of the physical effects (deterministic) models for flames and overpressures and one for a QRA with those models. In general the QRA approach uses a combination of probabilistic and deterministic models to evaluate the risk for a given system. The methodology uses traditional QRA probabilistic model approaches to assess the likelihood of various hydrogen release and ignition scenarios, which can lead to thermal and overpressure hazards. Several deterministic models are used together to characterize the physical effects for the scenarios. Information from the physical effect models is passed into probit functions that calculate consequences in terms of number of fatalities.

A significant value of HyRAM is that it supports calculation of the following key fatality risk metrics (Expected value) as shown on Figure 3.2 below:

- FAR (Fatal Accident Rate) – number of fatalities per 100 million exposed hours
- AIR (Average Individual Risk) – number of fatalities per exposed individual
- PLL (Potential Loss of Life) – number of fatalities per system-year

It also can calculate the following accident scenario metrics (Expected value):

- Number of hydrogen releases per system-year (unignited and ignited cases)
- Number of jet fires per system-year (immediate ignition cases)
- Number of deflagrations/explosions per system-year (delayed ignition cases)

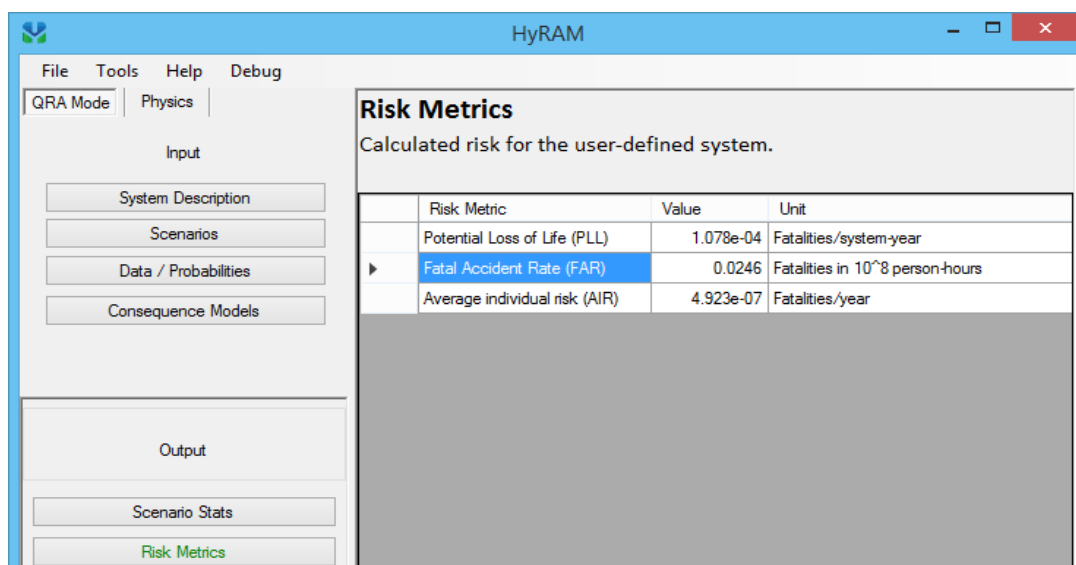


Fig. 3.2: Screenshot of HyRAM QRA Mode

In summary, HyRAM provides a platform, which integrates state-of-the-art; validated science and engineering models and data relevant to hydrogen safety into a comprehensive, industry-focused decision support system. The use of a standard platform for conducting hydrogen QRA ensures that various industry stakeholders can produce metrics for safety from defensible, traceable calculations. The physical models underlying the HyRAM platform have been experimentally validated with hydrogen in the parameter (e.g., pressure, temperature) range of interest for hydrogen systems. The probability data included in HyRAM have been developed by reference to systems using hydrogen as much as possible. The software architecture of HyRAM is modular, with the anticipated addition and revision of modules and data as the state-of-the-art advances.

### **3.2.1.1 Remaining Challenges and Barriers**

- On-going need for safety data and models:
  - Validated consequence models for hydrogen behaviours, including: liquid/cryogenic release behaviour; deflagration (unconfined) and detonation models; transition from deflagration to detonation (DDT); flow/flame surface interactions, barrier walls, and ignition. Note: This gap also relates to the HyRAM consequence models.
  - Operating experience or other information to generate data/probabilities for hydrogen system component failures, leak frequencies, detection effectiveness, etc.
- Need for additional features and models to enable deeper system-specific insights to enable overcoming station-siting barriers
  - Uncertainty & sensitivity analysis capabilities
  - Higher fidelity and depth of QRA models (e.g., Fault Trees, Event Sequence Diagrams, importance measures) - Capabilities to allow users to develop scenarios, root cause models, etc.
- Opportunities to partner to support formal software activities, validation, testing, training, design decision making....

#### **Long-term vision:**

- Partner with stakeholders to create a fully configurable, tested software product available for users to calculate hydrogen risk values and consequences;
- Able to support a wide range of activities within safety, codes, and standards.

### **3.2.2 Risk Assessment via Dynamic Modeling**

This topic was presented by Dr. Frank Markert from Denmark Technical University (DTU), who leads the subtask on human reliability analysis within IEA HIA Task 37.

Application of dynamic and dependent models as an alternative to QRA is based on the following approach:

- The event sequences trigger each other and are simulated concurrently
- Events taking place in one sequence change the conditions in the other sequences (dynamic interaction)

This approach is graphically presented on Figure 3.3 below:

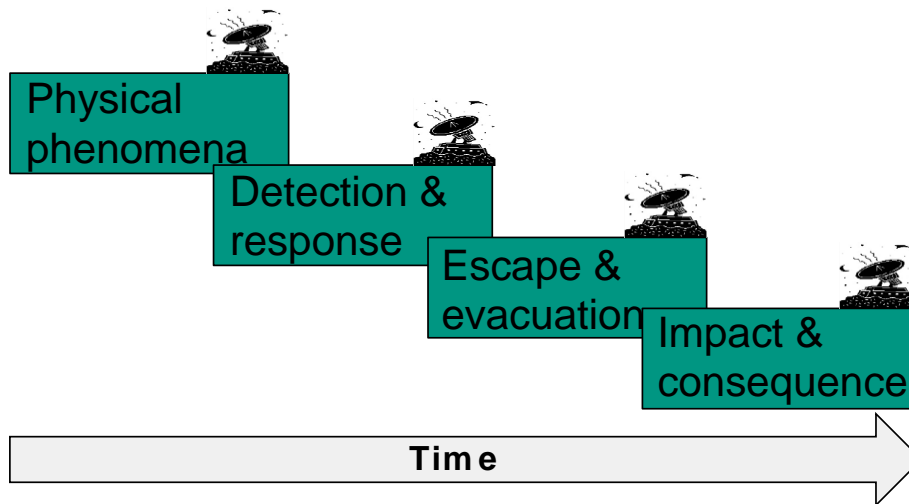


Fig. 3.3: Application of dynamic and dependent models.

The key motivation for alternative to QRA tools is related to limitations of conventional models.

Conventional systems analysis tools such as fault & event trees, Bayesian networks, cause-consequence and barrier diagrams have proven to be very effective tools for reliability and risks analyses. However, they cannot capture a number of features accurately:

- e.g. difficult to be applied to dynamic situations with:
  - dynamic demand: seasonal - daily changes
  - loss of partial performance
  - gas supply variations (amount gas delivered)
  - down times
  - residual time of gas delivery e.g. from line pack storage
  - gradual recovery after a failure

It is very well known that traditional QRA may result in significant uncertainty due to its reliance on accuracy of information and validity of assumptions. Starting from operational data, failure scenarios selection, modelling physical phenomena to probabilistic assessment based on available statistics – uncertainty increases every step of the way. For example, hydrogen ignition probability alone may differ by one to three orders of magnitude in various recorded QRA studies. Those are presumed to be discrete values within a wide range of operating parameters.

To the contrary, Discrete Event Simulations (DES) model continuous and dynamic characteristics and addresses multidimensionality of systems. Traditionally DES are employed to model e.g. manufacturing plants with machines, people, transport devices, conveyor belts and storage spaces in order to optimize manufacturing processes. Different ready-to-use commercial software packages are available on the market. DES opens new perspectives for reliability modeling that combines discrete and continuous technological and procedural aspects, e.g. it also includes human reliability.

Application field of DES models includes the following:

- Such models may provide more detailed answers to questions that depend on varying parameters
- The model retains geographical dependencies and time patterns

- The model may predict extremely rare events that may occur during the life time of an (pipeline) installation -> run time may cover millions of years.
- Possibility to include human operations as maintenance or any other task.
- Models can be extended to mimic the work flow on fueling stations incl. the varying fuel demand by customers.

DES modeling allows establishing interdependencies between various event trees, which helps achieving more accurate risk estimation.

An example of such established interdependencies is shown on Figure 3.4 below illustrating the escalation of a hazardous material release resulting in fatalities.<sup>5</sup>

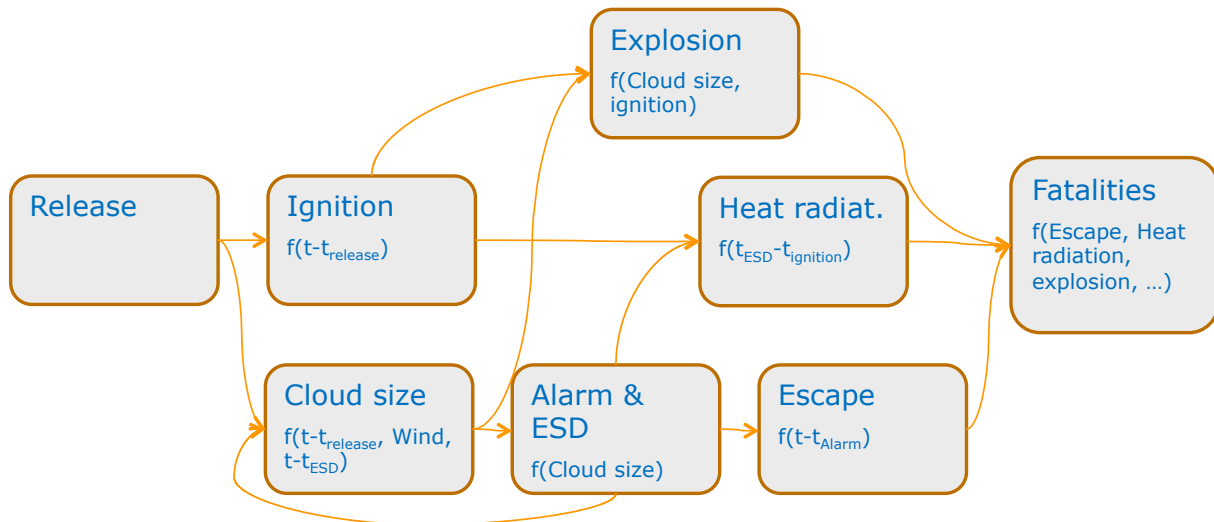


Fig. 3.4: Example of established interdependencies in DES model.

In summary, these are key features of DES modeling:

- Both processes and events are modelled
- Models are dynamic (vs. static conventional models)
- Data are sampled statistically, e.g. hole size, wind speed
- Easy housekeeping of models and results
  - transparency of calculations
- Animation and graphical scenarios contribute to understanding and confidence
- Domain experts understand models and influence their development
- Easy integration of the technical part and human performance
- Multiple runs are performed to extract risk numbers for assessing Individual Risk, Potential Loss of Life, Group Risk).

### 3.3 Consequence Modelling Tools

Consequence modeling tools were presented by Drs. Thomas Jordan (KIT), Katrina Groth (Sandia), Dmitri Makarov (UU) and Andrei V. Tchouvelev (AVT).

Consequence modeling tools were partially addressed via research area "Integration Platforms" that was ranked 7<sup>th</sup> as shown on Table 3.1.

Within "Integration Platforms" the following ranking of sub-topics was derived.

<sup>5</sup> Note: explosion used here describes a combustion event that results in significant overpressure.

Table 3.4: Expert ranking within Integration Platforms from 2014 RPW report.

Topic Number	Topic	Number of Votes	% of Votes Received
7.2	Model verification and validation	22	55%
7.1	Platform completeness	10	25%
7.3	Software testing	8	20%

It should be noted here that Consequence modeling tools are split between engineering tools and CFD.

### 3.3.1 Progress Summary

(Available) Engineering Tools:

- H2FC Cyberlab SAGE Network (provides some first models)
- NETTOOLS (project application under FCH2-JU was successful and plans to continue H2FC Cyberlab development).
- HyRAM consequence models (“Physics mode”)
- University of Ulster suite of engineering models and
- Canadian toolkit (UQTR and AVT)

CFD Tools:

- SUSANA FCH-JU project SUSANA provided the basis for CFD validation
- FireFOAM user basis is growing
- GexCon has been working on an integrated approach for FLACS

### 3.3.2 Status and Important Findings

#### 3.3.2.1 SAGE-based Network

SAGE based service got stuck after H2FC project stopped. Server was attacked, resulting on unstable service. Lack of modularity: referencing one notebook from another did not work smoothly.

#### 3.3.2.2 NETTOOLS

Work package will translate the PmWiki based BRHS/ Hydrogen Safety Handbook to Jupyter notebooks (see jupyter.org) to be used as a more open framework for the scientific community and as an academic educational tool.

#### 3.3.2.3 HyRAM Consequence Models

Hydrogen behaviour studies are at the foundation of HyRAM’s consequence modeling capabilities. The achieved progress since 2005 is graphically presented on Figure 3.5 below.

## Sandia Hydrogen Behavior studies

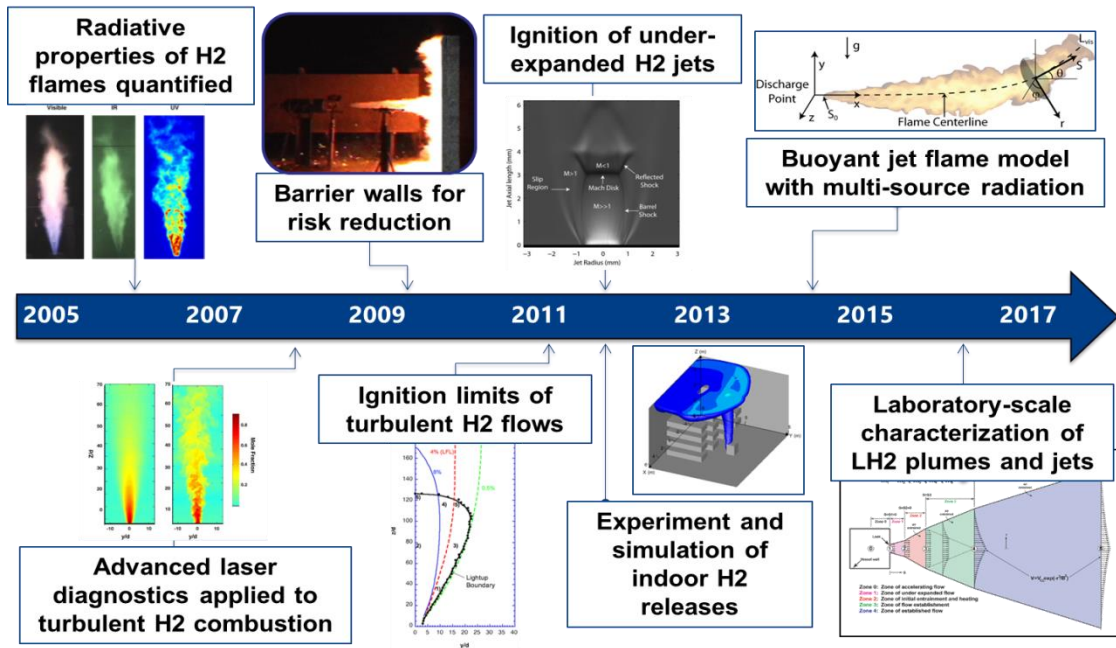


Fig. 3.5: Sandia progress in hydrogen behaviour development since 2005.

Within HyRAM, the following documented and validated models can be used from a simple user-interface in an engineering toolkit, or in physics (consequence) mode:

- Temperature-pressure-density calculations using the Abel-Nobel equation of state
- Tank mass flow-rate and blowdown, based on initial pressure and orifice size
- Under-expanded CGH<sub>2</sub> jet dispersion, with graphical representation of mean concentration boundaries
- Accumulation and layering in an enclosure, with layer height, flammable mass, and overpressure generated upon deflagration
- CGH<sub>2</sub> flame temperature profile
- CGH<sub>2</sub> flame radiation, with graphical representation of iso-heat flux contours

### 3.3.2.4 University of Ulster (UU) Suite of Engineering Models

Below is the list developed and validated engineering models by UU:

- Under-expanded CGH<sub>2</sub> jet parameters (in real and notional nozzles) [4, 5]
- The similarity law for CGH<sub>2</sub> concentration decay and hazard distances in axisymmetric expanded and under-expanded jets [6, 4]
- Tank blowdown dynamics as a function of volume, pressure, and leak diameter: adiabatic and isothermal releases [7, 4]
- Pressure peaking phenomenon for unignited release for: constant mass flow rate release and tank blowdown [8, 4]
- Flame length and three hazard distances (no-harm, injury, fatality) for jet fires [9]
- Passive ventilation in an enclosure with one vent [10, 11]
- Blast wave decay from high-pressure GH<sub>2</sub> tank storage [12]
- Vent sizing correlation for deflagration mitigations [13]

- Nomogram for effect of buoyancy on hazard distances [14, 15, 4]

UU has also been developing CFD tools for safety engineering. Their vision for open source CFD code is the following:

- License-free CFD code "HyFOAM" for academic research and industrial safety engineering design (financial support is required) based on OpenFOAM
- Legacy of EC FP7 H2FC project
- Collection of case studies, demos and tutorials:
  - Releases
  - Fires
  - Deflagrations
  - Detonations
  - etc.
- Current progress:
  - CGH<sub>2</sub> axisymmetric jet
  - Deflagration in open atmosphere

### 3.3.2.5 Canadian Toolkit (UQTR / AVT)

The partnership of UQTR and AVT developed a toolkit that includes a number of published and validated engineering models to predict hydrogen and methane dispersion, overpressure and thermal effects [16]. The strongest feature the tool kit includes is a prediction of the effect of either hydrogen and methane jet proximity to surface (both horizontal and vertical). A graphical sample of the Canadian toolkit screenshot showing the effect of the surface vs other models that do not take into account the surface effect is shown on Figure 3.6 below.

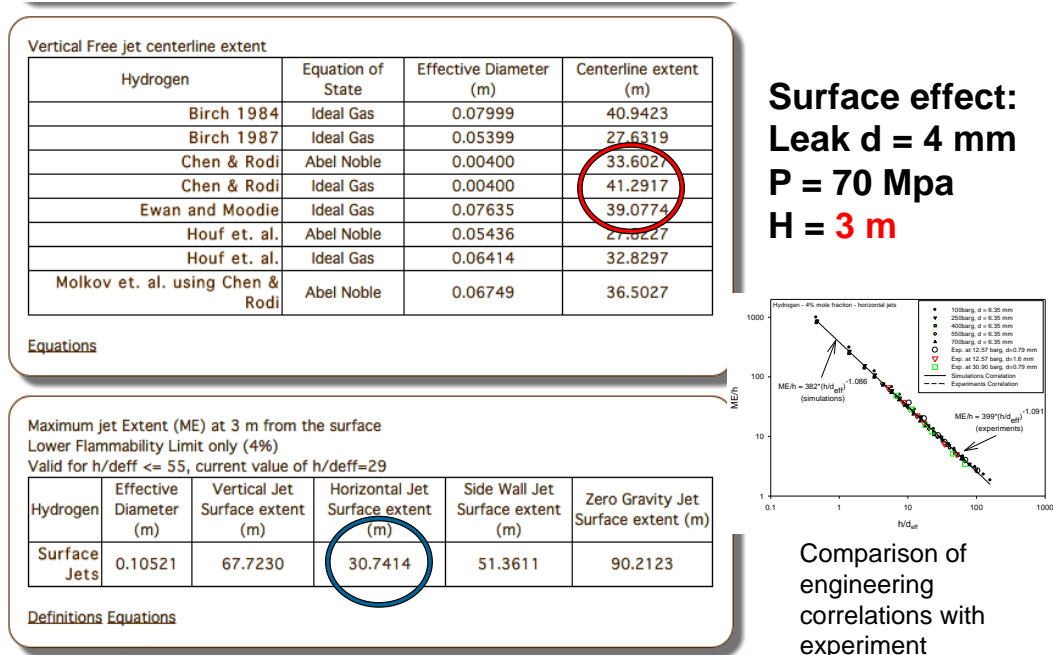


Fig. 3.6: Screenshot from Canadian toolkit illustrating the effect of surface on the extent of hydrogen jet.



## **3.4 Gaps and Next Steps**

### **3.4.1 QRA Tools: HyRAM 2.0 ++**

- Scoping algorithms for uncertainty analysis and dynamic QRA
- Incorporate software changes to assimilate IRIS software to allow users to edit Event Trees, Fault Trees & calculate importance measures
- Establishing process to enable external R&D community to contribute models and data, i.e. as plug-ins

### **3.4.2 Consequence Modeling Tools**

- Defining the validation basis in particular for engineering tools to be used for HFS and other H<sub>2</sub> applications.
- Develop sound course material for HyRAM and offer courses to the community (potential activity of the IA-HySafe educational committee, provided agreement by SNL)
- Introducing Uncertainty Quantification UQ for the CFD in the consequence analysis tools (although these type of uncertainties are small compared to the uncertainties in the statistical basis for QRA in general). There are new methods for UQ in CFD applied in particular for nuclear safety assessments

#### ***3.4.2.1 Engineering Tools To Be Developed***

Models available:

- Forced ventilation system parameters
- Upper limit of hydrogen inventory in closed space [17]
- Mitigation of localised non-uniform deflagration by venting
- Blowdown time as a function of storage pressure, volume and TPRD diameter

Models not yet available:

- Pressure peaking phenomenon for ignited releases
- Radiation from hydrogen fireball after high-pressure CGH<sub>2</sub> tank rapture in a fire
- Effect of buoyancy on jet fire hazard distances

It is also critical to develop and validate engineering models for high pressure hydrogen in enclosures. Available validated enclosure models are not relevant to realistic conditions of high pressure hydrogen systems.

## 4 Accident Physics – Gas phase

Chair: Jay Keller (ZCES, DOE) - Participants and contributors: Katrina Groth (SNL), Ethan Hecht (SNL), Dmitriy Makarov (UU), Chris San Marchi (SNL) and Trygve Skjold (Gexcon)

### 4.1 Introduction

This section addresses issues involving gas phase unintended releases; topics include Venting, Pressure Peaking, Blast Waves, Jet Fires, and reduced order modeling for use in integrated software tools. Understanding unintended gas phase releases under realistic scenarios has been central to ensuring the safe deployment of hydrogen technologies. As will be described below, we have made great progress in understanding this behaviour and hence, have been able to design systems to safely deploy hydrogen technologies. This topic was ranked 5<sup>th</sup> @ 8% between the topics at the 2014 RPW. Ranking within this topic is shown in Table 4.1.

Table 4.1 Expert ranking within Unintended Gas Release topic from 2014 RPW report.

Topic Number	Topic	Number of Votes	% of Votes Received
5.5	Effect of ignition location in gradient mixtures	11	22%
5.1	Validation of notional nozzle models in real configurations	10	20%
5.7	Radiation hazard from jets, etc.	9	18%
5.6	Effect of transition from momentum- to buoyancy-generated jet of deterministic separation distances	8	16%
5.4	Blow-down times in built-up areas	7	14%
5.2	Validated turbulence models	3	6%
5.3	Behavior and dispersion of cryogenic jets	2	4%

### 4.2 Progress – State of the Art

#### 4.2.1 Venting

The work of Molkov et.al. at the University of Ulster (UU) have developed impressive set of predictive models of venting scenarios [11]. These models do a good job at calculating the ventilation geometry needed for appropriate ventilation requirements. Including a variable neutral plane does a good job of predicting the flow for lighter than air gasses, this allows for analysis of concentration gradients in the enclosure. Predicting vented overpressures is a bit of a challenge. The EU Fuel Cell Hydrogen Joint Undertaking (FCH-JU) is funding a project "HyIndoor" to investigate this exact problem.

#### 4.2.2 Pressure Peaking

Pressure peaking is a phenomenon that occurs if a tank releases its high pressure contents of light gases, which subsequently expand at a rate faster than venting can occur. This phenomenon is particularly acute with high pressure hydrogen. Molkov's group at UU has been studying this for several years and has developed very impressive validated models that can predict this behaviour well [11, 8].

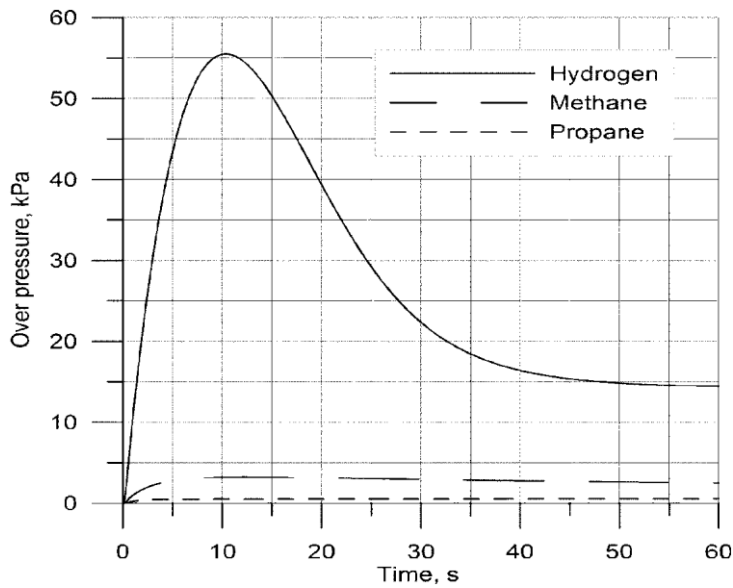


Fig. 4.1: Pressure peaking (calculation represents a 350 bar storage system, non-reacting release thru a 5.08 mm orifice, mass flow rate of 390 g/s)[18]

### 4.2.3 Blast Waves

The notion of a catastrophic tank failure is of concern to some AHJ's around the globe. The consequence of such an event is directly linked to the scenario under consideration. The tank release (with or without combustion) soon after a catastrophic tank failure has been studied by Molkov et.al. [18, 12].

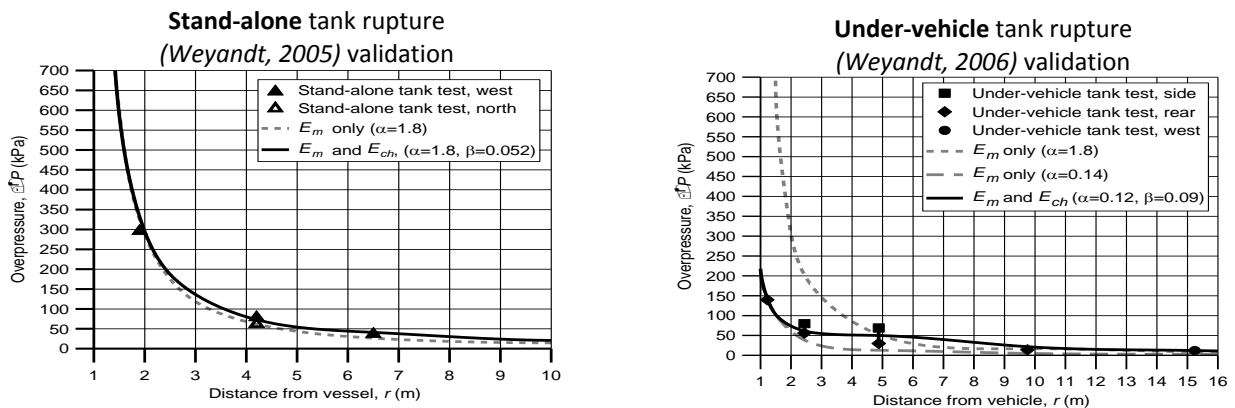


Fig. 4.2: Comparison of blast waves; simulation vs. experiment

### 4.2.4 Non-Premixed Combustion (Jet flames)

Non-Premixed combustion on a fundamental level has an excellent scientific basis. Sandia National Laboratories (SNL) has been organizing the turbulent non-premixed flame workshop for decades. These workshops provide a vehicle for modelers to compare and validate models against state-of-the-art experiments from around the globe. The turbulent combustion facility at SNL is such an example [19], it has capability to perform:

- High resolution Lab scale measurements of:
  - Temperature
  - Species (unignited reactants, major products, radicles, pollutants)
  - Velocity

- Variations in:
  - Orifice diameter
  - Flow rate / backpressure
  - Aspect ratio
- Example diagnostics are:
  - Rayleigh
  - Raman
  - Particle imaging velocimetry (PIV)
  - Laser induced fluorescence (LIF)
  - Visual and IR Imaging

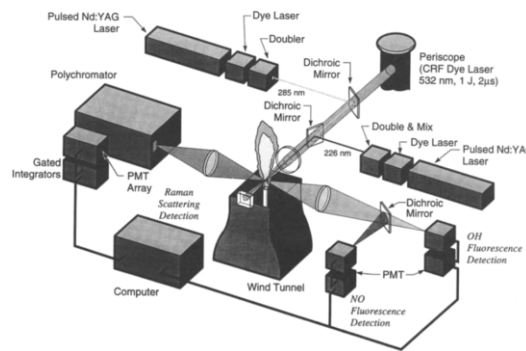


Fig. 4.3: SNL non-premixed flame measurements and experiments (from [19])

Hazard characteristics from flames have also been well characterized [20];

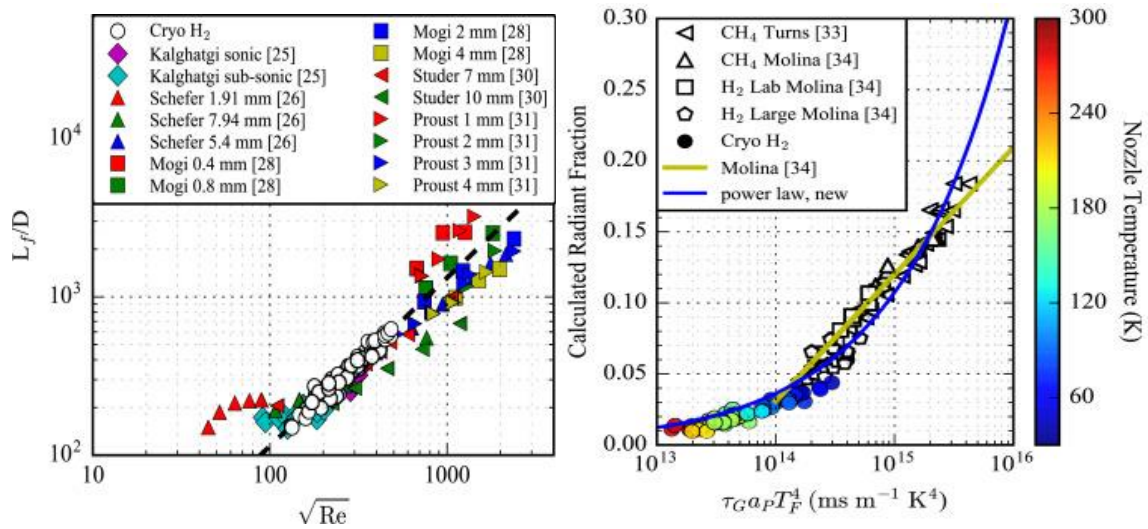


Fig. 4.4: Experimental results for flame length and radiant fraction (from [20])

Figure 4.4 on the left shows flame length and on the right a calculated radiant fraction used to calculate radiative heat flux.

- Quantified hazards include:
  - Temperature
  - Radiative heat flux
- Lab scale and field measurements:

- Length
- Width
- Temperature
- Heat Flux
- Reduced correlations for
  - Flame dimensions
  - Radiant fraction (to calculate heat flux)

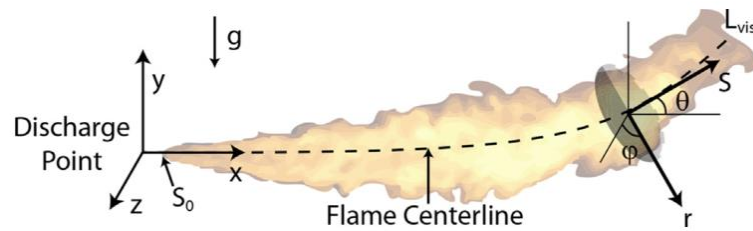


Fig. 4.5: Reduced order model of jet flame with buoyancy to capture the radiative flux (from [21]).

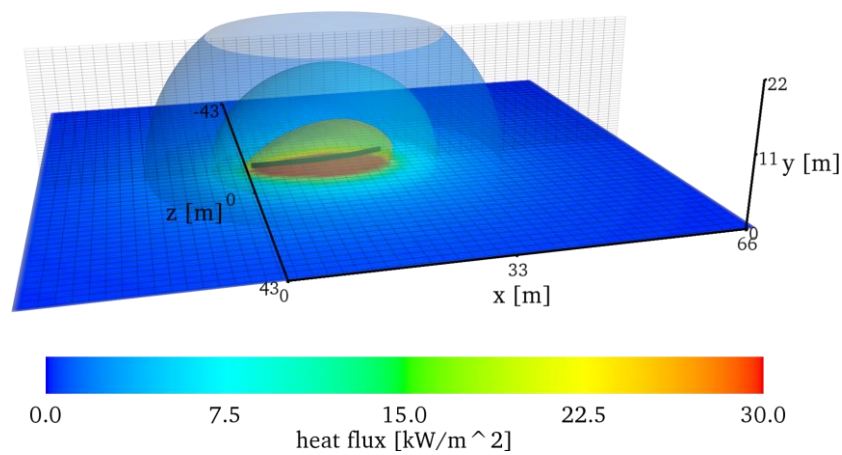


Fig. 4.6: Reduced order model of jet flame; output from HyRAM [1] showing heat flux contours  
 These reduced order models are designed to be used in fast running integrated model packages like HyRAM [21], where multiple scenarios can be rapidly simulated using a PC. The use of notional nozzle is getting much better, the model developed by Molkov et. al. is able to predict the jet behaviour as shown in Figure 4.7.

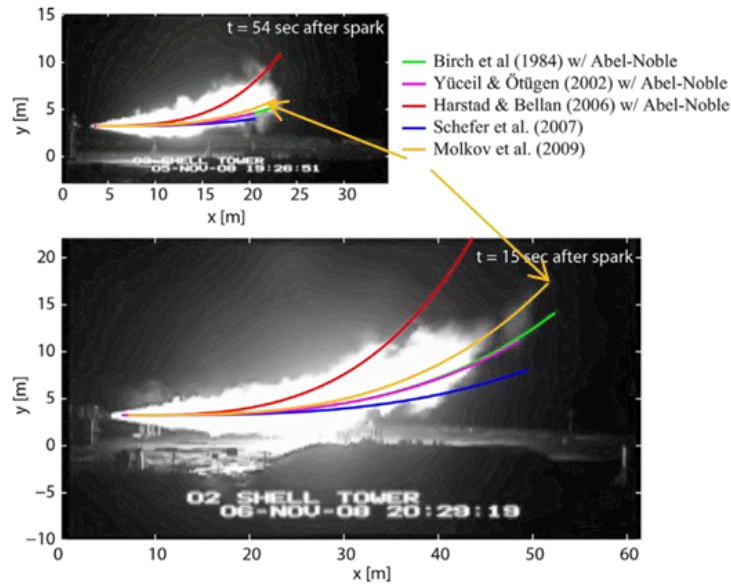


Fig. 4.7: Reduced order model of jet flame; output from HyRAM showing heat flux contours (from [21]).

## 4.2.5 Ignition

### 4.2.5.1 Forced Ignition

Forced ignition of a non-premixed jet is reasonably well understood. The ensuing jet is full of complex turbulent features, as the jet mixes with the ambient air features will be characterized by a wide range of mixtures from pure hydrogen to pure air. Due to the low minimum ignition energy of hydrogen (0.02mJ), should an ignition source (spark) make contact with hydrogen above 4% mole fraction, it will ignite, forming a kernel of combusted gas ( $H_2O$ ). However, there may not be a contiguous propagation route of flammable hydrogen (see Fig. 4.8, central frame), or the flame speed may be lower than the convective velocity of the jet. If the flame speed is not fast enough for the flame to propagate up stream, the flame is said to “blow off”, and a jet flame will not form. However, should the ignition point be within the lightup boundary, then the combustion is robust enough to propagate centrally and upstream and form a stable flame. This is captured statistically by the flammability factor, which is the average of the probability of a concentration being between the lower and upper flammability limits for hydrogen (Fig. 4.8, right frame) [22].

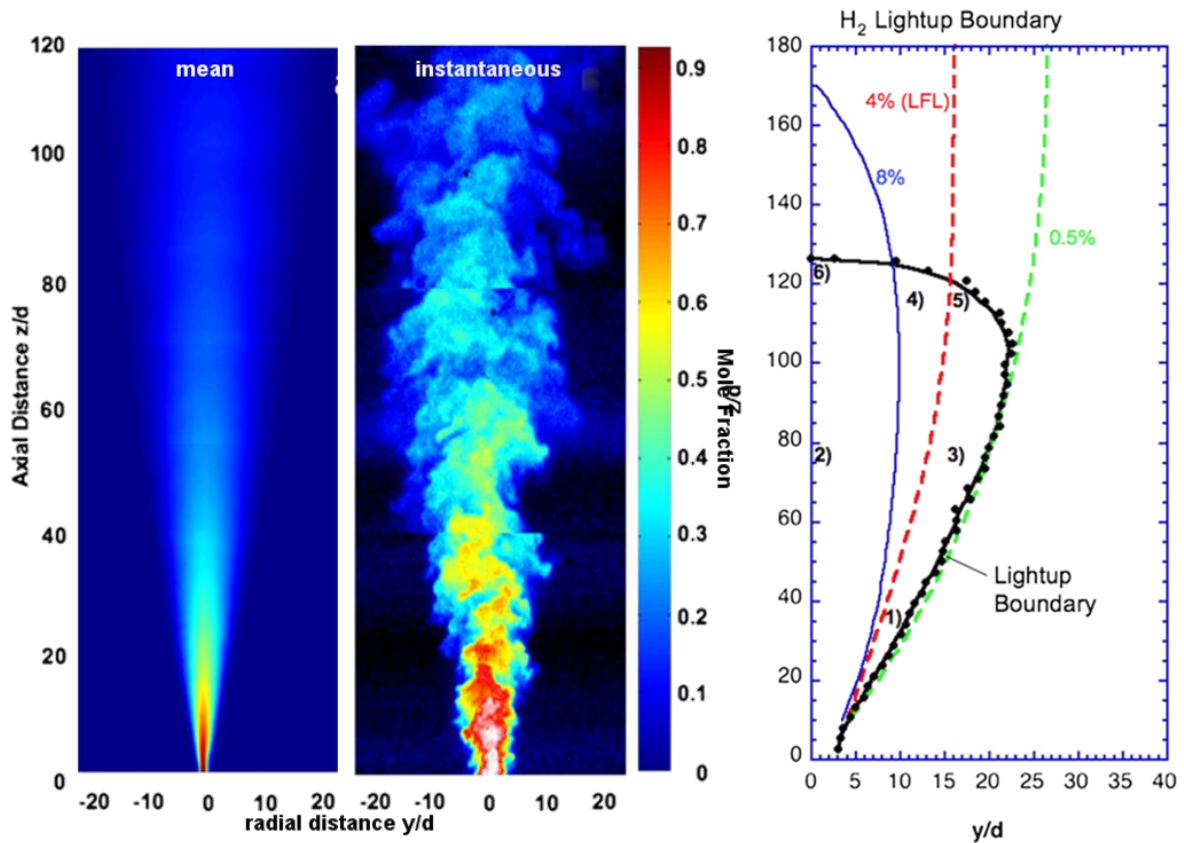


Fig. 4.8. Shown are unignited mole fractions of hydrogen, measured using planar laser Rayleigh scattering. On the left is a time averaged image, and middle is an instantaneous image showing the rich turbulent features of this flow. The graph on the right shows contours of the mean mole fractions along with the experimentally measured (symbols) and calculated using the flammability factor (solid black line) light up boundary (from [22]).

#### 4.2.5.2 Spontaneous Ignition

Spontaneous ignition of hydrogen air mixtures is not at all well understood. 81 ignitions of  $H_2$  releases have been reported in the Major Hazardous Incident Data Service (MHIDAS) database. The ignition source was identified in 11 cases (flame, electric, hot surface ...), while in the remaining 70, no ignition source was identified.

- The following have been proposed explanations for the observed ignition
  - Joule-Thomson heating (ruled out a 100 MPa release only increase the temperature by 53K not enough to reach the auto ignition temperature of  $\sim 858K$ )
  - Electrostatic discharge (discharge from charged particles)
  - Diffusion ignition (transient high-temperature shock waves)
  - Adiabatic compression (difficult to differentiate from diffusion ignition)
  - Contact with a hot surface
  - Catalytic reaction with materials present in the flow (iron oxide)

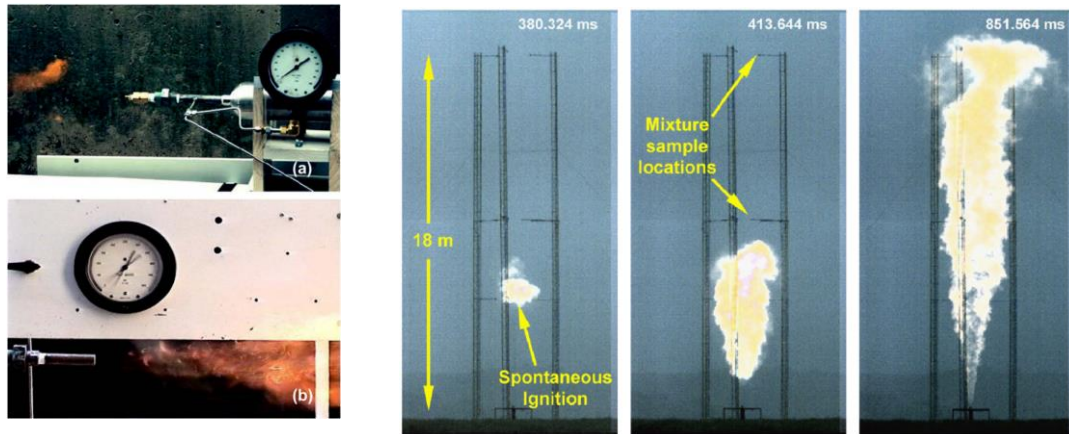


Fig. 4.9: On the left is an example of spontaneous ignition exiting a shock tube [23], ignition occurred 100% of the time – shock heating. On the right is a delayed spontaneous ignition from a choked flow exit the ignition point is in subsonic flow ignition occurred 100% of the time (shock heating is not the source) [24].



Fig. 4.10: Image of iron oxide static charge experiments at SRI field laboratory Livermore California. Across a wide range of experiments no ignition was observed.

## 4.3 Working Topics – Further Work

### 4.3.1 Releases and Jet Fires

- Transient solution for jet flame lift-off and blow-off
- Delayed ignition (advance the work of Houf et.al. [25])
- Effects of barriers on hazard distances

### 4.3.2 Blast Waves and fire balls

- Simulations accounting for real gas properties
- Thermal radiation effects on blast wave properties

### 4.3.3 Deflagrations and detonations

- Non-uniform vented deflagrations (model validation)
- DDT simulations



#### **4.3.4 Non-Premixed**

- Under expanded jet needs further work
- Need a "correct" equation of state

#### **4.3.5 Ignition**

##### **4.3.5.1 Forced**

- Lightup boundary can be predicted by using the Flammability Factor (FF), but we need to improve our modeling of the FF

##### **4.3.5.2 Spontaneous**

- We simply do not understand spontaneous ignition.

#### **4.3.6 Premixed Combustion – large scale**

- We need reliable engineering tools for consequence analysis
  - enclosures with obstructions
  - Open environments with obstructions
  - DDT modeling / prediction

#### **4.4 Gaps and Next Steps**

- Pressure Peaking phenomena
  - Model for ignited jet flames
  - Thermal loads to inside structures
- Passive ventilation
  - Model for multiple vents
  - Improved modeling of wind effects
- Blast waves
  - Wider Validation of modeling
  - Include broader scope of scenarios
- Deflagrations / detonations
  - Wider validation of modeling tools
  - DDT modeling and predictions
  - Engineering models for flame acceleration around obstacles
- Ignition – forced
  - Forced
    - Reduced order model for accurate prediction of flammable extent (FF)
    - Influence of hardware in the flow (igniter vs laser spark)
  - Spontaneous
    - Fundamental Mechanisms
    - Prediction

## **4.5 Summary**

The fundamental science basis for non-premixed flames is very good. The hazards from these flames are also well characterized. Reduced order models have been developed and work reasonably well to predict thermal load consequences and are being used in integrated platforms (HyRAM). Therefore the sub-topic of Non-Premixed Jet Flames is given a low priority for further investigation.

On the other hand it has been given a high priority to the sub-topic of Premixed Combustion for further investigation. The phenomena is well understood from a fundamental perspective but modeling for large scale applications with obstacles needs further work – particularly the understanding and modeling of DDT.

## 5 Accident Physics – Liquid/cryogenic behaviour

Chair: Phil Hooker (HSL) - Participants and contributors: Ethan Hecht (SNL), Jennifer Wen (UW) and Simon Jallais (Air Liquide)

### 5.1 Introduction

Liquid Hydrogen LH<sub>2</sub> has clearly been used in a number of industries for many years, having first been liquefied in the late 1800 by James Dewar. In addition to its best known use as rocket fuel (the Saturn V rocket utilising 1.2 Million liters of LH<sub>2</sub> for each of the Apollo missions) it is widely used in the electronics and other industries. In future however, it is clear that it can be used as a bulk fuel for a range of relatively energy intensive applications in the transport sector, which will require larger quantities of fuel to be stored on board, such as ships, trains etc.

From a hazards management point of view, the complexities and extreme conditions implied with liquid hydrogen handling put different demands on safety assessments and the modelling of accidental release, mixing and combustion. The quality and level of detail of experimental data available in literature are insufficient to allow complete and accurate validation of CFD. Unfortunately, criteria for model performance in other field (e.g. LNG) cannot be easily adapted. They need to be revised for LH<sub>2</sub> because of the significant differences in its physical properties.

#### 5.1.1 Properties of LH<sub>2</sub> and cryogenic hydrogen causing difficulties

There are a number of properties that distinguish the behaviour of LH<sub>2</sub> and cryogenic hydrogen from that of other cryogenic materials such as liquefied natural gas (LNG). Table 5.1 summarizes some key features, including the boiling and melting points, of hydrogen, methane, and major components of air.

As the table shows the boiling temperature of hydrogen is lower than the one of the main constituents of air, nitrogen and oxygen, and of methane. This low, cryogenic temperature implies that the production of LH<sub>2</sub> is quite energy intensive. Furthermore it makes handling of LH<sub>2</sub> quite complicated and direct contact of LH<sub>2</sub> or its very cold containers will generate new hazards to the ambient and human beings.

Table 5.1 Key thermodynamic properties of hydrogen, methane and main air components.

	Hydrogen	Nitrogen	Oxygen	Methane
Liquid density (kg/m <sup>3</sup> )	70	807	1141	717
Gas density at boiling point (kg/m <sup>3</sup> )	1.3	4.6	4.5	1.8
Boiling point (K)	20.28	77.36	90.19	111.6
Freezing point (K)	14.01	63.15	50.5	90.7

For example, the extremely low boiling point of hydrogen means that spills and releases cannot only cause condensation and icing of the atmospheric moisture but also of the components of air itself. These associated phase changes cause complications in understanding how such releases can be modelled. As shown by HSL experiments [26], the low temperature of spills of LH<sub>2</sub> freezes out nitrogen and, more importantly, oxygen from the air. Liquid Oxygen LOX in itself represents a serious hazard, in particular when in contact with flammable substances like LH<sub>2</sub>. The formation of condensed phase mixtures of LH<sub>2</sub> and solid / liquid air (Figure 5.1) has been observed to give rise to explosive behaviour even when the cloud of hydrogen gas is small, possibly due to oxygen enrichment in the condensed phase.



Figure 5.1 Solidified air formed during LH<sub>2</sub> release along the ground (from [26]).

### 5.1.2 Potential future applications

As already discussed, for scaling up the hydrogen supply infrastructure the transport of LH<sub>2</sub> is the most effective option due to its energy density. For the transport sector especially, with the planned large bus fleets, the emerging hydrogen fueled train, boat and truck projects and even for the pre-cooled 70 MPa car fueling, LH<sub>2</sub> offers higher energy densities, gains in efficiency and in some instances even a risk reduction when compared to a large scale compressed hydrogen supply infrastructure.

LH<sub>2</sub> implies specific hazards and risks, which are very different from those associated with the relatively well-known compressed gaseous hydrogen. Although these specific issues are usually well reflected and managed in large-scale industry and aerospace applications of LH<sub>2</sub>, experience with LH<sub>2</sub> in a distributed energy system is lacking. Transport and storage of LH<sub>2</sub> in urban areas and the daily use by the untrained general public will require higher levels of safety provisions accounting for its specific properties. The quite different operational conditions compared with the industrial environment and therefore also different potential accident scenarios will put an emphasis on specific related phenomena which are still not well understood. Specific recommendations and harmonized performance based international standards are lacking for similar reasons. For a safe scale-up of the described promising hydrogen solutions science based and validated tools for hydrogen safety engineering and risk informed, performance based, international standards specific for LH<sub>2</sub> technologies are imperative.

Therefore the potential for increased handling and distribution of LH<sub>2</sub> in the public highlights the need to address unanswered questions related to the respective prototypical accident scenarios via pre-normative research, thorough laboratory scale experimental and theoretical investigations. In particular, appropriate models for the flashing multiphase, multicomponent release phenomena, cryogenic plumes and jets, the potential for flame acceleration and deflagration-detonation-transition in these multiphase mixtures, have to be developed on a new experimental basis. The suitability of conventional mitigation techniques needs to be checked carefully and partially overly conservative safety distance requirements have to be revised on the basis of an improved understanding of the physics and with the help of the new models. The intrinsic safety advantages of LH<sub>2</sub> over compressed hydrogen offer indeed a high potential for

safer, more economic innovative solutions. However, this potential might be used only if the required knowledge base is provided.

## 5.2 Status at time of last workshop

At the time of the last workshop in 2014, the following list of issues was compiled as needing to be addressed.

- The complexities of liquid hydrogen put different demands on the modelling of releases.
- The quality and level of detail of experimental data available in literature are insufficient to allow complete and accurate validation of CFD.
- Criteria for model performance in other fields (e.g. LNG) need to be revised for hydrogen because of the significant differences in its physical properties.
- Analytical models have been developed but complete validation is missing

The behaviour of liquid and cryogenic hydrogen releases featured in two categories of the research priorities voting, with this being included in the "Indoor" category, as well as the specific "Unintended release-Liquid" category. "Indoor" ranked 3rd with 13%, and "Unintended release-Liquid" ranked 4th with 11%.

The specific areas of interest for these two categories are given in Table 5.2 and 5.3.

Table 5.2 Expert ranking within "Indoor Release" topic from 2014 RPW report.

Topic Number	Topic	Number of Votes	% of Votes Received
3.3	Behavior and dispersion of cryogenic jets	23	24%
3.1	Improve understanding of hydrogen behavior indoors	21	22%
3.10	Simplified model development for indoor accidents and incidents	14	15%
3.5	Passive ventilation approaches	9	9%
3.4	Validation of pressure peaking phenomenon for releases in realistic enclosures like garages	8	8%
3.7	Extinction of fire in a garage by water vapor generated during combustion of moderated release from TPRD in a garage	8	8%
3.9	Further numerical investigation of fire regimes indoors by taking into account water condensation	8	8%
3.6	Wind/vent modeling, two-vent model	5	5%
3.2	Validated turbulent models	0	0%
3.8	Effect of soft/acoustic absorbing walls/boundaries on flame acceleration and on DDT	0	0%

Table 5.3 Expert ranking within the topic “Unintended LH2 Release” from 2014 RPW report

Topic Number	Topic	Number of Votes	% of Votes Received
4.9	Laboratory tests for behavior of liquid hydrogen release: pools, spreading, “ice” formation, evaporation and fires	23	21%
4.1	Flashing liquid hydrogen jet releases	18	16%
4.7	Explanation of why windy conditions during spills could create conditions for explosion of non-gaseous phase	16	15%
4.2	Consequence modeling of liquid hydrogen release in congested areas	12	11%
4.3	Boiling Liquid Expanding Vapor Explosion or Fireball (BLEVEs)	11	10%
4.4	Carefully controlled cold hydrogen release data	11	10%
4.5	Accurate state modeling implementation	7	6%
4.8	Formation of liquid hydrogen/liquid oxygen mixes of hydrogen/hydride-air/water systems and behavior	7	6%
4.6	Multi-phase flow models with velocity slip	5	5%

## 5.3 Progress / Working topics

### 5.3.1 Cryogenic plumes/ jets

The behaviour of accidental releases of LH<sub>2</sub> is a key area where some studies have already been performed, but further investigation is still required. Three large scale experimental works are described below (Figure 5.2), and these provide data at a range of scales and also demonstrate the phenomena that occur.

#### Large experiments of LH2 releases have demonstrated condensation in plumes and ground cooling

Rapid release of 1500gal LH<sub>2</sub> at NASA White Sands

- Quickly warms, become buoyant and mixes with air
- Prolonged spills cool ground and can travel further


Witcofski and Chirivella, UHE, 1984

Large-scale releases (0.4 kg/s) at Battelle Ingnieurtechnik (BAM)

- Ignitable gas cloud significantly smaller than visible condensed water vapor cloud
- Little pooling observed
- Cooled ground significantly

Schmidtchen et al., Cryogenics, 1994  
Statharas et al., J. Haz. Mat., 200

Experiments at the Health and Safety Lab (HSL) in the UK observed condensed oxygen and nitrogen



- Pooling observed after surface cooled
- Releases at sufficient height evaporate before reaching ground
- Solid deposit ignited in one test (trapped H<sub>2</sub> in solid O<sub>2</sub>)

Royle and Willoughby, Proc. Safety and Env. Protection, 2011  
Royle and Willoughby, Health and Safety Executive, 2014  
Hall, Health and Safety Executive, 2014

Figure 5.2 Scales and key phenomena of LH2 releases

#### 5.3.1.1 Concentration profiles

Computational modelling has been used to simulate some of these large scale experimental works. For instance, ADREA-HF has been used to simulate HSL experimental work [27], see Figure 5.3.

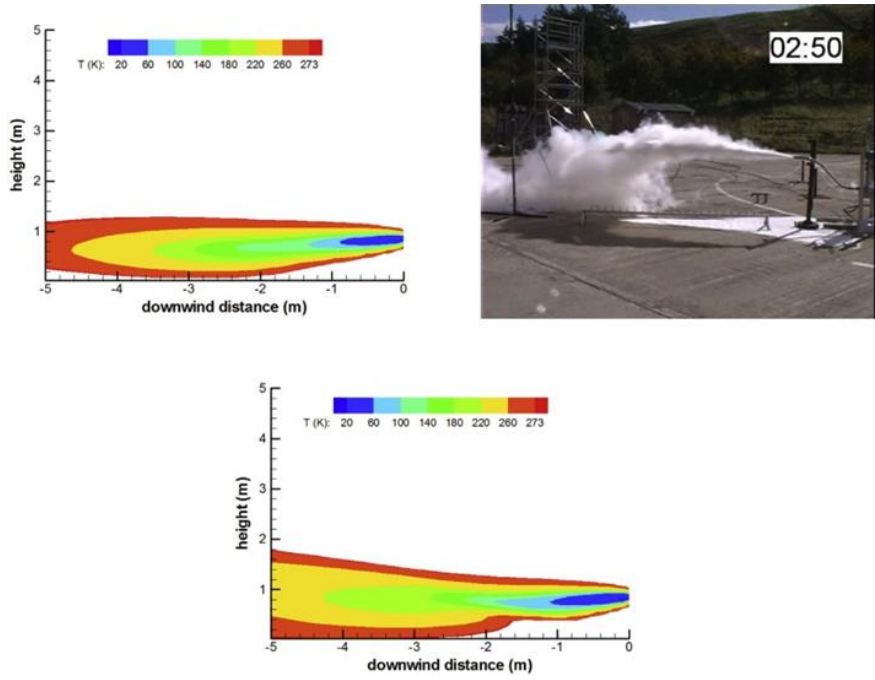


Figure 5.3. ADREA-HF Simulations of HSL experiments (from [27]).

Another example is the application of FLACS to model large scale LH<sub>2</sub> spills [28, 29] as shown in Figures 5.4 and 5.5.

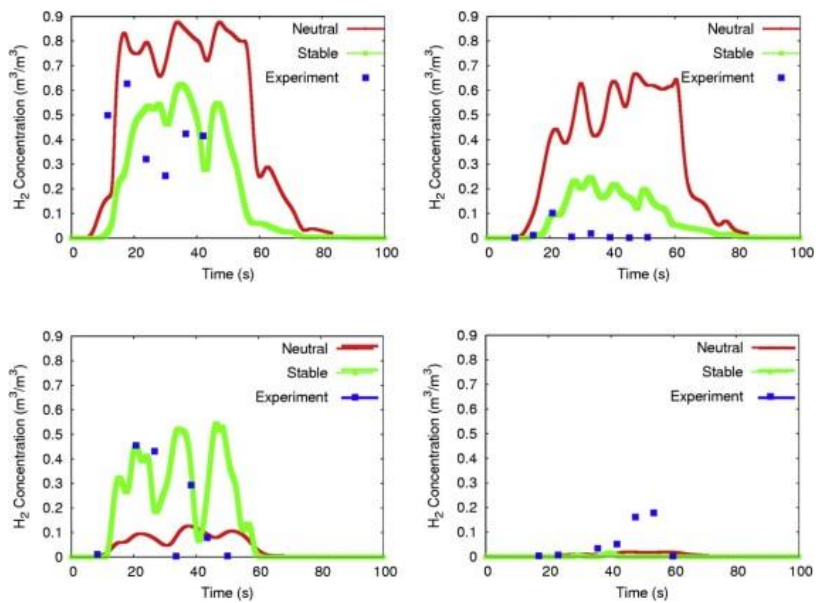


Figure 5.4: FLACS simulation results of LH<sub>2</sub> spills (from [28]).

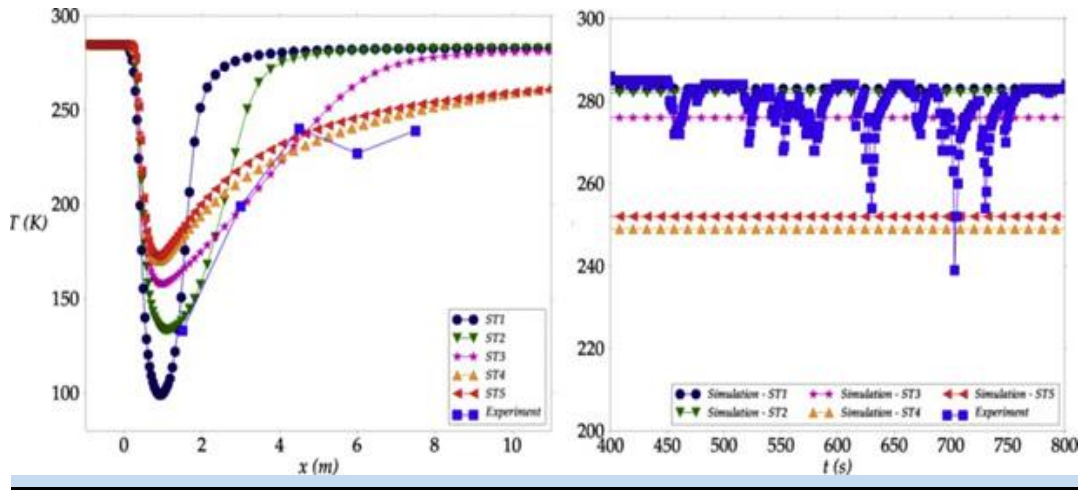


Figure 5.5: FLACS simulation results of LH2 spills compared to experimental data [29].

These kind of advanced codes are required to deal with the full range of relevant phenomena, including the impact of humidity, and the connection/slip between the vapour and non-vapour phases. Large scale experiments often suffer from variable wind, or other external factors, challenging their use for model validation. However, data from smaller scale experiments, with more control of boundary conditions, are sometimes more valuable for model validation [30]. Some small scale experiments have been performed, such as those at KIT [31] (Figure 5.6) that showed that the concentration decay is less rapid than for gaseous hydrogen, and those at Sandia (Figure 5.7) where an ignition and radiation study was performed on cryogenic hydrogen.

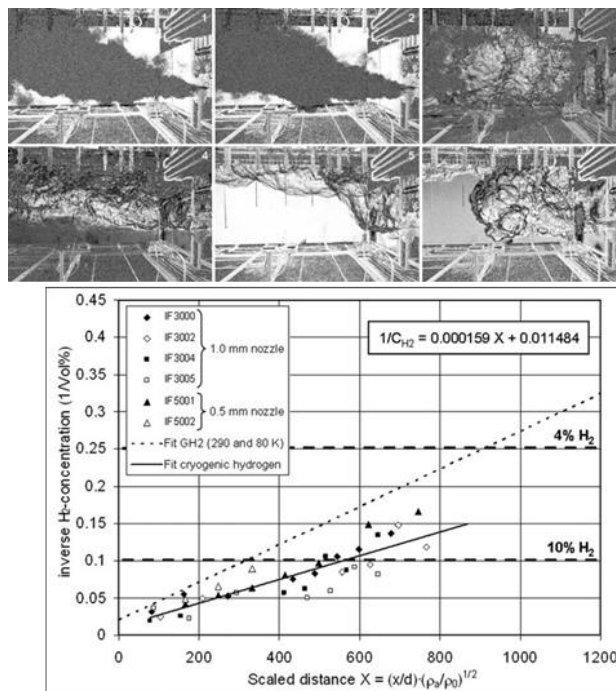


Figure 5.6 LH2 release experiments at KIT [31].



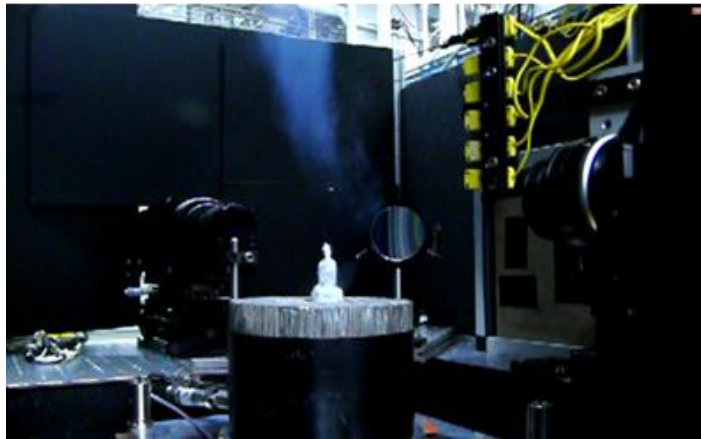
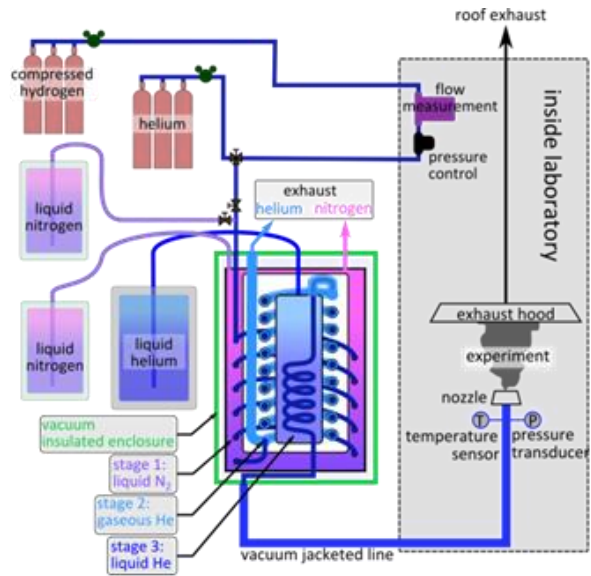


Figure 5.7 LH2 release experiments at Sandia

Distance to flammable limits for cryogenic hydrogen gas have been determined experimentally and correlations obtained for a range of temperatures and pressures [20] shown in Figure 5.8.

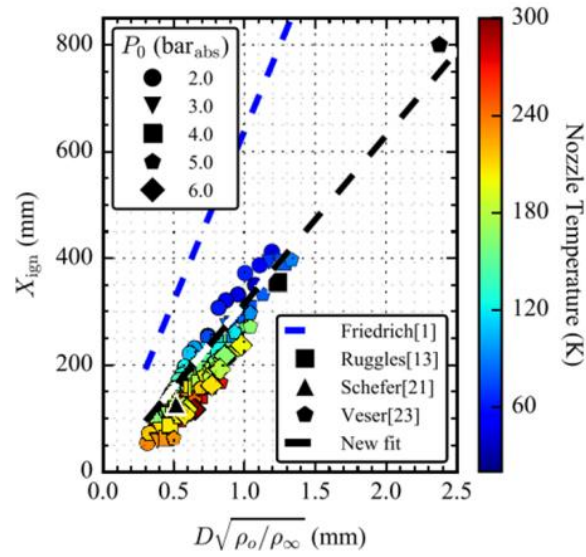


Figure 5.8 Correlation for distance to ignition for cryogenic hydrogen (from [20]).

A cold hydrogen dispersion model has been derived and integrated into HyRAM risk modelling tool [32]. However, it still requires further validation. The model does not account for any condensation of moisture or air and therefore it has been observed to over predict the centerline concentration compared to experimental data for releases at 80 K as shown in Figure 5.9.

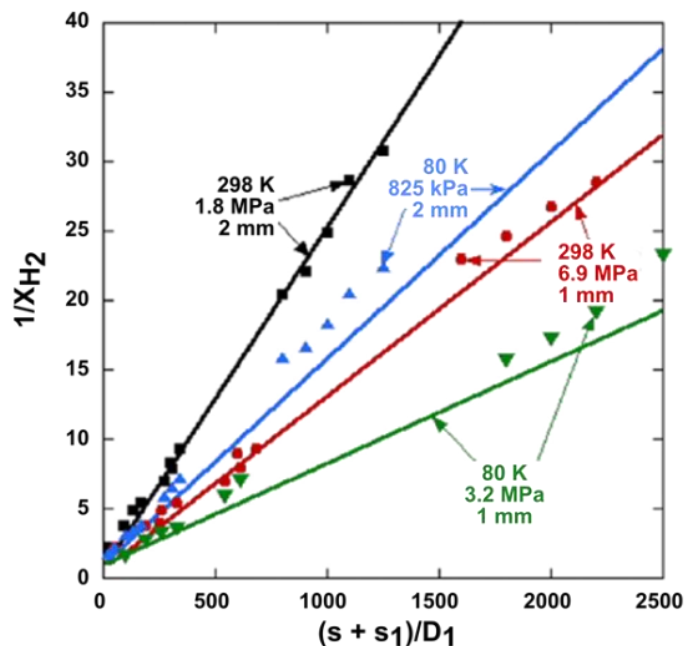


Figure 5.9: Centerline inverse concentration of hydrogen (from [32]).

Work has been carried out by University Warwick in developing SprayFoam for flashing LNG jets, within OpenFOAM, and some validation has been carried out with LPG jets. The

model could potentially be adapted for LH<sub>2</sub> but would require significant development. Other CFD modelling efforts have been performed by several other groups [33-35]<sup>6</sup>.

A major issue for model validation is the lack of good experimental data for initial source conditions (i.e. within the pipe).

A group of partners including The Linde Group, FP2Fire, LLNL, SNL and NREL are planning a series of large scale release experiments. The releases will be at height to simulate venting as a result of LH<sub>2</sub> delivery protocols. The aim of this working topic is to establish a robust sampling and analysis system, and obtaining data for model validation.

### 5.3.1.2 Jet-fire behaviour

The modelling of LH<sub>2</sub> and cryo-hydrogen jet fires have similar issues. Engineering models are available for LH<sub>2</sub> jet fires but the effect of liquid droplets is not fully understood. However, some work has been carried out to aid understanding. The work of Panda [20] on cryo-hydrogen jet fires showed that the gas viscosity has a larger influence in the existing flame length correlation previously determined [36] of flame length versus Reynolds number. The work of Panda also showed that the radiant fraction data for cryo-hydrogen plotted versus the flame residence time joins the data for ambient releases but the overall trend appears to follow a power law function rather than logarithmic as shown in Figure 5.10.

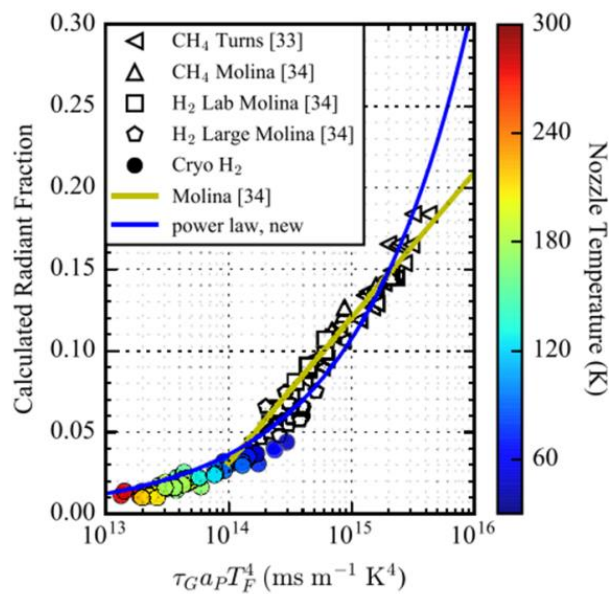


Figure 5.10: Radiant fraction data for cryo-hydrogen plotted versus the flame residence time [20].

## 5.3.2 Other hazards associated with liquid releases

There are a number of subjects that have previously been identified but for which little progress has been made in recent years.

### 5.3.2.1 Multi-phase accumulations, ignition and explosion potential

There has been a basic understanding of this phenomenon for some time. Experiments were carried out in the 1960s [37] to investigate the impact sensitivity of mixtures of LH<sub>2</sub> and condensed oxygen. The resultant mixture can be made to detonate with a yield by weight greater than that of TNT.

<sup>6</sup> See also the work presented during the "Liquid Hydrogen session" of the ICHS 2017 (Hamburg).

An explosion of ignited LH<sub>2</sub> / solid air mixture occurred in experiments at HSL under realistic release conditions. In that case the explosion occurred after several seconds of a running fire and is not believed to have been driven by impact [26]. Estimates of the explosion characteristics were made, although the experiment was not instrumented to study such behaviour.

However, no further progress has been made in really understanding the required conditions for this to occur, nor the consequences of such an event.

### **5.3.2.2 Pool fires**

There has been limited study of this phenomenon for LH<sub>2</sub>. Whilst there is a basic understanding, potential developments in applications may result in this being of more interest (see later).

### **5.3.2.3 BLEVE**

The potential for BLEVE behaviour of LH<sub>2</sub> storages has been considered in some quarters as not a viable event. This is primarily due to the fact that liquid hydrogen tanks are double walled and a direct impinging heat load on the inside tank is less probable. This heat load is necessary to "boil" the liquid inside the inner tank creating an over pressure which may lead to rupture of the tank and a subsequent vapour explosion.

Potentially initiating events have been observed. In one case the boil-off vent line was blocked as a result of water applied by firefighters freezing within it. Conceivably, the condensation of air may also result in a similar condition under the right circumstances. However, at least in the observed cases a subsequent vapour explosion did not occur.

## **5.4 Gaps and Next Steps**

Work has been carried out to define and refine the knowledge gaps in relation to modelling of hydrogen behaviour, including LH<sub>2</sub> and cryogenic hydrogen, via the EU SUSANA project.

Also, since the last workshop, there have been developments in potential applications of LH<sub>2</sub> and cryo-hydrogen.

These aspects are described in the following sections.

### **5.4.1 Modelling of LH<sub>2</sub> / cryo-hydrogen**

The SUSANA project listed the knowledge gaps pertaining to modelling. These are given below.

#### **Cryogenic compressed releases:**

- More research is required in modelling the two phase choked releases, problems with estimation of the mass flow rate.
- Evaluation and comparison of the performance of the different Equation of States (EOS) in the two phase choked flow approaches, in order to estimate the mass flow rate at the nozzle.
- A proper correlation for accurately calculating the specific heat capacity of hydrogen at low temperatures and high pressures should be further investigated and incorporated into CFD codes.
- Studies on humidity and air condensation during cryogenic compressed releases should be undertaken in order to inform modelling of these phenomena.

#### **Issues with liquid hydrogen releases can be identified in the following subjects:**

- Further development of pool spreading and evaporation models, coupled with vapour dispersion.

- Comparison between the models that solve the liquid pool separately and the models that do not solve the pool separately.
- Research should be directed at improving the modelling of ground heat flux in cases where a liquid pool is formed- for both solid and liquid (usually water) substrates.
- The radiative heat transfer and its contribution to the total heat transfer from the air and ground to the cold cloud should also be studied.
- The source modelling is another key parameter that needs further research (isenthalpic vs isentropic) to estimate the flashed vapour fraction.
- Study regarding turbulence intensity at the source.
- Humidity and air condensation phenomena need further exploration (effect on vapour dispersion and heat flux).
- Study effect of non-ideal behaviour of hydrogen on CFD predictions in liquid releases.
- Proper correlation for specific heat capacity of hydrogen at low temperatures required.
- Finally, it is essential to carry out additional experiments under more controlled conditions, in which all the above key parameters will be measured.

Many of the knowledge gaps in this area relate to understanding the source terms, particularly for two-phase releases at the outlet. Also, the need for high quality experimental data, with good control of variables, is required for model validation. The SUSANA project has started to compile an on-line library of experimental data for model validation.

Another aspect that has not been considered to any extent for LH<sub>2</sub> is the behaviour in nil-wind conditions. Experience has shown that other gases and vapours under such conditions can result in very small degrees of dispersion, but rather spreading of relatively high concentrations by gravity current. The dispersion, and explosion behaviour, of cold hydrogen in highly congested areas also warrants better understanding.

#### **5.4.2 Potential issues arising from new technologies**

As described in 5.1.2 large inventories of LH<sub>2</sub> may be present in public spaces, in congested areas such as railway tunnels, and in harbours, ports etc.

It has been observed for LNG that the extent of burning surface of a large pool fire is limited by the in-draft of air to the base of the fire. The understanding of this in relation to LH<sub>2</sub> could be of importance for deriving suitable safety distances where this kind of event could occur. Similarly, the potential for, and consequences of, BLEVEs of LH<sub>2</sub> storages in fire engulfment scenarios would warrant further understanding.

### **5.5 Summary**

Despite some significant improvement in understanding of some areas of the hazard behaviour of LH<sub>2</sub> and cryo-hydrogen, a number of knowledge gaps still exist in all of the areas including dispersion indoors and outdoors, jet and pool fires, solids (oxygen)/liquid hydrogen explosions, general ignition and BLEVE/fire resistance.

## 6 Applications

Chair: Thomas Jordan (KIT) - Participants and contributors: Wolfram Fleck (Daimler), Frank Graf (DVGW), Gerhard Krühsel (DLR), Pratap Sathiah (Shell) and Benno Weinberger (INERIS)

### 6.1 Status at the time of the previous workshop

Applications have been addressed only vaguely in the previous workshops and associated reports. In 2012 the industry representatives mainly highlighted their respective technology and only very limited insights in safety related issues were provided. The same applies to the 2014 version of the workshop, where Applications ranked on last position by common voting of the participants coming from research and from industry. One reason for this low rank might be that the whole process became rather phenomena and tools oriented and the scenarios dimension, which provided the actual motivation to certain phenomena, were actually lost. Consequently, no suitable sub-structure had been established within the application session. Only few applications were listed and voted in 2014, mainly motivated by corresponding presentations of workshop participants.

Table 6.1: Ranking of Sub-Topics within the Application Session 10 derived from the RPW2014 report

Topic Number	Topic	Number of Votes	% of Votes Received
10.3	Vehicle tank protection	12	50%
10.2	Gas turbines	5	21%
10.1	Power-to-gas	4	17%
10.4	Pre-combustion systems (PCS)	3	13%

In fact, only the Sub-Topic 10.3 "Vehicle tank protection" was discussed in more detail and therefore corresponding priorities have been derived in the RPW2014 report. One priority addresses the vehicle fire scenario and the protection of the vehicle tank against thermal loads. The second priority was suggested by a dedicated presentation, highlighting potential over-conservative requirements for the 700 bar cold filling standards (SAE).

### 6.2 Motivation of a dedicated "Application" Session

Differently from the workshop in 2014 this time an emphasis on applications was placed. The explanation is that applications bridge phenomena and safety issues, representing the research "sphere" with its phenomena thinking on one side, and the industry "sphere" with its predominant risk orientation on the other.

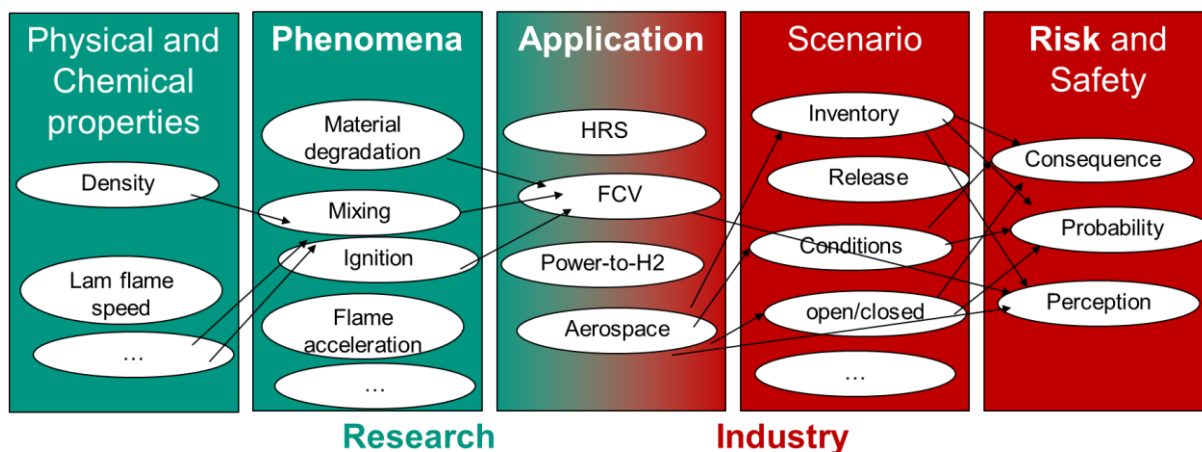


Fig. 6.1: Applications linking "Safety Research" and "Industry Risk" perspectives

For risk and finally safety assessments, the application has to be embedded in a set of real world scenarios. The application might then favor or suppress certain phenomena.

The engineer involved in a risk assessment of an innovative hydrogen application will select credible scenarios and then will try to identify what was the initiating event, driven by which phenomena, and what will be the consequences, again based on the phenomena which will be involved in the chain of events characterizing the whole incident. So the industry based engineer will always take the "industry" perspective, motivated by designing and marketing safe products, i.e. real world applications. The researcher on the other side wants to improve the understanding of the special behaviour of hydrogen, often independent of a specific product or application.

Although science always tries to be profound and complete, pre-normative work has to be driven by anticipating the innovative applications, which are close to enter the market. This is substantiated by the need of the industry to apply most suitable standards and, even beyond, to account for the state-of-the-art for designing, building and operating safe applications. So the relevant state-of-the-art and specific standards should reflect an appropriate level of understanding the relevant phenomena. The state-of-the-art is referring to published results of research, like validated physical models, which steadily extend the state of knowledge with respect to the relevant phenomena. So promising innovative applications (i.e. the middle of the Figure 6.1) define the relevant scenarios to be investigated by the industry based developers (right hand, red side of Figure 6.1). On the other side (i.e. left hand, green side of Figure 6.1) those scenarios highlight certain phenomena, which have to be addressed by research. Without real applications we cannot select credible scenarios, nor rank phenomena on a risk/safety dimension.

### 6.3 Sub-structure of the "Application" session

Following the background described above and based on input provided by industry the organisers and the chairperson decided to focus on the following applications, Sub-Topics respectively:

- a) Hydrogen Fueling Station HFS
- b) Fuel Cell Electric Vehicle FCEV
- c) Power-to-Hydrogen
- d) Aeronautics / Aerospace

For each application at least one representative expert from the respective industry was invited to report as panelist on recent findings, current work and new topics to be addressed.

### 6.3.1 Hydrogen Fueling Station (HFS)

#### 6.3.1.1 Progress

The panelist Pratap Sathiah, Shell, referred to several high pressure dispersion and explosion experiments performed in the past. Some of them have been used in validation and benchmarking exercises of CFD and risk assessment tools. However, in particular for high pressure releases there are still open issues, mainly when it comes to safety distances for jets interacting with neighboring structures, i.e. wall attachment or impingement.

Some modelling work has been done related to the effect of fast filling on the vehicle tank and pre-cooling on the coupling itself. Effective simplified calculation procedures for the temperature distribution and histories reached by the SAE standardized fueling or alternative protocols have been developed.

In the field of risk assessment, some first field experience with HFSs has been shared openly, helping to define credible scenarios, and some assessments of the special issues related to co-location, i.e. multi-fuel stations, has been published. Several papers presented at the ICHS2015 Special Session "Safety of Fueling" (Chair: Guy Dang-Nhu) reflect well the progress made by 2015, 2016 respectively [38-44]. In general, the recent activities of the Working Group 24 of ISO TC197, dedicated to the development of a new international standard for HFSs, stimulated further activities in these fields. Interestingly one of those recently adopted topics is dedicated to the potentially worst case scenario, the catastrophic failure of a vehicle on-board pressure vessel in the vicinity of a HFS, e.g. during fueling, and the ability of the fueling infrastructure to cope with this. Several accidents with CNG vehicles (see Figure 6.2 for instance) prove that such kind of accidents have to be included in the set of credible scenarios for a HFS also.



Fig.6.2: Lessons to be learnt from recent CNG vessel failure in Duderstadt,, Germany on 9.9.2016. Driver seriously injured; ARAL and other fuel suppliers stopped CNG fueling of all VW CNG cars. (Claims: "driver was informed before, not to fuel with CNG"; "there was no explosion"); Source: Arne Bänsch



### **6.3.1.2 Gaps and Next Steps**

The following list of open issues, new directions respectively, have been identified.

- Adverse effects on material and systems in below design, idling conditions (corrosion, low frequency and T cycles,...)
- Lack of engineering models accounting for mitigation measures appropriately
- Over conservative expensive design raising safety and efficiency concerns (e.g. alarm limits, electrical grounding of busses and cooling requirements)
- Still strong doubts about safety within authorities, public and users (drivers) caused in particular by the catastrophic rupture scenario of the vehicle tank
- Material and processing (welding) issues for high pressure components
- Effect of compressor vibrations on material, joints and pressure equipment in general
- Still open ventilation requirements for containers of compressor
- Suitable models for hydrogen dispersion, jet fire and explosion in particular for scale-up (large bus fleets, trains,...) and real world boundary conditions (jet wall attachment or impingement, wind conditions, etc) encountered at the HFS

### **6.3.1.3 Conclusions for the HFS application**

Most of the open issues are related to the phenomena mixing, ignition and combustion including mitigation strategies, few concern material compatibility. Scaling up HFS services implies including the effect of LH<sub>2</sub> in these investigations. Most relevant scenarios are fire, pressure vessel rupture and explosions including missile effects. For risk assessment the previously highest ranked topic of suitable engineering tools is valid as well., The required set of relevant models for these accidental phenomena has to be completed, integrated and validated urgently. Only this way the flexibility offered with the new performance oriented standards may be exploited for reaching required safety levels most economically.

## **6.3.2 Hydrogen (Fuel Cell) Electric Vehicles (FCEV)**

### **6.3.2.1 Reference point RPW2014**

As described in the introduction of the Application chapter the highest ranked and broadest discussed Sub-Topic at the RPW2014 was "Vehicle tank protection" (see Table 6.2 above). The main conclusion from the RPW2014 was that there exist considerably over-conservative pre-cooling requirements. Therefore, more detailed analyses of and better engineering models for the temperature evolution during standard (SAE) compliant fueling was suggested. Although this topic was already touched upon in the HFS application and shows up here again, it actually relates to the dedicated on-board storage session.

### **6.3.2.2 Progress**

Automotive OEMs invest in safety related research and development, but for several obvious reasons this work is not openly communicated, nor shared among their peers. Published work always relates to design independent issues, deals rather on an abstract level with phenomena or in best case relates to emerging standards or regulation.

Some modelling work has been done related to the effect of fast filling on the vehicle tank and pre-cooling on the coupling itself. Effective simplified calculation procedures for the temperature distribution and histories reached by the SAE standardized fueling or alternative protocols have been developed and presented.

At the ICHS2015 Special Session "Safety of Fueling" (Chair: Guy Dang-nhu) progress made by 2015 was captured in a few presentation [41, 42]. Further work has been done related to the bonfire test procedures of the GTR #13. Some results related to the thermal protection and some first ideas for identifying state of TPRD after fire/accident have been presented at ICHS2015 [43, 44].

Ongoing work is addressing Pressure Peaking Phenomena and effects of blast induced by rupture of high pressure on-board storage.

### **6.3.2.3 Gaps and Next Steps**

- Operations
  - **State of health monitoring** of pressure vessel (fatigue, after crash, thermal events, misuse), non-destructive testing
- Leakage/venting related tasks
  - H<sub>2</sub> leakage in **garages** or in **tunnels**
  - Venting of H<sub>2</sub> via TPRD in narrow spaces as a single car garage
  - Remotely initiated venting
- Fire
  - Complex accident situation in **tunnels**
  - Vehicle fire (different locations) and response of storage components to thermal excursion
  - Improved protection in particular of on-board storage against fire and thermal excursions
- Extreme events
  - Improved protection against extreme events
  - Pressure vessel rupture mitigation
- Rescue and first responders Post Crash event
  - Identification of tank SOC status (after fire or crash) to protect first responders
  - Identification of tank structure integrity after crash for first and second responders

### **6.3.2.4 Conclusions**

Most of the open issues are related to the topic "On-board Storage" which was treated separately in the workshop. However, from a scenario perspective the closed or partially closed scenarios: FCV involved in a fire in a private or public garage, in a tunnel or at a fueling stations still represent the most critical issues. These scenarios include the critical issue of safe strategies for first and second responders and concepts for avoiding or at least mitigating catastrophic pressure vessel ruptures.

## **6.3.3 Power-to-Hydrogen PtH**

### **6.3.3.1 Progress**

Several Power-to-Hydrogen injection plants were connected to the natural gas grid. In Germany, for instance several Power-to-Gas including 8 Power-to-Hydrogen demonstration projects are in operation. Hydrogen injection in natural gas grid is addressed in various initiatives (e.g. Hyready, HIPSNET) and the limits for the hydrogen fraction in the existing gas infrastructure have been investigated broadly (e.g. Naturalhy, GERG, DVGW). In a general conclusion 2 vol.-% hydrogen are considered non-critical for the existing gas infrastructure.

First national standards were realized (e.g. DVGW G 265-3 for hydrogen injection plants). However, the general picture with respect to standards still looks fragmented, at least when it comes to transnational or international frameworks.



Fig. 6.3: PtG (green logos) and Pth (blue logos) projects in Germany

For different blends of hydrogen in methane the following important characteristic properties have been determined<sup>7</sup>:

- Upper and lower flammability limits at SATP
- $P_{\max}$  and  $dp/dt_{\max}$  and limit concentration for gas mixture characterization (Hydrogen  $H_2$ - Natural Gas NG still in same class as NG)
- Flame temperatures, thermal radiation of the flame, viscosity of gas (mass flow) at SATP
- Minimum safety experimental gap / Minimum Ignition Current at SATP
- Flame length of  $H_2$ -NG mixtures

There is ongoing work related to the characterization of the detonation sensitivity of  $H_2$ -NG mixtures via measurements of the induction time in shock tubes and rapid compression machines.

<sup>7</sup> This work has been recently accomplished by the group of V. Schroeder, BAM and was presented at least partially at the WHEC 2016 in Zaragoza and at a DECHEMA conference in Freiburg: 15th International Symposium on Loss Prevention and Safety Promotion in the Process Industries and accompanying exhibition 5 - 8 June 2016 Konzerthaus Freiburg, Germany.

### 6.3.3.2 Gaps and Next Steps

The following list reflects the open issues identified at the RPW2016 related to the safety issues of the used gas grid, mainly pointing to H<sub>2</sub> embrittlement and assisted corrosion<sup>8</sup>:

- List of materials compatible with H<sub>2</sub>-NG systems, taking into account already collected data and available standardization deliverables such as the technical report ISO/TR 15916:2004 7.
- Behaviour of H<sub>2</sub> in H<sub>2</sub>-NG on plastics pipes, valves, fittings in house gas installations, storage cylinders - effect on components
- Metering (additionally supported by the recommendations of the EC RCS strategy coordination group) and mixture concentration and homogeneity control<sup>9</sup>
- Influence of hydrogen on integrity of underground pore storages
  - hydrogen induced microbiological reactions
  - permeation effects

For the bullet points on hydrogen storage in underground caverns, results have been provided by projects HyUnder and H2Store. Some additional insights might be derived from investigations of nuclear waste storage.

The common objective of the topics above is to reach a general consensus and suitable standards for hydrogen concentrations beyond 10 vol.-% in the gas supply infrastructure in the near future.

Further gaps or research directions relate to<sup>10</sup>:

- Testing procedures, such as the fatigue life test should be reviewed together with industry
- Materials compatibility with the Cr-Mg steels used for CNG vehicle tanks.
- Effects on industrial and residential burners, this also includes standardization and certification issues (use of test gases for example).
- Correlation between specimen and component tests for the characterization of susceptibility to hydrogen embrittlement and enhanced fatigue
- Effect of larger concentration of H<sub>2</sub> in H<sub>2</sub>/NG on flame stability in standard burners
- All kinds of mitigating safety measures (TPRD, Explosion Protection Systems, etc.) have to be certified for H<sub>2</sub>/NG
- Re-assessment of the ATEX Zoning should be standardized for H<sub>2</sub>/NG
- Collect available field data from Power-to-H<sub>2</sub> installations
- Training about the safety aspects of H<sub>2</sub>/H<sub>2</sub>NG

### 6.3.3.3 Conclusions

Most of the open issues are material related. Compared to the other applications, this application has matured considerably. In general, the impact of gas composition on end-users still has to be assessed. However, support for international harmonized standardization is required for transnational solutions and to demonstrate a common and openly communicated knowledge base related to this application. High temperature and

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<sup>8</sup> The following issue was not directly discussed during the Research Priority Workshop, but raised nevertheless by contributors afterwards:

- Hydrogen interaction with salt within the cavity and the surrounding rock mass
  - development of multi-scale numerical models able to describe and predict the geochemical and thermo-hydro-mechanical behavior of hydrogen in saline cavities and their surroundings

<sup>9</sup> A joint working group WELMEC WG 11, CEN TC 237, FARECOGAZ and MARCOGAZ is finalizing an overview on the expected behavior of the actual meter types when renewable gases like biogas, mixture of hydrogen and natural gas-hydrogen are used.

<sup>10</sup> The following gaps were not directly discussed during the Research Priority Workshop, but raised nevertheless by contributors afterwards:

- Analyze the conditions of economic viability of underground storage and their societal acceptability at European level
- Evaluate the safety conditions of hydrogen storage and put in place appropriate monitoring for risk management
- Effect of H<sub>2</sub> in H<sub>2</sub>/NG on flame kinetics and the acoustic influence on rotational machinery

pressure electrolysis will involve new safety issues which should be addressed appropriately.

### **6.3.4 Aeronautics / Aerospace**

Although this application is not directly pushing the general introduction of hydrogen as an energy carrier, hydrogen has been and still is the most promising fuel propellant for chemical space propulsion motors of space launch systems and an attractive alternative for fossil fuels in aircrafts. The invited Aeronautics expert cancelled the participation. This is why there is an Aerospace focus in this application domain.

Since 1990 the operational experience of LH<sub>2</sub> fueled rocket stages was continuously extended in Western Europe. The dimensioning of the test facilities, the necessary safety systems and safe operation conditions are challenges still today. Due to the large inventories and huge power ratings, test operation suffers from many limitations, for instance space. New technologies for measurement command and control of test processes are needed and if no suitable solutions are provided, the testing itself might impose limits to the actual application.

#### **6.3.4.1 Progress**

At DLR site Lampoldshausen a new test facility P5.2 was designed to test the Ariane upper stage. An engineering safety study contained a study of blast expansion either at atmosphere or at vacuum (confined) conditions. The worst-case scenario considered was a ruptured 70m<sup>3</sup> LH<sub>2</sub> tank structure where a sudden release and exposure of big quantity of LH<sub>2</sub> to ambience was assumed.

The study of blast expansion has been performed at EMI, Freiburg where computational tool Apollo has been applied. The yield of the blast depends on the amount of ignitable (premixed) hydrogen gas, which in this application has to be evaporated from liquid state. However, in particular the prediction of the phase change is very difficult and represents an open issue.

#### **6.3.4.2 Gaps and Next Steps**

Open issues related to multiphase phenomena:

- Evaporated fraction when large inventories of LH<sub>2</sub> are suddenly released to atmosphere. (Initial conditions for explosion and detonation)
- Multi-phase physical processes (heat transfer, mixing with air, initial thermodynamic status of the liquid) largely unknown
- Probability of occurrence of detonation with respect to heterogeneously premixed gaseous cloud
  - Under which conditions a deflagration may be assumed
  - Where are the limits of forecast (deflagration/detonation)?
- For the scenario of complete rupture of LH<sub>2</sub> and Liquid O<sub>2</sub> LOX tank, consequences of complete release inside the pool (at the bottom of the test facility)
  - Secondary effects and controlled burn down
  - LH<sub>2</sub>/LOX mixture behaviour

Open issues related to appropriate mitigation measures for the test cell design:

- Devices to restrict the amount of premixed hydrogen/air gas clouds
- Application of glow plugs near test specimen (spatial arrangement)
- Effect in case of ignition close to the test specimen (LH<sub>2</sub>/LOX stage)
- Detection of small intern/extern hydrogen leakages (maybe by visual methods)
- Devices for remote controlled detection of hydrogen leakages upstream/downstream at the filling line to the stage within 5 min

Safe operation of LH<sub>2</sub>/LOX upper stage

- Avoidance of sudden boil off situations inside the LH<sub>2</sub> liquid body inside a tank
- Releases with high LH<sub>2</sub> flow rates via vent/flare stack including the possibility to release liquid at the stack orifice (large scale vertical two-phase “flushing” releases)
- Large scale validation experiments for simulation of multiphase flow and heat transfer (application to “common bulkhead failure” scenario)

Besides the cryogenic state of hydrogen sub-atmospheric pressure environment represents another peculiarity of these applications. Open issues in this regard are:

- Hydrogen ignition (ignition conditions, flame propagation, ...) at sub-atmospheric pressure (some work has been done in this field by KIT for the fusion reactor application).
- Venting hydrogen outboard has to take into account airship safety (this situation may arise while in-flight and safety must still be ensured during such operation). Typical criteria to take into account are :
  - Lightning effects / protection means and strategies,
  - H<sub>2</sub> plume mixing (high velocity of aircraft) and size of ignitable plume,
  - Ignition physics (low external pressure, low temperature, ...),
  - Consequence of plume ignition on aircraft (flame characteristics, radiated heat, ...).

#### **6.3.4.3 Conclusions for the Aerospace/Aeronautics application**

The dominance of cryogenic LH<sub>2</sub> links this application to the problems, which are implied with the scale up of the hydrogen supply infrastructure for transport applications, i.e. the HFS application. The common issues related to LH<sub>2</sub> and the relatively limited understanding of associated phenomena yield highest rank for LH<sub>2</sub>.

## 7 Storage

Chair: Dr. Hervé Barthélémy (Air Liquide) - Participants and contributors: Prof. Dr. Jinyang Zheng (Zhejiang University) and Jan Kunberger (BMW)

Efficient storage of hydrogen is crucial for the success of hydrogen energy markets (early markets as well as transportation market). Hydrogen can be stored either as a compressed gas, a refrigerated liquefied gas, a cryo-compressed gas or in solids such as hydrides. This session focused on compressed and cryo-compressed storage. It gave an overview of hydrogen storage research & development status & priorities as discussed during IA-HySafe Research Priorities Workshop in Petten, September 2016.

### 7.1 Compressed hydrogen storage

#### 7.1.1 Overview compressed hydrogen storage

Hydrogen can be stored in four types of pressure vessels as presented in Figure 7.1. The pressure vessels are generally cylinders but they can also be polygons or toroid. Metallic pressure vessels are known as type I. Type II pressure vessels consist in a thick metallic liner hoop wrapped on the cylindrical part with a fiber resin composite. The fully composites materials based pressure vessels (designated by COPV) are made of a plastic or metallic liner wrapped with carbon fibers embedded in a polymer matrix (filament winding). When the liner contributes to the mechanical resistance (more than 5%), the COPV is of type III (mostly metal liner). Otherwise, the COPV is of type IV (mainly polymer liner or seldom extremely thin metal liner).

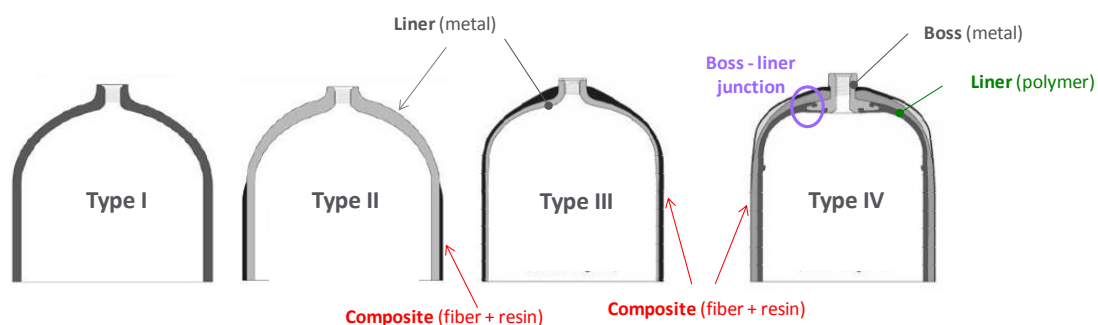


Figure 7.1: Representation of type I, II, III and IV COPV 11

#### 7.1.2 Key characteristics

The table 7.1 presents the main feature of the different type of pressure vessels.

Table 7.1: Key characteristics of compressed gas storage pressure vessels

	Technology maturity	Cost performance	Weight performance
Type I	Pressure limited to 50 MPa , ++	++	-
Type II	Pressure not limited, +	+	0
Type III	For $P \leq 45$ MPa-(difficulty to pass pressure cycling requirements for 70 MPa, [2])	-	+
Type IV	For $P \leq 100$ MPa – First commercial series – liner behaviour in gas to be further studied	-	++

#### 7.1.3 R&D status & challenges

The compatibility of the gas with the materials chosen and the impact of operating conditions on the materials and the tank structure have to be assessed. The whole

pressure lifecycle has to be considered: storage, transportation, use (emptying, handling, etc), filling steps including gas quality management, periodic inspection and maintenance. The objective is to prevent the risk of failure by burst or leak in service and guarantee the tank performance.

Table 7.2: Summary of R&D challenges

<ul style="list-style-type: none"> <li>▪ <b>General R&amp;D Gaps</b></li> <li>▪ Ageing models for lifetime assessment of materials &amp; structure</li> <li>▪ Need NDT for ensuring constant manufacturing quality and e.g. required performance (number of cycles, tightness, etc)</li> <li>▪ Recycling</li> <li>▪ Heat management during filling</li> </ul>	<ul style="list-style-type: none"> <li>▪ <b>Metal parts (boss, liner) =&gt; See Materials Compatibility Session</b></li> <li>▪ H<sub>2</sub> embrittlement (causes loss of fracture toughness) – H<sub>2</sub> enhanced fatigue</li> <li>▪ Premature failure in fatigue (due to HE and/or cycling, in particular at HP)</li> </ul>
	<ul style="list-style-type: none"> <li>▪ <b>Polymer liner =&gt; See Materials Compatibility Session</b></li> <li>▪ Gas permeation – Liner collapse</li> <li>▪ Mechanical loads and durability – Criteria for liner materials selection</li> </ul>
	<ul style="list-style-type: none"> <li>▪ <b>Boss-Liner Junction</b></li> <li>▪ Tightness of boss – liner junction</li> <li>▪ Bonding material selection &amp; qualification (if any)</li> </ul>
	<ul style="list-style-type: none"> <li>▪ <b>Composite Structure</b></li> <li>▪ Effects on damage &amp; lifetime of static &amp; cyclic pressure, temperature, environment, accidental loads (impact, fire)</li> </ul>

Composites pressure vessels have been operated for some decades for different applications. Commercial products are now available with 700 bar working pressure. Thanks to international R&D efforts, strong progress has been made in the different fields listed in table 7.2 [45, 46]. It has been emphasized during the workshop, that the results of those studies should be further shared with scientific, industrial and normative community. Questions remain mainly on:

- Need for ageing models considering liner collapse and other mechanical loads and influencing operating parameters => Definition of test protocols to define material selection test and criteria to qualify the solution for H<sub>2</sub> high pressure cylinder.
- Assessment of the effect of temperature excursions and overheating on cylinder lifetime.
- modelling damage induced by impacts and lifetime assessment (including metal liner) and structural health monitoring.
- Need Non Destructive Examination methods for ensuring constant manufacturing quality, e. g. required performance (number of cycles, tightness).
- need for new cylinder & fire solutions design for smart and reliable fire detection and protection (TPRD, protections, fire detections, heat conduction to promote liner melting, etc).
- need for modelling tools of fire scenarios (fire, temperature and radiative effect levels, temperature of the cylinder, etc). Predictive tools of burst time in fire have been recently developed in FiRECOMP FCH-JU project [47].
- Recycling.-

Note that the list above is not made by priority.

## 7.2 High Pressure Stationary Vessels<sup>12</sup>

Stationary hydrogen storage traditionally adopts seamless pressure vessels. However, seamless pressure vessels are limited in volume according to the ASME Boiler and Pressure Vessel Code VIII Rules for Construction of Pressure Vessels Division 1, UF and Appendix 22. Moreover, by increasing operating pressure, the problems of hydrogen embrittlement and cost become issues [48].

<sup>12</sup> This issue was discussed during the Research Priority Workshop, but not included in the priorities voting; however the organizers felt it was important to include it in this report.



In order to increase storage quantity, multi-vessel assembly is usually used, which inevitably increases hydrogen leak points, making management and safety monitoring more difficult [49].

Large composite pressure vessels can also be utilized for stationary hydrogen storage, which is expected to replace seamless pressure vessel for higher-pressure conditions, such as 45 MPa and 90 MPa. In order to achieve this objective, manufacturing costs will have to be reduced, especially the cost of carbon fiber [50].

Recently, a novel steel/concrete composite hydrogen storage vessel has been designed, which comprises a layered steel vessel encased in an outer pre-stressed concrete sleeve. Yet its reliability and safety still have to be further validated. A unique multifunctional steel layered vessel (MSLV) for stationary hydrogen storage was developed to deal with the aforementioned problems [51]. In addition, a Chinese national standard<sup>13</sup> was issued in 2011.

Compared with traditional seamless pressure vessels, MSLV is flexible in design, convenient in fabrication, safe in use and easy for online safety monitoring. The 77 MPa and 47 MPa MSLVs had been successfully used in hydrogen refueling station design.

### 7.3 Cryo-compressed storage

Cryo-compressed storage combines properties of both compressed gaseous hydrogen and liquefied hydrogen storage systems. It is developed to minimize the boil-off loss (dormancy) from liquefied hydrogen storage while retaining a higher system energy density. Hydrogen is stored in an insulated tank that can accept cryogenic temperatures (20K) and high pressure (at least 30 MPa) at ambient temperature. The fact that the tank is able to withstand high pressures allows greater pressure increases before hydrogen has to be boiled off. Such cryogenic pressure vessels significantly extend the time before starting evaporative losses when they are in operation and thus increase storage autonomy.

As an example, the BMW Group has started validation of cryo-compressed hydrogen storage for hydrogen vehicles with high energy and long range requirements [52, 53]. The diagram depicted in Figure 7.2 reported by BMW, shows that cryo-compressed H<sub>2</sub> enables high storage density (80 g/l). The cryogenic gas is denser than liquid hydrogen.

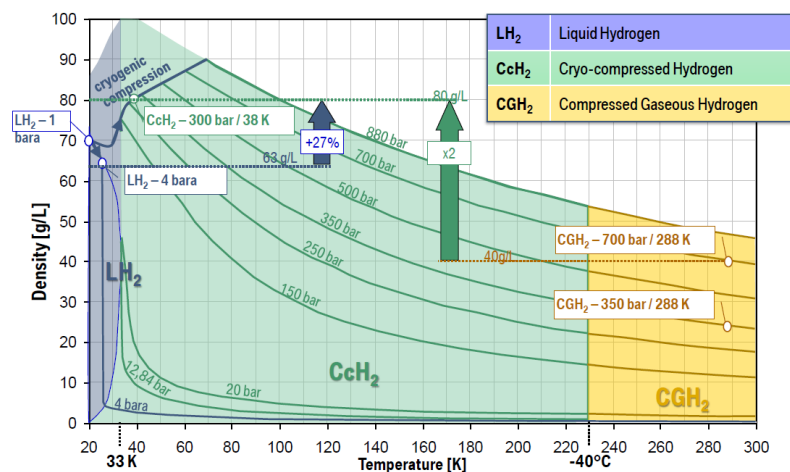


Figure 7.2: Hydrogen density versus pressure and temperature from BMW

The tank consists of a type III composite pressure vessel with a metallic liner that is encapsulated in a secondary insulated jacket, whose role is to limit heat transfer between the hydrogen and the environment. More details on the cryo-compressed storage tank design can be found in scientific literature [54].

<sup>13</sup> GB/T 26466-2011 Stationary flat steel ribbon wound vessels for storage of high pressure hydrogen

An identified gap is the improvement of the insulation function.

## 7.4 Gaps and Next Steps

Topic	Identified R&D Gaps
Compressed Storage	
Cylinder design & testing	-Need for ageing models considering liner collapse and other mechanical loads and influencing operating parameters => Designation of test protocols to define material selection test and criteria to qualify solutions for H <sub>2</sub> HP cylinder. -Effect of overheating on lifetime ?
Recycling	Need for recycling approach
Cylinder Manufacturing	Need for Non Destructive Examination methods for ensuring constant manufacturing quality, e. g. required performance (number of cycles, tightness)
Fire Safety	need for modelling tools of fire scenarios (fire, temperature and radiative effect levels, temperature of the cylinder, etc). Predictive tools of burst time in fire have been recently developed in Firecomp FCH-JU project.
Fire Safety	need for new cylinder & fire solutions design for smart and reliable fire detection and protection (TPRD, protections, fire detections, heat conduction to promote liner melting, etc)
Damage & inspection	Modelling damage induced by impacts and lifetime assessment (including metal liner) and structural health monitoring
Cryo Compressed storage	improvement of insulation function

## **8 Materials**

Chair: Iñaki Azkarate - Participants and contributors: Beatriz Acosta Iborra (JRC), Mathilde Weber (Air Liquide), Chris San Marchi (SNNL) and Laurent Briottet (CEA).

### **8.1 Hydrogen effect on Materials**

Materials for industrial applications are selected according to several factors, and service conditions have great impact on this choice. Hydrogen mainly affects materials in their mechanical properties. Depending of the material's nature, metal or polymer, hydrogen can impact it in different ways.

In the case of metals, the phenomenon behind hydrogen effects is the hydrogen molecule ( $H_2$ ) splitting into two atoms, which then enter the material in this atomic state and causes the deleterious effects.

This does not occur in the case of polymers, for which the effect is more based on the permeability, diffusivity and solubility of  $H_2$ .

Results can sometimes show the same kind of patterns (blisters, cracks,..), but the reasons behind these visible phenomena, can be based on different mechanisms.

#### **8.1.1 Hydrogen Damage in Metals**

##### ***8.1.1.1 Hydrogen induced cracking (HIC)***

Atomic hydrogen diffuses in the material and recombines to form  $H_2$  at specific sites (microcracks, inclusions,..). This molecular hydrogen ( $H_2$ ) can accumulate and develop high pressures. In ductile materials, these pressures can deform the material producing blisters. In the case of materials with low ductility, cracking can occur. It can then propagate in a stepwise manner (Stepwise Cracking, SWC)

##### ***8.1.1.2 Hydrogen reaction***

Hydrogen can also react with metallic phases forming hydrides (Ti, Zr,..) or react with non-metallic phases (carbides) forming methane ( $CH_4$ ) or other compounds

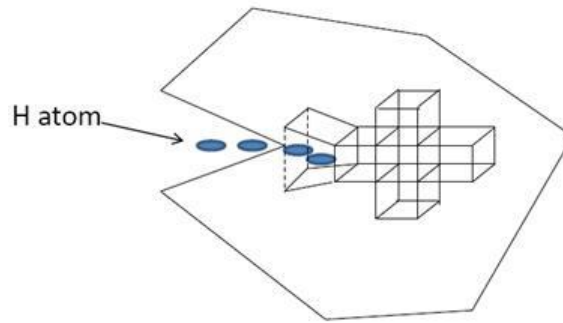
##### ***8.1.1.3 Hydrogen Embrittlement (HE) or Hydrogen Stress cracking (HSC)***

This type of failure can take place when atomic hydrogen enters in contact with a material that is under stress (applied or residual). In fact sometimes is considered as a type of Stress Corrosion Cracking (SCC). If a component already has a crack, it is possible for hydrogen stress cracking to begin at the already existing crack.

##### ***8.1.1.4 Mechanisms of Hydrogen Embrittlement in metals.***

In the following more details on the mechanism behind hydrogen damage in metal will be given [55-60].

### - Hydrogen Enhanced Decohesion Mechanism (HEDE)



The decohesion mechanism is one of the earliest mechanisms proposed for hydrogen embrittlement (HE).

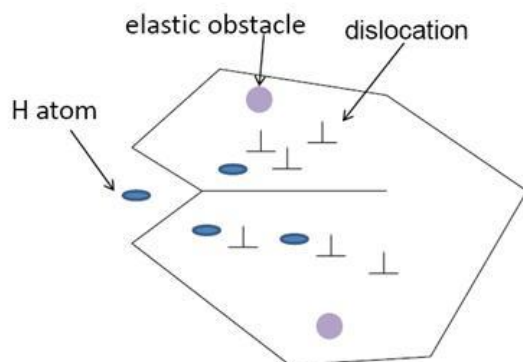
This mechanism is based on the postulate that solute hydrogen decreases the forces required to separate the crystal along a crystallographic plane.

There is a decrease in atom binding forces of the metal lattice, which can result in premature brittle fracture. The brittle fracture may be in the form of either intergranular or transgranular cleavage.

The decohesion mechanism considers that there is a critical concentration of hydrogen atoms for which brittle fracture occurs.

This mechanism could be applied for intergranular fracture, where high concentration of hydrogen accumulates at grain boundaries (reaching the critical concentration for brittle fracture)

### - Hydrogen Enhanced Localised Plasticity Mechanism (HELP)



According to this model the failure occurs by locally ductile processes.

This mechanism is based on the fact that the presence of hydrogen in solid solution increases the mobility of dislocations and creates localized high deformation regions.

The reason of this increased mobility is attributed to reduction of interactions between dislocations and between dislocations and other obstacles (such as carbon atoms, grain boundaries) when hydrogen is present.

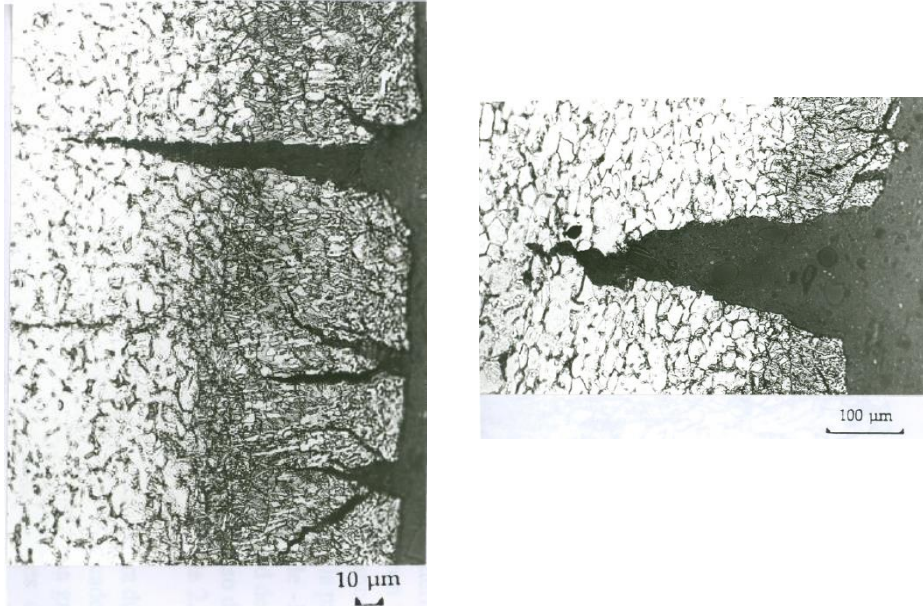
Dislocations thus move closer to each other, and closer to obstacles, and produce denser or more compact pile-ups when hydrogen is present.

The result of this is that microscopic regions of high deformation (where hydrogen increases the mobility of dislocations) are surrounding less ductile zones where dislocations are closely packed. The applied stress is then concentrated on these hard

zones that represent only a small portion of the cross section. When the tensile stress in these small portions is higher than the ultimate tensile strength, failure occurs.

At present there is a large amount of experimental observations, by in-situ transmission electron microscopy that are supporting this mechanism. The fact that the effect of hydrogen on dislocations mobility is not dependent on the type of dislocation (edge, screw or mixed) and that it is present for different crystallographic structures, suggests that the HELP mechanism could be universal.

### - Hydride Induced Embrittlement



Hydride-induced embrittlement is a second-phase mechanism that involves the nucleation and growth of an extensive hydride field ahead of a crack.

It has been observed that hydrides first nucleate in the stress field of a crack and then grow to large sizes not by the growth of individual hydrides but by the nucleation and growth of new hydrides in the stress field.

The auto-catalytic process of hydride nucleation and growth together with their brittle nature seems to be the main cause of embrittlement of V, Nb, Ti and Zr.

### 8.1.2 Hydrogen Damage in Polymers

There are many differences between metals and polymers. The properties of polymers depend not only on their chemical structure, but on a variety of other factors. The most important of these are molecular weight (and molecular weight distribution) of polymer chains, and processing history.

For example, the degree of crystallinity of a polymer is affected by its cooling rate from the molten state. Processing techniques like extrusion can induce orientation and extension of polymer chains, influencing properties. Fillers, plasticizers, crosslinking agents, and other additives are often incorporated to modify polymer's properties. Thus a tremendous variety may be associated with a single polymer.

Unlike metals, polymer properties are affected by hydrostatic pressure.

Polymers are not subject to hydrogen embrittlement in the same ways as metals. Hydrogen absorbed by polymers exists as a diatomic molecule; it does not dissociate as it is known to do in metals.

Four classes based on polymer microstructure are considered in the following. Two thermoplastics, and two crosslinked into networks by curing treatment.

- Semicrystalline thermoplastics (PE, HDPE, PP, PEEK, PTFE,..)
- Fully amorphous thermoplastics (PVC,..)
- Elastomers (rubbers, butadiene, chloroprene, fluoroelastomers,...)
- Epoxies (epoxy resins)

## **8.2 Materials and hydrogen in standards**

Main standard considering materials in a general way and their suitability for hydrogen service is ISO TR 15916:2015 Basic considerations for the safety of hydrogen systems.

### **8.2.1 Recent Progress**

Recent progress in other standards has been carried out in:

- ASME Article KD-10: hydrogen pressure vessels. Fracture mechanics approach (fatigue crack growth and fracture),
- SAE J2579: on-board hydrogen fuel systems. Fatigue life approach (includes slow strain rate tensile testing),
- CSA CHMC1: general test methods in gaseous hydrogen (metallic). Fracture, fatigue and tensile testing for metallic materials,
- CSA HPIT1: gaseous hydrogen fuel systems for industrial trucks. Guidance specific to Cr-Mo pressure vessel steel with conservative design philosophy,
- ISO 11114-4: specific to transportable gas cylinders. Several methods to evaluate transportable pressure vessel steels.

### **8.2.2 Current Activities**

Activities are currently under way in:

- ASME Article KD-10: hydrogen pressure vessels. Expanding scope to ASME SA-723 steels (international partnership),
- SAE J2579: on-board hydrogen fuel systems. Developing testing capability for low-temperature fatigue and coordination of testing activities through SAE and national programs,
- CSA CHMC1: general test methods in gaseous hydrogen (metallic). Evaluating fatigue-life methods by exploring parameter space (e.g., temperature, frequency, load ratio),
- CSA CHMC2: general test methods in gaseous hydrogen (polymers). Committee not yet active.

Test method development is underway at US DOE National Laboratories, but limited in scope.

### **8.2.3 Gaps and Next Steps**

Some gaps are identified:

- ASME Article KD-10: hydrogen pressure vessels. Available data is limited. Poor efficiency of fatigue crack growth testing methods. Fracture method is not conservative.
- SAE J2579: on-board hydrogen fuel systems. Still evolving: lacks consensus on methods and metrics. Existing metrics are overly conservative (precludes rational basis for selection of materials).
- CSA CHMC1: general test methods in gaseous hydrogen (metallic). Lacks internationally accepted metrics for qualification of materials.

- ISO 11114-4: specific to transportable gas cylinders. Methods are not equivalent and may not be conservative (new version coming soon). Does not address fatigue. Cannot be applied to other materials, systems or components.
- In general: No standards for hydrogen compatibility of polymer materials

### **8.3 Research Priorities**

Main contributors to results and comments provided below were the following organizations:

Metals: Air Liquide, CCS Global, CEA, CSM, ENSMA, Hydrogenius, I2CENER, JRC, KRISS, Kyushu University, LSPM, NPL, SINTEF, SNL,TECNALIA, Tenaris, TWI, VTT.

Polymers: Air Liquide, Hexgon-Lincoln/HSECOE, JRC, NREL, Nanosonic, ORNL, PNNL, PPRIME ISAE-ENSMA, SNL, Toyota.

### **8.4 Progress made in the last three to four years**

#### **8.4.1 Metals**

The evaluation of test methods to define mechanical properties in H<sub>2</sub> environment: toughness, fatigue, fretting fatigue (definition of specimens) and understanding of the most appropriate testing parameters (pressure, frequency) based on:

- fracture mechanics (toughness: KIC, KIH, fatigue: da/dN vs.  $\Delta K$ )
- non-cracked samples (fretting fatigue, disc-fatigue samples)

have been carried out.

The Effect of High Pressure on the selection of materials has been considered in these studies. Sufficient studies of fatigue crack growth data for Cr-Mo pressure vessel steels to enable qualification have been carried out FCH-JU project MATRYCE results on full-scale fatigue testing of type 1 (metallic) pressure vessels with defects demonstrates susceptibility for crack propagation under hydrogen of low-stress pressure vessel designs. MATHRYCE has defined a methodology for metallic cylinders design/lifetime assessment based on lab-scale tests and taking into account hydrogen enhanced fatigue, which have been presented to ISO/TC 197, WG 15 and an annex has been provided for the current draft ISO/CD 19884 standard based on the use of a hydrogen sensitivity factor to be applied to the life of a component tested under hydraulic loading [61].

The effect of gas impurities has been considered in the studies on material compatibility. Effect of CO, O<sub>2</sub> and H<sub>2</sub>O on H<sub>2</sub> embrittlement has been determined [62].

#### **8.4.2 Polymers.**

Improved liners using polyamide PA 6 resin have been reported (Toyota) to deliver better performance for hydrogen permeation (an order of magnitude superior to high density polyethylene, HDPE) and excellent mechanical performance, in terms of durability in withstanding sudden changes in tank temperature from filling and discharging hydrogen, and shock resistance in extreme cold environment. PA 6 has good mechanical properties (ductility, long term heat resistance, impact resistance at low temperature, creep resistance...) for H<sub>2</sub> tank liner and low costs. On the other hand PA 11 is used in pipeline liners.

The influence of operating conditions (depressurization rate) on liner buckling and strategies to avoid it as the liner configuration designs as part of tanks and installation/operation guidelines have been recently studied in several research projects [63, 64].

## **8.5 Research topics on-going and planned at near term**

### **8.5.1 Metals**

International partnership to evaluate high hardenability Ni-Cr-Mo pressure vessel steels:

- Fatigue crack growth and fracture (ASME KD-10 design method),
- Industry partners from US, Europe and Japan.

Fundamental understanding of surface effects and impurities on hydrogen embrittlement:

- Fundamental work in US and Japan.

Fatigue-life testing and methodology development:

- US, Japan and Germany (national labs and academic institutions),
- Coordination through SAE committees.

H<sub>2</sub> compatibility of high-strength pipeline materials and welds:

- Taking into account the role of residual stresses in welded materials and considering influence on the selected test method.

### **8.5.2 Polymers**

Evaluation of polymeric materials physical properties and mechanical performance changes under High Pressure hydrogen exposure (static) at long term exposure to large pressure gradient experiments (35-100-35 MPa) with and without temperature cycling (-45 to 85°C) is being studied in the US DoE project "Compatibility of Polymeric Materials used in the Hydrogen Infrastructure" [65].

Studies on permeability, diffusivity and solubility of H<sub>2</sub> in liners materials to understand the conditions for blister formation in type IV tanks are actually being carried out in several projects [66].

Characterization tests for polymers used for gaskets, seals & O-rings (H<sub>2</sub> permeability, diffusivity and solubility) and exposure tests to high pressure hydrogen are on-going. In 2017 evaluation of combined effects of pressure and extreme temperature (-40 °C and 100 °C ) is foreseen.

Physical & Chemical analysis of hydrogen refuelling station (HRS) hoses before and after accelerated life testing (cycling under mechanical, pressure, temperature and time stress) are being studied by NREL in a US DoE [67]. First results indicate that after a number of chilled cycles (1856) leaks develop at both hose ends (dispenser and nozzle).

A cryogenically flexible, low-permeability, hydrogen delivery hose is studied in DoE Project PD101 at Nanosonic [68]. The aim is to develop a flexible hose for H<sub>70</sub> (Hose for 700 bar pressure) service reliable at -50 °C and 875 bar; with optimised ruggedness, cost and safety, standing 70 fills/day and more than 2 year service life. The prototype is tested and qualification test with OEM dispenser/nozzle for safety and environmental durability are ongoing. Deployment is expected in 2017.

Neutron scattering & X-ray scattering to investigate molecular dynamics of H<sub>2</sub> solvated polymers and to identify microscopic properties critical to polymer performance/prediction of failure mode studies are being carried out at ORNL.

Initial observations and studies of damage accumulation in elastomers have been performed. Despite these efforts, results are not generalized, standardized methods are still missing and selection criteria are not systematically developed.

## **8.6 Gaps and Next Steps**

Taking into account the information provided and the discussions held at the workshop the following comments and research lines were stated.



### 8.6.1 Metals

A future project should validate the testing methodology used in different laboratories to characterize hydrogen compatibility in view of international standardization.

- More projects facilitating the increase of understanding on Fatigue Crack Initiation and Propagation of small cracks under hydrogen pressure would be valuable.
  - Testing to evaluate fatigue crack initiation under low stress intensity factor  $\Delta K$  requires long time and modelling will help to define key tests for model validation. Studying of the effect of hydrogen pressure on the  $\Delta K$  threshold is also important.
  - Finally, a data base providing fatigue data for the most probable materials to be used for hydrogen pressure vessels would be very useful. Efficient accelerated test methodologies are desirable.
- Work to update design rules and test protocols should be continued, especially for the fatigue crack initiation stage (short cracks), both in terms of mechanism and early propagation rate (due to fast propagation step in hydrogen afterwards).
- Continue to study scalability of fatigue testing, taking into account the effect of deep (low  $R=P_{\min}/P_{\max}$  ratio) versus shallow (high R ratio) cycles, and  $H_2$  accelerating effect for laboratory (specimen) and full scale test (pressure vessel). Shallow cycles require longer testing times and a correlation between shallow and deep cycles requires validation and acceptance.
- International consensus on metrics for qualification of metals for specific applications is required:
  - Onboard vehicles, Fueling stations (storage, compression, components, etc). Acceptance criteria of low-cost materials that are "embrittled" but adequate for the operation range should be considered.
- Role of impurities and inhibitors has to be assessed:
  - This is an important issue that has been recently studied and needs further research. Can impurities "protect" a system under all operating conditions? This information is especially needed for hydrogen/natural gas mixtures.
- The industrial technology for liquid hydrogen storage and distribution is well developed (for large capital projects), but may not be adequate for large-volume commercial sector (stations).

The use of existing natural gas pipeline networks for gaseous hydrogen delivery and transmission should be evaluated for blends and pure hydrogen. The materials used for pure  $H_2$  delivered to customer (residential and industrial) should be evaluated.

### 8.6.2 Polymers

Blistering/swelling behaviour has been shown to be caused by hydrogen sorption and formed during decompression. Some further studies are needed to confirm these findings.

Study mechanical performance of polymers under hydrogen: HDPE elasticity modulus yield strength is considerably lower under high hydrogen pressure, while ductility increases. The evolution is not permanent; the material recovers the original characteristics after the end of exposure. Harmonized methods for measuring properties of polymers at high pressure in  $H_2$  environment and metrics to quantify the effect of  $H_2$  are required.

Influence of High temperatures in tanks, the question is if polymer liners can resist higher temperatures than 85 °C while still performing at temperatures down to -40 °C (in terms of liner mechanical properties and permeability).

Study the effect of temperature excursions (does exceeding the range -40 to 85 °C a number of times during tank lifetime affect performance at end of life?) and assess tanks resistance to operational and accidental thermal shocks (e.g. hot tank fill with very cold H<sub>2</sub> or very fast emptied; cold tank filled in a very short time/with non-precooled H<sub>2</sub>).

Characterization of thermal Fatigue and Hydrogen effect: Evaluation of long term exposure and degradation at end-of-life is needed

Understanding of failure modes and development of efficient accelerated test methodologies are also required There is the need for ageing models for materials and structure considering mechanical and environmental loads (including liner collapse) to define lifetime of the components and optimize design and testing protocols. Methods for degradation and ageing assessment and end-of-life criteria are still needed.

Fit for purpose tests (both on samples and components) need to be developed: this requires knowledge of operating and accidental conditions and the feedback from e.g. OEMs, hydrogen fuelling infrastructure operators, etc..

Non-destructive methods for liners evaluation (blisters / cracks / buckling) and criteria for "healthy" tank and pipeline need to be developed and qualified for in-service inspection.

Further assessment on the interaction of tanks materials and robust sealing concepts might be required.

Variability of material properties depending on the supplier (for a given polymer) is still an open issue.

Other open topics are:

- embrittlement of elastomers at low temperature
- Hydrogen compatibility for materials in appliances operating at low pressure, but subjected to temperature excursions (home fuelling).

## 9 General Aspects of Safety

Chair: Frank Markert (DTU) - Participants and contributors: William Buttner (NREL), Eveline Weidner (EC-JRC), Franck Verbecke (AREVA) and Nick Barilo (PNNL)

### 9.1 Introduction

The topic comprises hydrogen safety training, mitigation including sensor and human behaviour. The latter is a new topic taken into account, while the first two topics were separately analyzed in the prior Research Priorities Workshop 2014 under the headlines: "Hydrogen Safety training" ranked 8<sup>th</sup> in 2014 and "Materials Compatibility/Sensors" ranked 9<sup>th</sup> in 2014.

### 9.2 Status at the time of previous workshop

The sub-topics for "Hydrogen Safety Training" achieved the following priorities on RPW 2014. "Higher education in hydrogen safety engineering" and "Establish an international forum to facilitate discussion on FR training [...]" received the highest and second highest votes, respectively. Closely followed by topics of hydrogen safety in enclosures (topic 8.9 and first responder training in topic 8.7), as seen in Table 9.1.

Table 9.1: Expert voting on "Hydrogen Safety Training" of the RPW 2014

Topic Number	Topic	Number of Votes	% of Votes Received
8.4	Higher education in hydrogen safety engineering	16	17%
8.10	Establish an international forum to facilitate discussion on FR training with a focus on user experiences, needs and products	11	12%
8.9	Research issues identified by the Hydrogen Safety Panels work on enclosures (i.e., ventilation, leak rates, explosion protection, separation distances, etc.)	10	11%
8.7	First responder training	10	11%
8.2	Fitter/operator training	9	10%
8.8	Publication of textbooks in different areas of hydrogen safety	9	10%
8.3	Identify better hydrogen leak rate data	8	9%
8.11	Needs based on the NFPA Research Foundation Report	7	8%
8.6	Establishment of European or International University of Hydrogen Safety	5	5%
8.1	Identify minimum natural ventilation rates for enclosed space	5	5%
8.5	Interaction of water spray and flame front	2	2%

The results of the second topic "Materials / Compatibility / Sensors" are shown in Table 9.2. Further work on sensors were recognized as a significant research topic to improve safety, since the highest and second highest scores achieved topic "Reliability testing and validation of sensors for specific applications" and "Sensor placement to maximize effectiveness in specific applications", respectively. While the topic 9.7 "Hydrogen- metals interaction studies [...]" and the topic 9.5 "Comply Educational and online interactive training [...]" are ranked 3<sup>rd</sup> and 4<sup>th</sup> place.

Table 9.2: Expert voting on “Materials Compatibility / Sensors” of the RPW 2014

Topic Number	Topic	Number of Votes	% of Votes Received
9.1	Reliability testing and validation of sensors for specific applications	17	22%
9.3	Sensor placement to maximize effectiveness in specific applications	16	21%
9.7	Hydrogen metals interaction studies need to be expanded to further alloys of interest, and fundamental research is still needed to understand the role of all parameters	12	15%
9.5	Complex and overbearing code requirements/limited international harmonization	11	14%
9.6	Improve understanding of embrittlement of hydrogen service candidate materials (metallic, non-metallic)	9	12%
9.8	Degradation modeling	8	10%
9.4	Reduce sensor cost and identify common performance metrics for cross-cutting applications	5	6%
9.2	Introduce testing of sensors for high concentration releases	0	0%

### 9.3 Progress /Closed gaps

Progress is documented by the given references [69-77]

#### 9.3.1 Progress “Hydrogen Safety Training”

This topic was presented by Franck Verbecke (AREVA, France).

The prioritized topics as described for topic 8 “Hydrogen Safety training” are followed up on several points. University Ulster provided an educational and online interactive training and the International Curriculum on hydrogen safety training for First Responders (FRs) has been established.

Additionally, education materials have been developed for First Responders for on-site and web based training:

- State-of-the-art in hydrogen safety science and engineering and develop science-informed training materials dedicated to FRs
- RCS-informed training materials
- Intervention strategy and tactics for assessing accident scene status and decision making
- Web-based course and exercises

The operational training platform (EHSTP) build and driven by AREVA, France, is shown in Figure 9.1. It consists of an area of 2500 m<sup>2</sup> and enables to simulate 109 different scenarios and enabling fuel comparison using hydrogen, CNG and LPG at different pressures.



Figure 9.1: European Hydrogen Safety Training Platform (EHSTP). 2500 m<sup>2</sup>; fuel comparison using hydrogen (700, 350 and 200 bar), CNG (200 bar) and LPG (20 bar)

Furthermore, a Virtual Reality training platform (CRISE) has been established to provide virtual training scenarios for real world situations for realistic potential accident scenarios involving hydrogen, as e.g. in tunnel accidents as shown in Figure 9.2.



Figure 10.2: CRISE scenario

This enabled three face-to-face training sessions involving 71 trainees from 15 countries (Germany, Austria, Belgium, Croatia, Spain, USA, France, Italy, Norway, The Netherlands, Poland, Portugal, UK, Sweden, Czech Republic). Additionally, these sessions had 21 observers from 10 countries (Germany, Belgium, Denmark, Spain, France, The Netherlands, Portugal, USA, Japan and Taiwan). The instructions were provided by 15 instructors / lecturers being IA-HySafe partners and experts in the respective fields.

The above-described activities are supplemented with an “Emergency Response Guide” shown in Table 9.3 below. All the activities resulted in an international collaboration with various stakeholders as listed below:

- International Association of Fire and Rescue Services (CTIF)

- Commission "Extrication and New Technologie"
- European Fire Services
- Automotive car manufacturer
- Toyota
- US DOE and PNNL
- HySUT (Japan)
- Taiwan

Table 9.3: Emergency Response Guide

SOP	Acts or elementary actions	Objectives:
Reconnaissance	Identify	- Make contact with the safety manager of the installation to obtain clarifications concerning the incident; - Take into account the risk of an H <sub>2</sub> explosion in confined premises; - Take into account the risk of anoxia in confined premises.
	Forbid	- Forbid windward progression and imperatively establish an exclusion zone at 50 m; - Ban non-ATEX electrical or electronic apparatus in the exclusion zone (cell phones, beepers, walkie-talkies, etc.).
	Inspect	- Cut off external power sources in the building.
Rescue	Intervene Isolate	- <u>If confined premises and H<sub>2</sub> leak:</u> <ul style="list-style-type: none"> <li>• wearing of isolating breathing apparatus (ARI) obligatory;</li> <li>• evacuate the victim outside of the exclusion zone as rapidly as possible.</li> </ul>
Establishment/ Attack		- <u>If risk of victim electrocuted:</u> <ul style="list-style-type: none"> <li>• use emergency electrical hazard equipment to remove the victim;</li> <li>• avoid any contact between the rescuers and the electrical elements.</li> </ul>
Protection		- Confirm or re-define the exclusion zone first (50m); - Perform measurements with an explosimeter (from the top to the bottom of the installation or storage system). - <u>Actions with a risk of anoxia:</u> <ul style="list-style-type: none"> <li>• close the H<sub>2</sub> supply valves;</li> <li>• ventilate the premises favoring natural drawing (do not use electrical or machine means of smoke removal).</li> </ul>
Removal Surveillance		- <u>Actions with an electrical hazard</u> → Actuate the emergency stop pushbutton (timeout of 20 min with presence of current remaining). - The surveillance phase ceases as soon as you are assured of the following: <ul style="list-style-type: none"> <li>• the level of oxygen in the premise is normal (about 20%);</li> <li>• the absence of ATEX by explosimeter measurements;</li> <li>• the electrical installation is secured and taken in charge by a technician.</li> </ul>

### 9.3.2 Progress "Materials Compatibility/Sensors"

William Buttner (NREL) presented this topic in cooperation with Eveline Weidner (EU-JRC (Petten)).

Hydrogen sensors are a critical element for the safe implementation of hydrogen as an alternative fuel. As an independent safety element that is not an operational part of the hydrogen system, sensors provide an indication of a hydrogen leak at an early stage before it becomes dangerous, such as through audible alarms, flashing indicator lights, or electronic signals to a central control center. In addition to warnings, sensors can activate corrective and protective measures, including activation of the ventilation system or shutting off the hydrogen fuel supply. There are numerous reports of a sensor

alarm successfully preventing a potentially serious event. Thus, it is important to use sensors to protect relevant infrastructures and vehicles. Within the United States, the use of sensors is mandated for several specific hydrogen applications by national codes as NFPA 2 and IFC. Although not explicitly required within Europe, sensors are one means to achieve a required SIL (Safety Integrity Level). A number of common commercial H<sub>2</sub> sensor platforms have been developed as listed in

Table . Each sensor platform has its advantages as well as limitations. Since no individual platform will be good for all applications, end-users must evaluate sensor options for their specific requirements. However, this is challenging because commercial models may have comparable manufacturer specifications, but exhibit significantly different behaviour when deployed. This is illustrated in Figure 9.3 which compares different sensor models in both clean and industrial environments. In addition to sensor selection, it is also critical that sensors be properly used, including placement. There is however, no validated guidance document on sensor placement. It needs to be stressed that any sensor only will work if it is used properly.

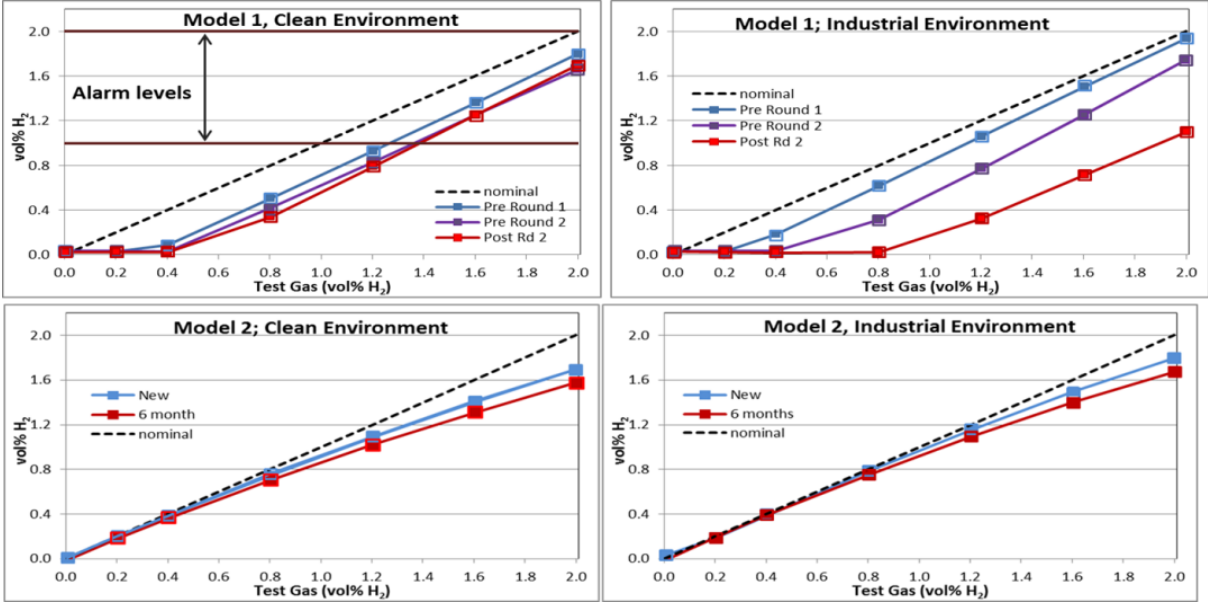


Fig. 9.3: Test for sensor responses (final indications) to various hydrogen levels prior to and following deployment [78].



Table 9.4: Commercial hydrogen sensors

<b>Common Sensing Element Platforms</b>			
	<b>Electrochemical Sensors</b>	<b>Combustible Gas Sensors</b>	<b>Thermo-conductivity sensors</b>
<b>Features</b>	<b>EC</b>	<b>CGS</b>	<b>TC</b>
Transduction Mechanism	Faradaic e <sup>-</sup> transfer (current)	Catalytic combustion ( $\Delta R$ induced by $\Delta T$ )	Heat Transfer ( $\Delta R$ induced by $\Delta T$ )
Advantages	Good LDL, Linear	Robust	Fast response time
Disadvantages	Prone to poisoning, drift	cross-sensitivity	non-selective (sensitive to $\Delta[H_2]$ )
Applications	Low level detection; personal monitors; ESIF	Industry Standard; HRS, Repair Facilities	Modeling studies; controlled environ., vehicles

	<b>Metal Oxide Sensors</b>	<b>Palladium Thin Film Sensors</b>	<b>Hybrid Platforms</b>
<b>Features</b>	<b>MOX</b>	<b>PTF</b>	<b>HP</b>
Transduction Mechanism	semiconductor doping ( $\Delta R$ )	Sel. H <sub>2</sub> adsorption; multiple platforms	Multiple platforms (integrated)
Advantages	Low cost versatile sensor	Selectivity	Broad Range (LDL and UDL)
Disadvantages	Perceived instability; cross sensitivity	Prone to poisoning; still expensive	Limited availability (market support)
Applications	General Deployment; containers	Petroleum Industry, specialized applic.	Vehicle

### 9.3.3 Progress concerning Human behaviour

Frank Markert presented this topic, who leads activities within this topic within IEA HIA Task 37.

The topic was not subject of the former PRW 2014. The human behaviour as part of the evaluation of general safety aspects concerning hydrogen safety is limited. There are some studies such as a study on human error assessment of hydrogen fueling technologies and studies on the perception of hydrogen technologies. Nevertheless, the topic is generic. Therefore, application of studies and methodologies from other scientific / technical fields are possible. There was and still there is work done in connection with the nuclear field; a number of error estimate models that were first applied in other fields are still being developed and most likely will be applicable also in the field of hydrogen safety. Strong activities are found in the transport safety research area as aviation and maritime industries. Human behaviour research is also found in the field of process industries, which provide a direct link to hydrogen processing and industrial installations. The EU ARAMIS project developed a QRA methodology including human and organizational aspects. In Norway the BORA methodology was developed to improve offshore maintenance including human error (e.g. during maintenance).

Human behaviour is an important factor in various hydrogen activities; it is seen as an organizational factor that organize activities from leading level to the operational level. Humans in the end contribute strongly in maintaining safety as they are controlling processes e.g. during the design phase for new applications and during the operational phase for established ones. Generic estimates on the probability that human error is the

primary causal factor in industrial and transport accidents is reported between 50 and 90%. Castiglia [71] found human behaviour in hydrogen incidents is due to one or more of the following factors:

- Lack of personnel training on specific equipment, systems and operating scenarios
- Inadequately training of personal regarding the properties of hydrogen and the potential consequences of their actions
- Daydreaming and complacent actions by personnel operating hydrogen and related equipment
- Personnel not following written procedures, because of personal reasons or bad procedures

Of special importance are safety barriers established to prevent or mitigate accidents. Safety barriers are only active when something goes wrong. Malfunctions may not be recognized or repaired as timely as processing malfunctions that usually are recognized immediately. Safety barriers including the action of humans are therefore included here under the "human behaviour" label. The type of dependency on human behaviour varies for different safety barrier types as shown in Figure . It is a weaker dependence for passive barriers, but very strong for preventive barriers as "respect for safety zones".

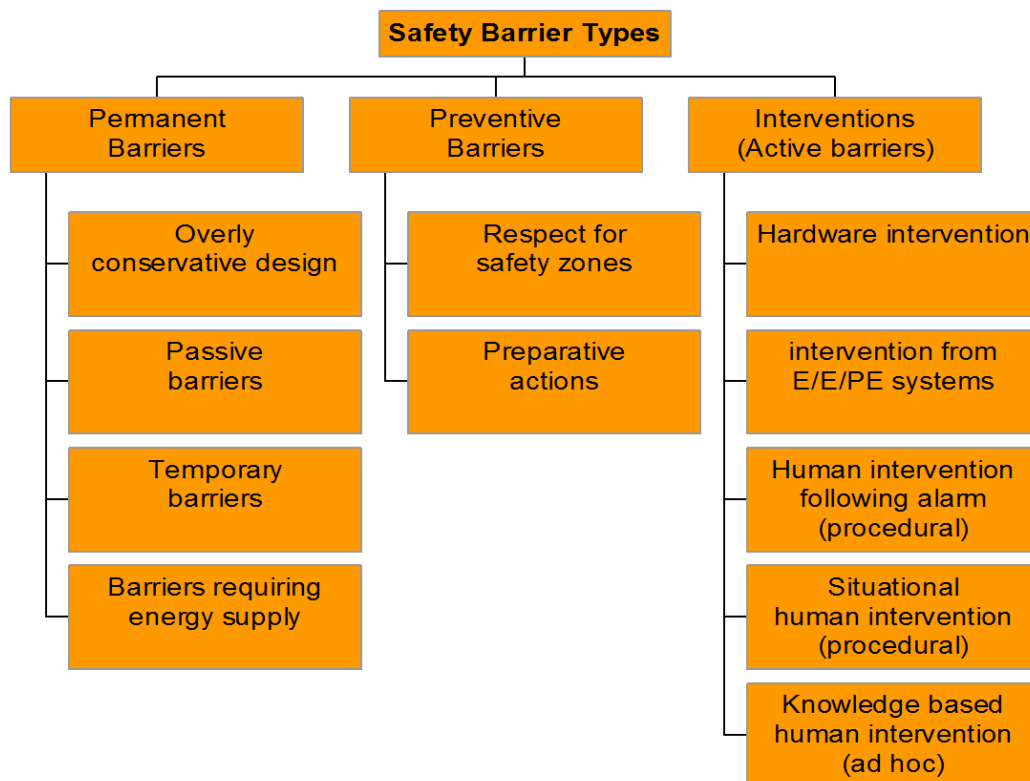


Figure 9.4: Safety Barrier types including barriers influenced by human behaviour

## 9.4 Gaps and Next Steps

### 9.4.1 Hydrogen Safety Training

In order to develop this topic a portfolio of hydrogen safety trainings is suggested to be developed. They should focus on:

- Different population e.g. operators vs firefighters
- Different levels e.g. basic firefighters vs. high-rank officers

- Different type of application i.e. stationary vs. transport applications
- Different training duration e.g. 2 days vs. 1 week
- Estimating a cost/trainee for each training
- Promoting training through networking channels

It is seen as an important priority to establish training/teaching courses for first responder trainers and Hazmat officers. That is, persons that will be responsible for the establishment of national hydrogen safety training programs using their national language and regulations. This type of education will benefit from the already established educational program described above using the operational and virtual reality platforms developed in the frame of the HyResponse project.

Another priority, is “opening” the HyResponse training platform to the hydrogen community. It will support a demystification of hydrogen risks due to real experiences concerning hydrogen safety issues. This is addressing e.g. operators, site managers, Firefighter, persons involved in the permitting process. The training platform could be opened and used for R&D collaborations, e.g. research to improving operational methods.

#### **9.4.2 Mitigation including sensors**

Hydrogen Sensors are currently and successfully being deployed to assure safety. Nevertheless, the sensor technology still provides some critical gaps, as identified by feedback within the community (e.g. the H2Sense project). In the following these critical gaps are briefly listed and categorized as part of the performance metrics. It is evaluated that the impact of existing gaps in sensor technology probably can be exacerbated in more specialized fields such as within power-to-gas field and the C&S support in pre-normative research.

The critical gaps found can be categorized in the following domains.

- 1) Analytical Metrics
  - a. Long term stability of sensors
    - Field performance due to long-term impact of temperature, pressure, hydrocarbons and other chemicals
  - b. Lack of predictors
    - Insufficient knowledge on mode of sensor failure, ALT and end-of-life indications
  - c. Selectivity
  - d. Perceived performance
- 2) Operational Metrics
  - a. Calibration and maintenance
- 3) Deployment Metrics
  - a. Sensor selection and use
    - Sensor test protocols; Guidance on deployment/ placement of (array of) sensors; Networking vs. WAM; Certification costs and harmonization; Market sustainability

There is on-going research within the gap 3a) to develop a guidance document for sensor placement with integrated empirical and theoretical modelling of hydrogen releases performed by NREL, JRC and AVT. The first step in the project is to assess small indoor facilities to develop guidance in the framework of NFPA 2. It is recommended for the future to enlarge the guidance to cover large area facilities and to allow for minimization of the number of sensors used without compromising safety.

### **9.4.3 Human behaviour**

Generic research has been and still is conducted on human behaviour. Actually, it is the main focus in the fields of road, train and maritime transportation. Many of the approaches may be applicable also for the hydrogen safety area, but some more verifications are needed. The application of safety barrier categories and the influence on their functionality due to human behaviour, should be re-assessed for hydrogen applications and technologies. Improved methods that better predict safety barriers probability of failure taking into account human errors, need to be developed.

Many countries allow for a performance based evaluation in the permission process for new buildings and installations. Another direction is seen in the development of Monte Carlo simulation based probabilistic models that can handle dynamic systems in a more appropriate manner. Such approaches can help to better identify worst case damages and their likelihood. Furthermore, human behaviour in evacuation situations could be better assessed with better predictions of the available and required time to escape. This is essential for risk assessment and permitting of hydrogen applications in larger infrastructures such as tunnels and car parks.

## 10 Priorities

The concluding summaries of the session chairs presented above have been combined with the results of the survey, given in detail in the Annex, to derive the following priorities.

The first set of priorities deals with the accident physics and material issues which are the indispensable basis for improved risk assessment and management methodologies and for safer applications in general. Therefore, these fundamental issues are reflected in the subsequent prioritisation chapters.

### 10.1 General Physics and Material Issues

With respect to general accident physics involving hydrogen in its gaseous phase, premixed combustion is given highest priority for further investigation. The phenomena is well understood from a fundamental perspective but modeling of flame acceleration and DDT and associated pressure effects for large scale applications with obstacles and interaction with mitigation techniques, in particular venting and water sprays, needs further work (1<sup>st</sup> and 2<sup>nd</sup> rank in 1) Accident Physics – Gas).

In contrast the fundamental science basis for non-premixed flames is very good. The hazards from these flames are well characterized. Reduced order models have been developed and work reasonably well to predict thermal load consequences and are being used in integrated platforms (HyRAM). Therefore the sub-topic of non-premixed jet flames is given a low priority for further investigation. Only exception from this general statement is the radiation properties of large scale fire balls and jet fires. Validation data is lacking for these phenomena.

Regarding the liquid hydrogen behaviour a number of knowledge gaps still exist and validated models are lacking for all accident phenomena. Validated models for multiphase releases (choked flow/jets) and accumulations in particular in congested areas indoors and outdoors have highest priority (1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> rank in 2) Accident Physics – Liquid, supported by 4<sup>th</sup> rank topics all with similar >10% votes). Second priority is attributed to pool spreading and fires as well as BLEVE and fire resistance of cryo-containers. Although some efforts and little progress in the dispersion modelling could be made with few large scale experiments performed by HSL, these experiments also generated new open points in particular regarding the multiphase characteristics of the pool and spontaneous ignition.

In general for both, hydrogen in its gaseous and liquid phase, realistic boundary conditions (congestion and confinement) as well as the ignition physics are highlighted directly or at least indirectly.

Setting up and filling a database of fatigue data (fatigue crack initiation and propagation) for the most relevant pressure vessel materials has been given highest priority in the material session (1<sup>st</sup> and 2<sup>nd</sup> rank in 5.2) Performance Assessment of Material). Highly correlated is the need for better understanding the influence of pressure, purity and temperature on these data and to agree on suitable qualification metrics and test strategies. (1<sup>st</sup> rank in 5.1) Testing of materials).

For polymers appropriate models for lifetime prediction under realistic conditions (pressure swing, temperature excursions, etc), standard test protocols and selection criteria have been prioritized on a similar high level (2<sup>nd</sup> rank (out of 5) in 5.1) and 3<sup>rd</sup> rank (out of 8) in 5.2)).

### 10.2 Risk Assessment

With respect to Risk Assessment considerable progress could be achieved with the QRA Tool HyRAM. As the QRA Tools topic had been prioritized strongly in the previous workshop (Washington 2014) several related activities have been initiated or enforced worldwide. However, highest maturity is achieved with the US DoE supported HyRAM

tool. However, for all of these tools frequency data, highest priority (1<sup>st</sup> rank in 3) Integration Computational Tools), and suitable models for accounting for mitigation measures, 2<sup>nd</sup> priority (2<sup>nd</sup> rank in 3) Integration Computational Tools) are lacking. The lack of consequence modeling tools obviously refers to the open issues in the general physics session listed above. In general validation concepts have to be developed for these tools (3<sup>rd</sup> rank in 3) Integration Computational Tools). Possibly some results of the FCH-JU Project SUSANA for the validation of CFD codes for risk assessment could be transferred.

### **10.3 Applications**

The different applications add special technical aspects to the general physics prioritized above. Intentionally, at the workshop and in the priority survey no application has been prioritized against another. However, within an application topic the issues have been prioritized as follows.

For public supply infrastructure, i.e. hydrogen fueling stations the expected scaling up and efficiency requirements of the fueling services implies increasing usage of LH<sub>2</sub>. Therefore most relevant scenarios include LH<sub>2</sub> related phenomena (like safe transfer of LH<sub>2</sub> from trucks to the stations), but also general fire, pressure vessel ruptures and explosions of premixed systems including direct and missile effects at the HFS. First priority is to account for cascading effects, presence or accident initiation with conventional fuels (multi fuel stations) and the complex and partially confined real scenarios (large bus fleets, trains, etc.) in the applied risk assessment (1<sup>st</sup> rank in 7.1) Application HFS). Appropriate models for mitigation concepts should eliminate unnecessary over-conservatism and avoid raising unjustified safety concerns in the public (2<sup>nd</sup> rank in 7.1) Application HFS). Obviously, the HFS topic also links to the material issues. In particular the welding processes for steels suitable for high pressure, high purity application deserves further attention (3<sup>rd</sup> rank in 7.1) Application HFS).

For the hydrogen vehicles in particular accidental scenarios in confined or partially confined environment, like tunnel, garages, repair shops or at fueling stations, have been given highest priority (1<sup>st</sup> and 3<sup>rd</sup> rank in 7.2) Application FCV) These scenarios include the critical issue of safe strategies for first and second responders and concepts for mitigating catastrophic pressure vessel ruptures.

With the onboard storage representing the most critical component of a hydrogen vehicle this topic is highly correlated with general safety topics of hydrogen storage. There improved protection against fire or thermal excursions has highest priority (2<sup>nd</sup> rank in 7.2) Application FCV and 1<sup>st</sup> rank in 6) Storage). This priority is supported by the required upgrade of the GTR n°13 where definition of more realistic car fires (heat flux measurements and testing) is required to standardize the corresponding testing appropriately. Structural health monitoring has 2<sup>nd</sup> priority in the Storage topic and - also closely related to the Materials issues - modeling of ageing and thermal degradation with a special focus on liner stability and permeability has 3<sup>rd</sup> priority (see corresponding ranks in 6) Storage).

Most of the open issues of the Power-to-Hydrogen PtH application are material related. Compared to the other applications, this application has matured considerably. Safety relevant parameters of hydrogen/natural gas blends have been evaluated or are just on the way to be published. However, support for international harmonized standardization is required for transnational solutions and for demonstration of a harmonized common knowledge. To this end collection of field data is considered the most important action (1<sup>st</sup> rank in 7.3) Application PtH). Introduction of significant volumes of natural gas/hydrogen mixtures can have a significant impact on the currently used infrastructure and connected applications. Respondents also prioritized (2<sup>nd</sup> and 3<sup>rd</sup> position) potential concerns in terms of performance of current applications and safety (e.g.: flame stability).

Hydrogen aerospace and aviation applications are mainly applying LH<sub>2</sub> for gravitational performance reasons. Therefore these applications refer to the same gaps in the basic understanding and in the modeling capabilities as introduced above for the general LH<sub>2</sub> related accident physics.

#### **10.4 General Aspects of Safety**

This chapter addresses general risk management and mitigation concepts including sensors.

Hydrogen sensors are currently and successfully being deployed to assure safety. Nevertheless, the sensor technology still provides some critical gaps, as identified by feedback within e.g. the H2Sense project. Among quite a few open issues highest priority is attributed to providing appropriate guidance on selection and placement of sensors in the different applications (1<sup>st</sup> rank in 4) General Aspects of Safety).

Risk management includes human behaviour, education and training. For first responders training there have been serious efforts and progress worldwide (HAMMER facility and HyResponse project, for instance). However, in relation to the hydrogen vehicle priorities additional efforts are needed for first responders training in special environments (2<sup>nd</sup> rank in 4) - see also General Aspects of Safety in particular addressing tunnel and large garage scenarios. Strategies for second responders have to be developed too, when considering recent catastrophic events with natural gas vehicles.

In general human behaviour is key for safety also in hydrogen application. Therefore this factor has to be included in all efforts for improving the safety culture and overall safety performance.

## **11 Summary**

This report on the Research Priorities Workshop 2016 summarized the discussion during the workshop and the ranking of research priorities subsequent to the workshop. It identifies the state-of-the-art in topical areas relevant to hydrogen safety to accelerate the deployment of hydrogen technologies. The topics were carefully chosen from previous workshops and to cover emerging gaps as the deployment of hydrogen technologies evolve. The workshop identified current research focus areas, those areas where current research topics need to mature, and those areas where the technical community felt there were serious gaps in our efforts to ensure safe deployment. See the Annex Survey results for a discussion of the survey and tabulated results.



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## Annex - Priority Survey

### Introduction

The Research Priority Workshop on Hydrogen Safety organized in Petten in September 2016 was followed by a survey addressed to experts in the field of the hydrogen safety. The experts were identified by the workshop organizers and were asked to prioritize among selected topics. This exercise has the aim to set a rank of priorities from the current gaps in hydrogen safety topics. It creates a tool which can be used by interested parties and it can be used to assess consensus on priorities as expressed by a wide international community of specialists in the field.

### Survey Methodology

The categories were chosen by the workshop organizers and were based on the topics which emerged during the workshop.

Each respondent had to prioritize the first five topics he/she deemed most relevant in each category. A score from one to five was assigned according to ranking. The first preference was assigned a score of five, the second one a score of four, the third one a score of three the fourth one a score of two and a score of one was assigned to the fifth preference.

The final ranking for each category was obtained by adding up the singles scores.

Contrary to the previous exercise, it was decided to avoid an overarching ranking among the various session. The reason for this is a) that it would have been a rather in-homogeneous comparison, i.e. applications versus physical phenomena, b) some of the topic appears in more than one session.






#### 1.3 Results

As a general remark, in each session some topics seem to stand out with respect to the others. Usually one topic receives a higher score, while two other topics are close behind and with a shorter distance among them.

In the following, the results are presented already divided into the different sessions. The score and the percentage of points attributed to each topic within a session are summarized in a table for each session.











1 Accident Physics – Gas	
1.0.1	Venting cannot be accurately predicted when coupled with premixed combustion overpressure
1.0.2	Statistical approaches to ignition need further refinement to improve reduced order predictions
1.0.3	Spontaneous ignition is not at all understood
1.0.4	Premixed combustion - further modelling studies are needed for large scale applied problems with obstacles, – particularly for DDT, Flame acceleration in confined and obstructed spaces and Blast Waves
1.0.5	Jet flames

Accident Physics - Gas	tot	%	
1.0.1	86	22.93	
1.0.2	70	18.67	
1.0.3	67	17.87	
1.0.4	90	24.00	
1.0.5	62	16.53	










## 2 Accident Physics – Liquid

- 2.0.1 Knowledge and experience related to indoor releases and dispersion
- 2.0.2 Knowledge and experience related releases involving large quantities
- 2.0.3 Knowledge and experience related releases in congested areas
- 2.0.4 Multi-phase accumulations with explosion potential (LH<sub>2</sub> can condense and freeze oxygen. The resultant mixture can be made to detonate): conditions for occurrence and their consequences are not understood
- 2.0.5 BLEVE (Boiling Liquid Expanding Vapour Explosion or Fireball): knowledge on fire resistance and prediction of consequences are needed.
- 2.0.6 Studies on humidity / air phase change during LH<sub>2</sub> and cryogenic compressed hydrogen releases should be undertaken in order to inform modelling of these phenomena
- 2.0.7 Correlations for accurately calculating the specific heat capacity of hydrogen at low temperatures and high pressures should be further investigated and incorporated into CFD codes.
- 2.0.8 CFD validation especially for complex obstructed industrial environments and various weather conditions (wind speed atmospheric stability class)
- 2.0.9 Modelling of the two phase choked releases, in particular for achieving a reasonable estimation of the mass flow rate
- 2.0.10 Further development of pool spreading and evaporation models, coupled with vapour dispersion. Research should be directed at improving the modelling of ground heat flux in cases where a liquid pool is formed- for both solid and liquid (usually water) substrates. The radiative heat transfer and its contribution to the total heat transfer from the air and ground to the cold cloud should also be studied. Liquid hydrogen pool fire not well characterised
- 2.0.11 Evaluation and comparison of the performance of the different Equation of States (EOS) in the two phase choked flow approaches should be attempted

Accident Physics - Liquid	tot	%	
2.0.1	28	7.47	
2.0.2	38	10.13	
2.0.3	47	12.53	
2.0.4	62	16.53	
2.0.5	40	10.67	
2.0.6	23	6.13	
2.0.7	10	2.67	
2.0.8	44	11.73	
2.0.9	38	10.13	
2.0.10	39	10.40	
2.0.11	6	1.60	

### 3 Integration Computational Tools







- 3.0.1 Develop suitable models for accounting for the effects of different mitigation measures appropriately
- 3.0.2 Data/probabilities for hydrogen system component failures (e.g.: leak frequencies, detection effectiveness, etc.) from operative experiences
- 3.0.3 Features and models to enable deeper system-specific insights to enable overcoming station-siting barriers: i) uncertainty & sensitivity analysis capabilities and ii) higher fidelity and depth of QRA.
- 3.0.4 Develop validation, testing, training and design decision making strategies of such QRA tools
- 3.0.5 Uncertainty Quantification (UQ) for the CFD in the consequence analysis tools
- 3.0.6 Models based on fault & event trees, Bayesian networks, cause-consequence and barrier diagrams are still not able to handle dynamic events
- 3.0.7 Models for accurate prediction of pressure-peaking phenomena for ignited releases
- 3.0.8 Models for accurate prediction of radiation from hydrogen fireball after high-pressure CGH<sub>2</sub> tank rapture in a fire
- 3.0.9 Models for accurate prediction of buoyancy effects on jet fire hazard distances

Integration Computational Tools	tot	%	
3.0.1	65	17.33	
3.0.2	92	24.53	
3.0.3	27	7.20	
3.0.4	49	13.07	
3.0.5	30	8.00	
3.0.6	26	6.93	
3.0.7	30	8.00	
3.0.8	35	9.33	
3.0.9	21	5.60	



#### 4 General Aspect of Safety

- 4.0.1 Training of First Responders' trainers and Hazmat Officers
- 4.0.2 Guidance on sensor placement
- 4.0.3 Long-term stability and accelerated stability testing for sensors
- 4.0.4 Selectivity testing for sensors to be used with complex gas mixtures
- 4.0.5 Development of Monte Carlo methods using simplified models for RA of dynamic systems
- 4.0.6 Addressing safety barrier types and their PFD (Probability of Failure on Demand) changes by human behaviour














General Aspect of Safety	tot	%	
4.0.1	78	20.80	
4.0.2	93	24.80	
4.0.3	53	14.13	
4.0.4	53	14.13	
4.0.5	29	7.73	
4.0.6	69	18.40	

## 5 Material – 1: Testing aspects related to the characterization of materials

- 5.1.1 Methodology validation on several metals and components between different laboratories. (priority also relevant for future international standardization efforts)
- 5.1.2 International consensus on metrics for qualification of metals for specific applications
- 5.1.3 Definition of test protocols, Selection criteria and relevant standards for polymer materials
- 5.1.4 Development of non-destructive test methods for liner evaluation
- 5.1.5 Activities on seals, gaskets, hoses, valves and joints. They should receive similar attention to the tank material and their behaviour tested under different and realistic conditions











## Material – 2: Performance assessment of materials

- 5.2.1 Better understanding on Fatigue Crack Initiation and Propagation. In particular focusing on small cracks and better understanding of the effect of hydrogen pressure on the threshold of the stress intensity factor range. Special attention to low-temperature / high-pressure conditions. From a general point of view a better understanding of materials behaviour under mechanical stresses is needed
- 5.2.2 Database providing fatigue data for the most probable materials to be used for hydrogen pressure vessels
- 5.2.3 Scalability of fatigue testing: effect of deep vs shallow cycles, hydrogen accelerating effect for lab (specimen) versus full scale testing (pressure vessel)
- 5.2.4 Evaluation and assessment of integrity of existing pipeline networks for pure hydrogen
- 5.2.5 Mechanical performance of polymers under hydrogen has to be better characterised (including blistering, swelling). Also studies on the reversibility of these materials
- 5.2.6 Better understanding of the role of impurities and inhibitors
- 5.2.7 Assessment of materials for specific liquid hydrogen applications
- 5.2.8 Definition of appropriate models for lifetime predictions for polymers. In particular, correlation between the behaviour of polymers under low hydrogen pressures and high hydrogen pressures and effects of temperature peaks (or valleys) and temperature excursions in tanks containing polymers. Correlations between permeation and pressure/temperature conditions, especially with the aim of achieving prediction capabilities

Material - 1	tot	%	
5.1.1	73	19.47	
5.1.2	85	22.67	
5.1.3	76	20.27	
5.1.4	66	17.60	
5.1.5	75	20.00	
Material - 2	tot	%	
5.2.1	55	15.28	
5.2.2	72	20.00	
5.2.3	37	10.28	
5.2.4	43	11.94	
5.2.5	44	12.22	
5.2.6	15	4.17	
5.2.7	44	12.22	
5.2.8	50	13.89	

## 6 Storage

- 6.0.1 Ageing models considering mechanical loads and all influencing operating parameters, including liner collapse (this will also assist improvement of test protocols defining material selection criteria to qualify H<sub>2</sub> cylinder design)
- 6.0.2 Modelling the damage induced by impacts on high-pressure tanks
- 6.0.3 Fires: new solutions for smart and reliable fire detection and protection systems (TPRD, protections, fire detections, heat conduction to promote liner melting, etc.)
- 6.0.4 Understanding effect of overheating on the structural performance and lifetime of the whole storage systems in case of extreme hot filling scenarios, and other temperature excursions.
- 6.0.5 Structural health monitoring of pressure vessels for operative conditions (fatigue, creep, etc.) and accidental conditions (after crash, thermal events and misuse).
- 6.0.6 Non-destructive-techniques for ensuring constant manufacturing quality and required performance (number of cycles, tightness, etc).
- 6.0.7 Testing of and advanced testing methodology for TPRD, to identify failure modes and frequencies.
- 6.0.8 Hydrogen conversion system (for blow off hydrogen), improve availability and operating range in cryo-compressed storage systems
- 6.0.9 Burst impact mitigation
- 6.0.10 Extreme impact loads: event statistics, protection on vehicle side, pressure vessel robustness
- 6.0.11 Improvement of insulation function in cryo-compressed storage systems

Storage	tot	%	
6.0.1	51	13.08	
6.0.2	28	7.18	
6.0.3	76	19.49	
6.0.4	48	12.31	
6.0.5	53	13.59	
6.0.6	30	7.69	
6.0.7	34	8.72	
6.0.8	11	2.82	
6.0.9	27	6.92	
6.0.10	26	6.67	
6.0.11	6	1.54	

## 7 Application – 1: Hydrogen Fueling Station

- 7.1.1 Adverse effects on material and systems in 'below-design', idling conditions (corrosion, T cycles, etc.)
- 7.1.2 Reduction of the over conservative expensive design raising safety and efficiency concerns (e.g. alarm limits, electrical grounding of busses and cooling requirements)
- 7.1.3 Material and processing (welding) issues for high pressure components
- 7.1.4 Compressor: ventilation requirements for compressor containers
- 7.1.5 Compressor: effect of compressor vibrations on material
- 7.1.6 Cascade effects: effect of various accidental releases in case of scale-up, complex real geometry (large bus fleets, trains, etc.)

## Application – 2: Fuel Cell Vehicles






























- 7.2.1 State of health/monitoring
- 7.2.2 Hydrogen venting via TPRD in garages (especially a single car garage)
- 7.2.3 Complex accident situation in tunnels
- 7.2.4 Pressure vessel rupture mitigation
- 7.2.5 Understanding vehicle fires and the response of storage components to thermal excursion
- 7.2.6 Improved protection of vehicles hydrogen systems against fire, thermal excursions and other extreme events
- 7.2.7 Remotely initiated venting

## Application – 3: Power to Hydrogen

- 7.3.1 List of materials compatible with H<sub>2</sub>/NG systems, taking into account already collected data and available standardization deliverables such as the technical report ISO/TR 15916:2004 7
- 7.3.2 Behaviour of H<sub>2</sub> in H<sub>2</sub>/NG on plastics pipes, valves, fittings in house gas installations, storage cylinders - effect on components
- 7.3.3 Metering and mixture concentration and homogeneity control
- 7.3.4 Influence of hydrogen on integrity of underground storages
- 7.3.5 Review of testing procedures such as embrittlement and the fatigue life test for H<sub>2</sub>/NG
- 7.3.6 Correlation between laboratory specimen and component tests for the characterization of susceptibility to hydrogen embrittlement and enhanced fatigue
- 7.3.7 Effect of larger concentration of H<sub>2</sub> in H<sub>2</sub>/NG on flame stability in standard burners
- 7.3.8 All kinds of mitigating safety measures (TPRD, Explosion Protection Systems, etc.) have to be certified for H<sub>2</sub>/NG
- 7.3.9 Re-assessment of the ATEX Zoning should be standardized for H<sub>2</sub>/NG
- 7.3.10 Collection of available field data from Power-to-H<sub>2</sub> installations
- 7.3.11 Training on the safety aspects of H<sub>2</sub>/NG

## Application – 4: Aerospace / Aviation

- 7.4.1 Multi-phase physical processes (heat transfer, mixing with air, and initial thermodynamic status of the liquid) are largely unknown for large liquid hydrogen releases
- 7.4.2 Determining the probability of detonation with inhomogeneously premixed gaseous clouds
- 7.4.3 Behaviour of liquid hydrogen and liquid oxygen mixtures
- 7.4.4 Appropriate design of test cells including suitable mitigation concept
- 7.4.5 Physics of hydrogen ignition and flame propagation for low external Pressure and temperature (aircraft conditions)

Application - 1			tot	%	
7.1.1		48		12.80	
7.1.2		71		18.93	
7.1.3		62		16.53	
7.1.4		60		16.00	
7.1.5		39		10.40	
7.1.6		95		25.33	
Application - 2			tot	%	
7.2.1		45		11.54	
7.2.2		65		16.67	
7.2.3		81		20.77	
7.2.4		52		13.33	
7.2.5		49		12.56	
7.2.6		70		17.95	
7.2.7		28		7.18	
Application - 3			tot	%	
7.3.1		26		7.22	
7.3.2		29		8.06	
7.3.3		35		9.72	
7.3.4		39		10.83	
7.3.5		16		4.44	
7.3.6		13		3.61	
7.3.7		44		12.22	
7.3.8		42		11.67	
7.3.9		21		5.83	
7.3.10		52		14.44	
7.3.11		43		11.94	
Application - 4			tot	%	
7.4.1		95		25.75	
7.4.2		82		22.22	
7.4.3		73		19.78	
7.4.4		50		13.55	
7.4.5		69		18.70	

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