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LECTURE. Unignited hydrogen releases, their prevention and mitigation

Contents

Introduction

An unwanted hydrogen release can be caused either by an equipment failure or by a loss of leak tightness of a FCH system. The consequences of this event can be different, depending on the characteristics of the release and the location of a source of the leak, i.e. outdoors or indoors. If initially the release is unignited there is still a possibility that it will ignite, after a certain delay, if an ignition source is present in the path of the release. If hydrogen release occurs indoors the consequences will be more severe compared with the releases happening outdoors as an explosive atmosphere may build up in a confinement. All these consequences can affect people, structures and environments. Minor incidents may escalate leading to catastrophic outcomes.

This lecture is mainly focused on unignited hydrogen releases in the open. The classification of compressed hydrogen leaks is presented in the current lecture as well as some useful terminology. First Responders are introduced to the similarity law and under-expanded jet theory, which will allow them to evaluate hydrogen concentration decay and determine hazard distance from the point of release to the lower flammability limit or any other concentration of interest. The means of reducing the hazard distance from a source of hydrogen release are detailed in this lecture. It also discusses prevention and mitigation/detection measures for unignited hydrogen releases from compressed hydrogen storage vessels.

Objectives of the lecture

By the end of this lecture First Responders will be able to:

- Classify unignited hydrogen releases (leaks/jets) and distinguish between permeation leaks, sub-sonic, sonic and super-sonic jets; expanded and under-expanded jets, momentum- and buoyancy-controlled jets;
- Evaluate hydrogen concentration decay in the momentum-controlled jets using corresponding nomogram;
- Predict the distance, at which hydrogen jet becomes buoyant;
- Calculate the size of hydrogen flammable envelope, i.e. to determine the furthest point from the source of leak, at which a jet can be ignited;
- Assess a safe size of a PRD with the view to avoid the formation of a flammable hydrogen layer under a ceiling in the enclosure;
- Calculate the blow-down time for compressed hydrogen tanks of different capacities;
- Recognise the means of reducing hazard distances from the point of the release;
- State the main prevention techniques for hydrogen jets;
- Recognise the mitigation measures of hydrogen leaks consequences;
- Point out the detection means of hydrogen releases.

Useful definitions

Blow-down is a process where the storage pressure decreases with time during a leak.

Expanded jet is a jet with a pressure at the nozzle exit equal to atmospheric pressure.

Mach number (M) is a dimensionless number equal to the ratio of a local flow velocity to the local speed of sound

Permeation is the movement of atoms, molecules, or ions into or through a porous or permeable substance.

Hazard distance is a distance from the (source of) hazard to a determined (by physical or numerical modelling, or by a regulation) physical effect value (normally, thermal or pressure) that may lead to a harm condition (ranging from "no harm" to "max harm") to people, equipment or environment (as per draft ISO TC197 definition).

Under-expanded jet is a jet with a pressure at the nozzle exit above the atmospheric pressure.

Compressed hydrogen leaks

As it is already known from previous lectures FC vehicles are equipped with on-board hydrogen storage tanks pressurised up to 70 MPa, and a refuelling infrastructure operates at pressures up to 100 MPa [2]. Due to the small size of its molecules hydrogen is prone to leakage. Predominantly hydrogen releases/leaks originate from valves and connections [3]. They may occur both indoors and outdoors. The releases can be unignited (i.e. non-reacting) or ignited (i.e. reacting). Although a full-bore rupture of a pipe or vessel is a rare event, it should be considered as a credible worst-case scenario. Special efforts should be made to prevent the unwanted hydrogen releases. A release of hydrogen either through a PRD or from a pipe rupture will result in a high-pressure jet.

Table 1 summarises the types of leaks and equipment or components generating hydrogen leaks [4].

Table 1. Leak sources and scenarios developed by EIGA (2007) [4]

Equipment/component	**Type of leak**
Pipework	Pinholes, pipe split
Flange's	Gasket failure, thermal movement, material creep
Weld connection	Weld crack
Solder connection	Solder crack, solder melt
Union connection	Thermal movement, leak
Screw connection	Leak, sealant failure, creep, material split
Hose connection	Seal leak, material split, human error
Valves	Stem leak, seal leak, bonnet/housing split opened by impact
Hoses	Perforation split
Instruments	Element rupture
Regulators	Diaphragm rupture, seal leak, downstream rupture (overpressure)
Solenoid valves	Seal leak
Pumps	Perforation, seal leak
Cylinder	Perforation, rupture, permeation leak

Typical flow rates of hydrogen releases vary significantly, from 10^{-5} g/s for permeation leaks to 10^{5} g/s for leaks on hydrogen pipelines. According to the European Regulation for type approval of hydrogen-powered vehicles (2010) the *safe permeation rate* for FC vehicles at 20 ^{o}C is limited to 6 mL/hr per L of a storage tank capacity [5]. It means for 170 L capacity of hydrogen storage permeation rate will be of 25.3×10^{-6} g/s. A flow rate for a leak from a broken pipe (on a 150 kW FC) will be around 3 g/s. A release from an industrial pipeline (diameter 30 cm) at p=2.5 MPa will have a flow rate of 100 kg/s.

Currently, a release via a PRD (with diameter of 5.08 mm) from a storage tank at 35 MPa will generate a flow rate of 390 g/s.

A permeation-induced release of hydrogen differs from plumes and jets: hydrogen releases slowly, in very small amounts, equally along the surface of a storage tank. The rate of hydrogen permeation through a particular material depends on: the temperature, internal pressure and the membrane thickness. The higher the storage pressure the higher is the permeation rate (please refer to Lecture 'Safety of hydrogen storage'). Three main phenomena drive the dispersion of permeated hydrogen: buoyancy, diffusion, and natural ventilation. Permeated hydrogen is distributed homogeneously in a garage-type enclosure [6]. Maximum allowable permeation rate at 20 ^{o}C for a passenger car is 8 mL/hr/L and for a FC-bus 5 mL/hr/L in a garage-type enclosure [7]. The simulations carried out at HySAFER (UU) demonstrated that with this level of permeation rate the hydrogen dispersion in a typical garage is not a problem [6].

An unscheduled release of hydrogen stored at high pressures can produce a highly under-expanded (pressure at the nozzle exit is above atmospheric pressure) turbulent jet that behaves differently compared to the expanded jets (pressure at the nozzle exit is equal to atmospheric pressure), which was extensively studied in the past. The schematic representation of a hydrogen release from high-pressurised storage vessel is shown in Figure 1.

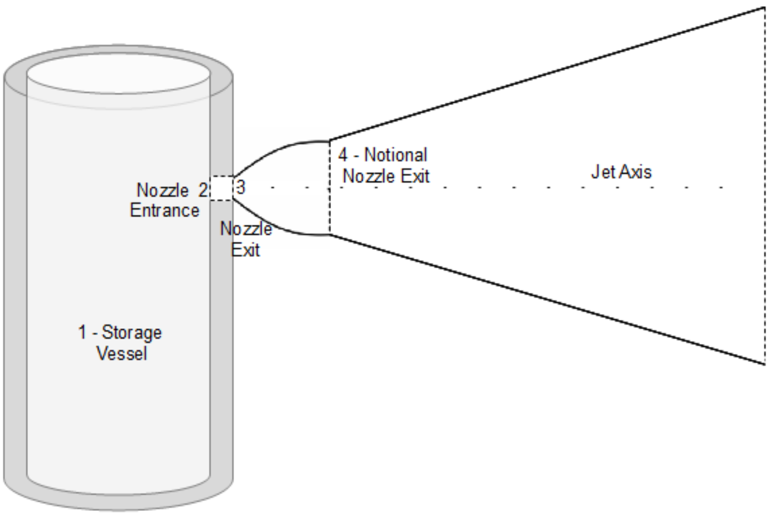


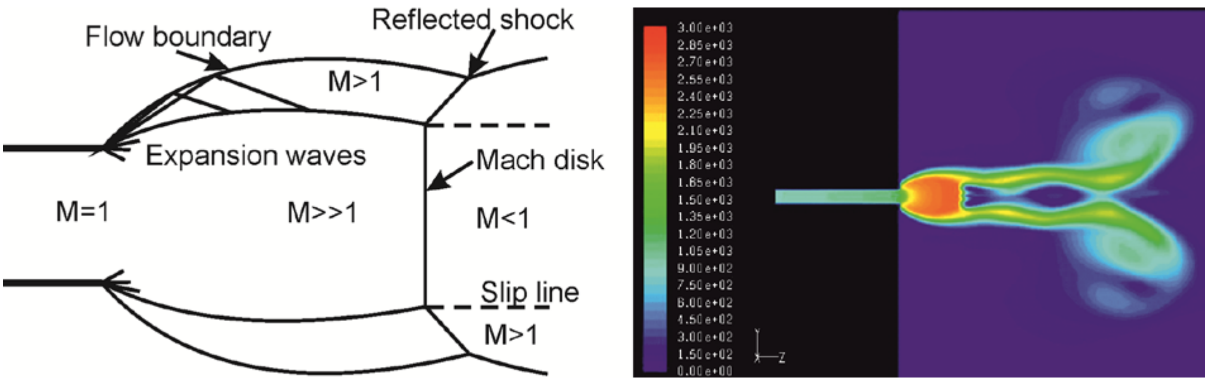
Figure 1. A scheme of a hydrogen release from high pressure hydrogen storage vessel.

The majority of leaks from hydrogen storage and equipment will be in a form of an under-expanded jet, at least at the beginning [2].

Expanded and under-expanded jets

Hydrogen jets can be expanded or under-expanded. An *expanded jet* is a jet with a pressure at the nozzle exit equal to atmospheric pressure. In an *under-expanded jet* a pressure at the nozzle exit has not fully dropped to the atmospheric one. At high pressures a velocity at the exit from the nozzle remains locally sonic, but the exit pressure rises above ambient. As the result the expansion down to ambient conditions takes place outside the nozzle [2].

For under-expanded jet the flow expansion occurs near the nozzle exit and is characterised by the complex shock structure, which is well documented and published elsewhere [8]. The schematic for an under-expanded shock structure is presented in Figure 2a. In this diagram one can see a distribution of the *Mach number* (M), which is a dimensionless number equal to ratio of a local flow velocity to the local speed of sound. *Mach disk* is a strong shock, which is normal to the under-expanded jet flow direction. A numerically simulated initial stage of hydrogen under-expanded release is presented on Figure 2b, for pressure ratio in a storage tank and the atmosphere 160.



(a) (b)

Figure 2. (a) The schematic of an under-expanded jet structure [8]; (b) an initial stage of under-expanded jet release at 16.1 MPa through a channel of 0.25 mm with a mass flow rate 0.46 g/s [2].

As it is shown in Figure 2a the local sonic velocity is established at the nozzle exit with the Mach number M=1. Then, the outflowing gas undergoes a rapid expansion and quickly accelerates to high Mach numbers (>>1, up to M=8 for 70 MPa storage pressure) accompanied with the decrease in pressure and density. A series of expansion waves are formed at the nozzle exit edge. These expansion waves are reflected as compression waves from the free surface at the jet flow boundary, coalesce and form a barrel shock and a Mach disk. Repeating barrel shocks and Mach disks structures downstream of the first Mach disk appear intermittently at pressure ratios below 20. For typical hydrogen storage pressures a short structure with only one Mach disk can be expected at the beginning of the *blow-down* (i.e. a process where the storage pressure decreases with time during a leak). As the gas with very high Mach number crosses the Mach disk, it undergoes a sudden decrease in velocity to subsonic speeds and increases in pressure (to the atmospheric) and density. The resulting flow structure after the Mach disk comprises a subsonic core (M<1) surrounded by supersonic shell (M>1) with shear layer called slip line dividing these two regions.

Sub-sonic, sonic and supersonic jets

The Mach number of the jet, which is equal to a jet velocity (U) divided by the speed of sound in the gas (C) exiting into the ambient air, is an important parameter in determining its behaviour. For jets with a *subsonic flow* $U<C$, $M<1$; the pressure at the exit plane is just equal (or very close) to atmospheric pressure. As stated earlier, many leaks from high pressure storage form an *under-expanded* jet with the *sonic* (choked) flow at the jet exit (when $U=C$, and M=1). The *supersonic* jets are characterized by the velocity larger than the speed of sound ($U>C$).

At high pressures the exit velocity remains locally sonic, but the exit pressure rises above ambient with the result that expansion down to ambient conditions takes place outside the nozzle. For hydrogen

the critical pressure ratio for sonic (choked) flow of compressible gas is 1.89 at STP (γ =1.405) and 1.89 at NTP (γ =1.39) according to the theoretical equation for choked flow conditions:

$$\frac{P_R}{P_N} = \left(\frac{\gamma+1}{2}\right)^{\gamma/(\gamma-1)}, \quad (1)$$

where P_R and P_N are pressure in the reservoir and the nozzle exit respectively, and γ is the ratio of specific heats. The equation (1) can be applied to estimate the pressure at the leak (nozzle) exit P_N if the storage pressure at the reservoir P_R is known [2].

Ishii et al. (1999) reported that jets of a diatomic gas (γ=7/5) exhausted from an open-end of the test tube tend to be: *subsonic matched* jets for the ratios of pressures in the high- and low-pressure chambers (the only parameter controlling the jet strength) between 1 and 4.1; *sonic under-expanded* jets for pressure ratios in the range from 4.1 to 41.2; and *supersonic under-expanded* jets for pressure ratios above 41.2 [9]. Pressure ratio of 4.1 is above the critical ratio 1.9 for sonic (choked) flow. However, there is no contradiction: each of two pressure ratios (high-pressure chamber to tube exit, and tube exit to low-pressure chamber) can be P_R/P_N =2.05, which is close to the theoretical critical pressure ratio of 1.9 for sonic flow. The difference could be attributed to losses between high- and low-pressure chambers.

Momentum- and buoyancy-controlled jets

All jets can be divided into three types depending on the effect of buoyancy. These jet types are shown schematically in Figure 3 for a horizontally-oriented jet. Fully *momentum-controlled jets* are not affected by the buoyancy, whilst fully *buoyancy-controlled jets* are diverted fast from horizontal to vertical direction of flow. The third type is a *transitional jet*, which has a momentum-controlled part located close to the nozzle exit, and a buoyancy-controlled part of the flow further downstream, when the jet velocity decreases and the diameter of the jet increases. It is important to know the moment when this transition takes place because it will have an impact on the hazard distance in particular and on first response strategy and tactics in general [2].

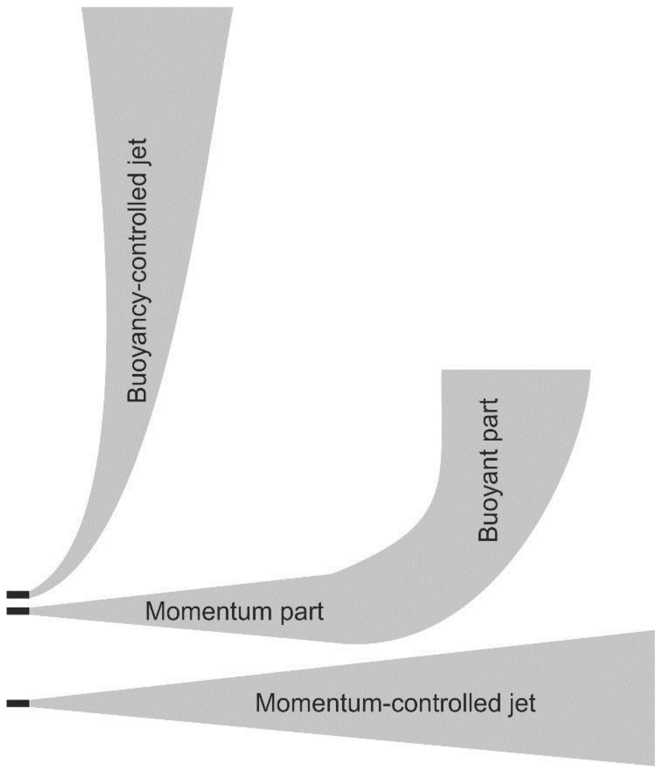


Figure 3. The schematic representation of: momentum-controlled, transitional and buoyancy-controlled jets [2].

Hydrogen concentration decay in momentum-controlled jets

The concentration of hydrogen in a jet decays from 100% at the nozzle (i.e. at a point of leak) to the lower values along the jet axis and from axis to periphery. For some calculations it is more convenient to substitute an under-expanded jet from an actual nozzle with an expanded jet from so-called *effective* or *notional nozzle*. There are a number of notional nozzle theories. The most cited model is the one suggested by Birch et al. in 1984 [10]. However, the former models are built on the ideal gas equation of state, and thus are not applicable to the storage pressures above 10-20 MPa, when the non-ideal behaviour of a gas must be accounted for. The first theory of under-expanded jet that accounts for a non-ideal behaviour of highly compressed hydrogen was published by Schefer et al. (2007) [11]. The notional nozzle diameter calculations by Schefer et al. (2007) are similar to Birch et al. (1984), yet the Abel-Noble equation is applied and the assumption by Birch et al. about the speed of sound at the notional nozzle is relaxed [10,11]. As a result the theory of Schefer et al. (2007) predicts uniform super-sonic velocities at the notional nozzle exit at high storage pressures [2].

Molkov et al. (2009) [12] developed an under-expanded theory, alternative to the one suggested by Schefer et al. (2007) [11]. This theory is based on the mass and energy conservation equations rather than on mass and momentum ones. Similar to Birch et al. (1984) [10], the model developed by Molkov et al. (2009) [12] is based on the assumption of a uniform sonic flow through the notional nozzle. The calculation scheme used for the under-expanded jet theory [12] is shown in Figure 4.

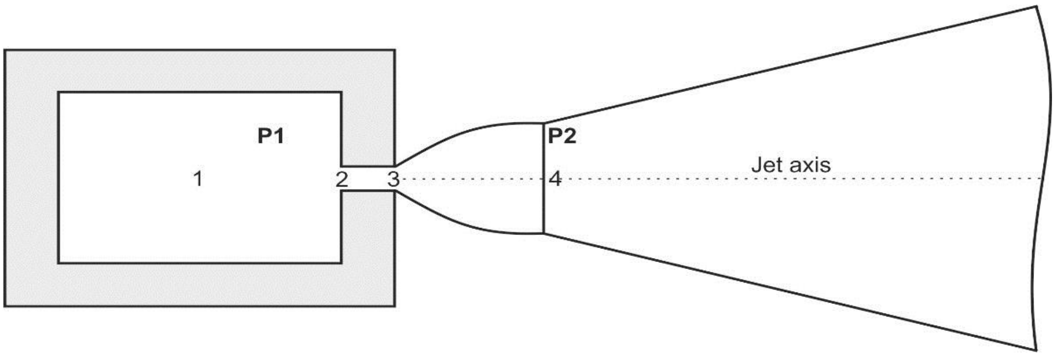


Figure 4. The scheme of an under-expanded jet: 1 - high pressure vessel; 2 - nozzle entrance; 3 - nozzle exit (= notional nozzle entrance); 4 - notional nozzle exit (3-4: no entrainment); P1 - storage pressure; P2 - atmospheric pressure (after the jet expansion) [2].

It is assumed that the flow velocity in the storage reservoir (1) is zero. The flow parameters at the entrance to the leak channel, nozzle entrance, are referred to as (2), and at the actual nozzle exit - as (3). For sonic and super-sonic flows the parameters at the nozzle exit (3) are those for choked flow and therefore the nozzle exit velocity is equal to the local speed of sound (Mach number M=1). The notional nozzle is between the actual nozzle exit (3) and the notional nozzle exit (4). At the notional nozzle exit (4) jet parameters correspond to a fully expanded jet with the pressure equal to the ambient one and uniform flow velocity equal to a local speed of sound. In some cases, the essential minor and friction losses, in the flow pathway (2)-(3), cannot be neglected, for example in the case of a very narrow crack [2].

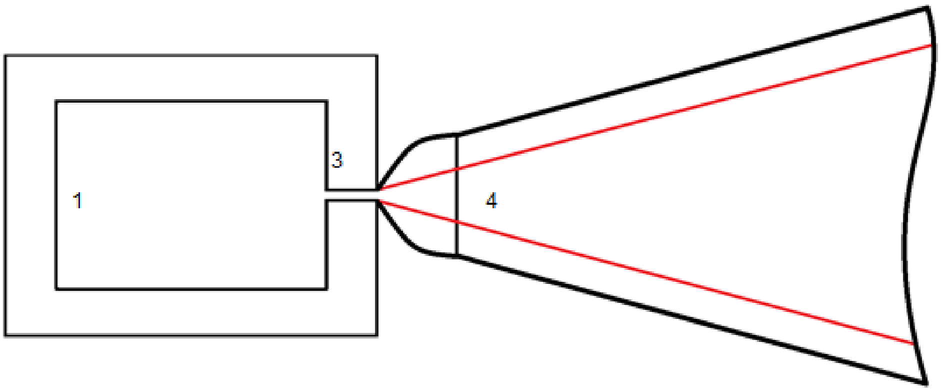


Figure 5. The scheme representing both expanded (red) and under-expanded (black) jets: 1 – reservoir; 3 – nozzle; 4 – effective nozzle diameter, only for under-expanded jets.

As discussed previously combustion is generally of a primary concern when considering harm criteria. An unscheduled hydrogen release from high pressure equipment and infrastructure will form a highly under-expanded jet. This could lead to a formation of a large *flammable hydrogen-air envelope*. The size of the flammable envelope is the deterministic hazard distance from the source of the release. In the event of its subsequent ignition people, structures, equipment and environment may be involved in a fire. The presence of an ignition source within the envelope could initiate severe *jet fires*, *deflagration*, and, potentially, *deflagration-to-detonation transition*. It has to be noted that thermal effects of jet fires and pressure effects of deflagration or detonation could override the hazard distance determined by the size of flammable envelope [2]. Thus, the knowledge of the laws related

to hydrogen dispersion and a flammable cloud formation, including *axial concentration decay* for arbitrary jets with various parameters is essential for decision making for First Responders.

If the flammable envelope reaches a location of an air intake in high-rise buildings, the consequences for occupants and building structure may be catastrophic. Thus it is important to determine the furthest point from the leak at which a jet can be ignited. This is generally defined by hydrogen concentration of 4 vol. %, i.e. by the *lower flammability limit* (LFL). Although this choice of hydrogen concentration is subject to debate, direct flame contact as a result of a flash fire will also occur if a person is within the 4 vol. % hydrogen envelope when hydrogen ignition occurs. The flammable envelope size, i.e. distance to LFL of 4 vol. %, increases proportionally to the diameter [2].

The *similarity law*, discussed below, is used for the prediction of the axial concentration decay of a leaking gas for sub-sonic, sonic, and super-sonic jets. The similarity law is shown to be valid in a wide range of conditions from expanded to highly under-expanded jets. It can be applied for calculation of *hazard distances* informed by the size of the flammable envelope. The non-ideal behaviour of hydrogen at high pressures and the under-expansion of the flow in a nozzle exit are taken into account. In earlier publications by Molkov and his colleagues these distances were referred to as separation or safety distances the definitions of which varied from one document to another. Some examples of the definitions are given below:

"a minimum distance, which separates specific targets (e.g. people, structures or equipment) from the consequences of potential accidents related to the operation a hydrogen facility" [1].
"a minimum separation between a hazard source and an object (human, equipment or environment) which will mitigate the effect of a likely foreseeable incident and prevent a minor incident escalating into a larger incident" [4].
The following factors affect the hazard distances:

- the nature of the hazard,
- the operating conditions and the design of the analysed equipment/facility,
- the type of target/object (people, structures, equipment),
- the environment between the latter and the source of hazard. In this way, the harm potential for people or structures can be evaluated and compared with the harm criteria.

In order to define where the flammable hydrogen-air mixture is formed, it is important to know how the concentration decays, from 100 vol. % at the nozzle to the LFL, i.e. to 4 vol. %. The original form of the similarity law (equation 2) for the axial concentration decay in the expanded round jets was suggested by Chen and Rodi, 1980 [13]:

$$C_{ax}^{m} = 5.4\sqrt{\frac{\rho_N}{\rho_S}}\frac{D}{x}, \qquad (2)$$

where C_{ax}^{m} is the axial mass fraction of hydrogen in the jet at the distance *x* from the nozzle,
ρ_S is the density of the surrounding gas, i.e. air (1.205 kg/m^3 at NTP),
D is the real nozzle diameter exit,
ρ_N is hydrogen density in the nozzle exit (the only unknown parameter).

The "unknown" density ρ_N can be calculated with the use of the *under-expanded jet theory* developed and validated at the HySAFER center, Ulster University. The distance to the LFL is proportional to the

leak diameter. Thus, the design of FCH systems has to satisfy technological requirements to mass flow rate and at the same time to take into account the requirement to minimise the internal diameter of piping to decrease potential hazard distance as it follows from (2). One should keep in mind that ρ_N also affects the flammable envelope size of 4 vol. % (i.e. mass fraction C_m of 0.00288) – the larger operating pressure of a FCH application, the larger notional nozzle density ρ_N, and, consequently, the longer hazard distance.

It can be concluded from the similarity law (2) that for hydrogen jets released to a stagnant air from a given storage pressure (i.e. fixed value of ρ_N) the ratio of a distance to a fixed concentration, $x=L$, expressed as a percentage by mass, to the nozzle diameter, D, is a constant, i.e. L/D=const. This means that the hazard distance is proportional to the leak diameter. Please note that the mass fraction (C_m) can be calculated from the equation (3) based on the volumetric (mole) fraction (C_V):

$$1/C_m = 1 + (1/C_V - 1)M_S/M_N, \tag{3}$$

where M_S and M_N are the molecular masses of a surrounding gas (28.84 g/mol is accepted for air) and nozzle gas (hydrogen), respectively. For example, the mass fraction of 0.0282 corresponds to the volumetric fraction of 0.295 (29.5 vol. % of hydrogen in air, i.e. a stoichiometric mixture); the mass fraction of 0.044365 corresponds to the volumetric fraction of 0.401 (40.1 vol. %, i.e. to a mixture with a maximum burning velocity), 0.013037 – 0.16 (16 vol. %), 0.008498 – 0.11 (11 vol. %), 0.005994 – 0.08 (8 vol. %), 0.00288 – 0.04 (4 vol. % - LFL), 0.00141 – 0.02 (2 vol. %), 0.0007 – 0.01 (1 vol. %).

In the case of fully expanded, round jets the similarity law (2) gives the following ratios of a distance to particular axial hydrogen concentration (in vol. %), L, to the characteristic nozzle size, D (for atmospheric nozzle pressure and expanded subsonic jets, with density ratio ρ_S/ρ_N=14.38: $(L/D)_{30\%}$=49.1; $(L/D)_{4\%}$=491; $(L/D)_{2\%}$=1003; $(L/D)_{1\%}$=2019. For example, the distance to the LFL of hydrogen in air (4 vol. %) in the momentum-controlled expanded jets is equal to 491 nozzle diameters. Please note that the correlation (2) by Chen and Rodi (1980) [13] was validated by concentration measurements in vertical jets up to the ratio of L/D=50 only. Its applicability above this range should be confirmed [2].

If the similarity law by Chen and Rodi, 1980 [13] is applied in its original form (2) to the expanded jets, then the calculation of hazard distances for unignited hydrogen round jets would be straight forward: by using the equation (2) with hydrogen density at the nozzle exit ρ_N=0.0838 kg/m^3 (NTP). However, for the under-expanded jets there is one unknown parameter, the density of the gas in the actual nozzle exit, ρ_N. This density can be calculated by the under-expanded theories, either without losses [12] or with losses [14].

The similarity law for hydrogen concentration decay along the axis of the momentum-controlled jets as well as the experimental data for hydrogen under-expanded releases are shown in Figure 6.

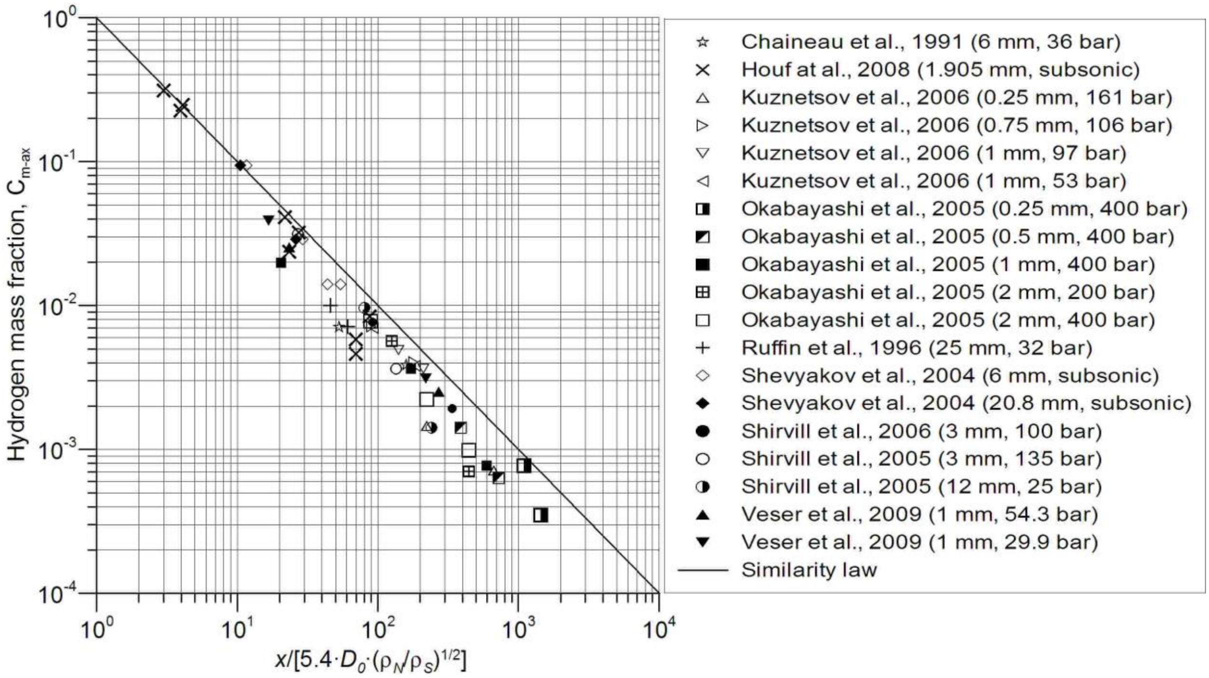


Figure 6. The similarity law (straight, solid line) and the experimental data (symbols) on the axial concentration decay in the momentum-controlled expanded and under-expanded hydrogen jets [2].

The experimental data on the axial concentration decay of pure hydrogen in momentum-controlled sub-sonic, sonic and super-sonic jets, released from the vessels of different volume pressurized up to 40 MPa, and through nozzles with diameters ranging from 0.25 to 100 mm are reported in [3]. The concentration of hydrogen in the air was in the interval between 1 and 86.6 vol. %. The similarity law was validated to the ratios *x/D* in the range from 4 to 28,580. Laminar and turbulent, expanded and under-expanded momentum-controlled jets were used to validate the universal character of the similarity law [3]. Please note that the similarity law is conservative in relation to the experimental data points, which is due to the effect of friction and minor losses in the experiments.

As indicated earlier, the mass fraction of hydrogen corresponding to the LFL (4 vol. %) is 0.00288. If we use this value along with the air density of 1.205 kg/m^3 (NTP) the equation (2) will be simplified to the following formula:

$$x_{4\%} = 1708 \cdot \sqrt{\rho_N} \cdot D \quad , \qquad (4)$$

which can be used to evaluate the size of flammable envelope to 4 vol. % of hydrogen (hazard distance for unignited hydrogen release).

The extent of the unignited hydrogen release can be calculated using two methods:

1. The nomogram for hydrogen concentration decay.
2. H2FC Cyber laboratory tools 'Hydrogen jet parameters' and 'Axial concentration decay' (http://h2fc.eu/sageserver).

The *nomogram* for the graphical evaluation of hydrogen concentration decay with the use of the similarity law and the under-expanded jet theory without losses is shown in Figure 7. The nomogram consists of four main graphs entitled: "Volumetric to mass fraction", "The similarity law", "Choose leak

diameter", and "Choose density in the nozzle exit", and one additional graph "Calculate density in the nozzle exit by storage tank pressure and temperature" (based on calculations by the under-expanded jet theory without losses).

The use of the nomogram for the calculation of the distance from the nozzle (for example 1 mm in diameter) to the 4 vol. % of hydrogen in air (blue-coloured dash line) along the axis of the release from a storage tank at a pressure of 70 MPa and temperature 300 K is demonstrated below.

1. Draw the vertical line downward from the point on the horizontal axis "Hydrogen volumetric fraction", corresponding to the concentration of interest (4 vol. % or 0.04), until the intersection with the line of the graph "Volumetric to mass fraction" (left-hand, top corner in Figure 7).
2. Draw the horizontal line from this intersection point to the intersection with the similarity law line in the right-hand top corner graph "The similarity law" (Figure 7).
3. Draw the vertical line downward from the intersection point obtained on "The similarity law" graph until the intersection with line corresponding to 1 mm diameter on the graph "Choose leak diameter" (Figure 7). Please note that there are eight lines on the "Choose leak diameter" graph, which correspond to the following leak diameters (from top to bottom): 15 mm, 10 mm, 5 mm, 3 mm, 2 mm, 1 mm, 0.5 mm, 0.1 mm). These figures are shown at the right side of the graph.
4. Calculate the density using the additional graph "Calculate density in the nozzle exit by storage tank pressure and temperature" located at the bottom of the nomogram using given pressure (in our example - 70 MPa) on the ordinate axis and a line corresponding to the chosen temperature (300 K). This is shown by two thick grey arrows on the "Calculate density in the nozzle exit by storage tank pressure and temperature" graph. The density calculated graphically at the nozzle exit for 70 MPa and 300 K is about 23 kg/m^3

5. Coming back to the “Choose leak diameter” graph, draw the horizontal line from the intersection point on the line “1 mm” until the intersection with an imaginary line corresponding to 23 kg/m^3 (located between two lines, 20 kg/m^3 and 50 kg/m^3, shown in the graph). Please note that there are five lines at the graph corresponding to the densities of 1 kg/m^3, 3 kg/m^3, 10 kg/m^3, 20 kg/m^3, and 50 kg/m^3 from top to bottom, respectively. These values are shown at the left side of the graph.
6. Draw the vertical line downward from the intersection point with the imaginary line corresponding to 23 kg/m^3 to the intersection with the abscissa axis ‘Distance to concentration of interest’ on the “Choose density in the nozzle exit” graph. Thus, the calculated graphically distance from the nozzle exit to hydrogen concentration of 4% by volume is about 7.7 m.

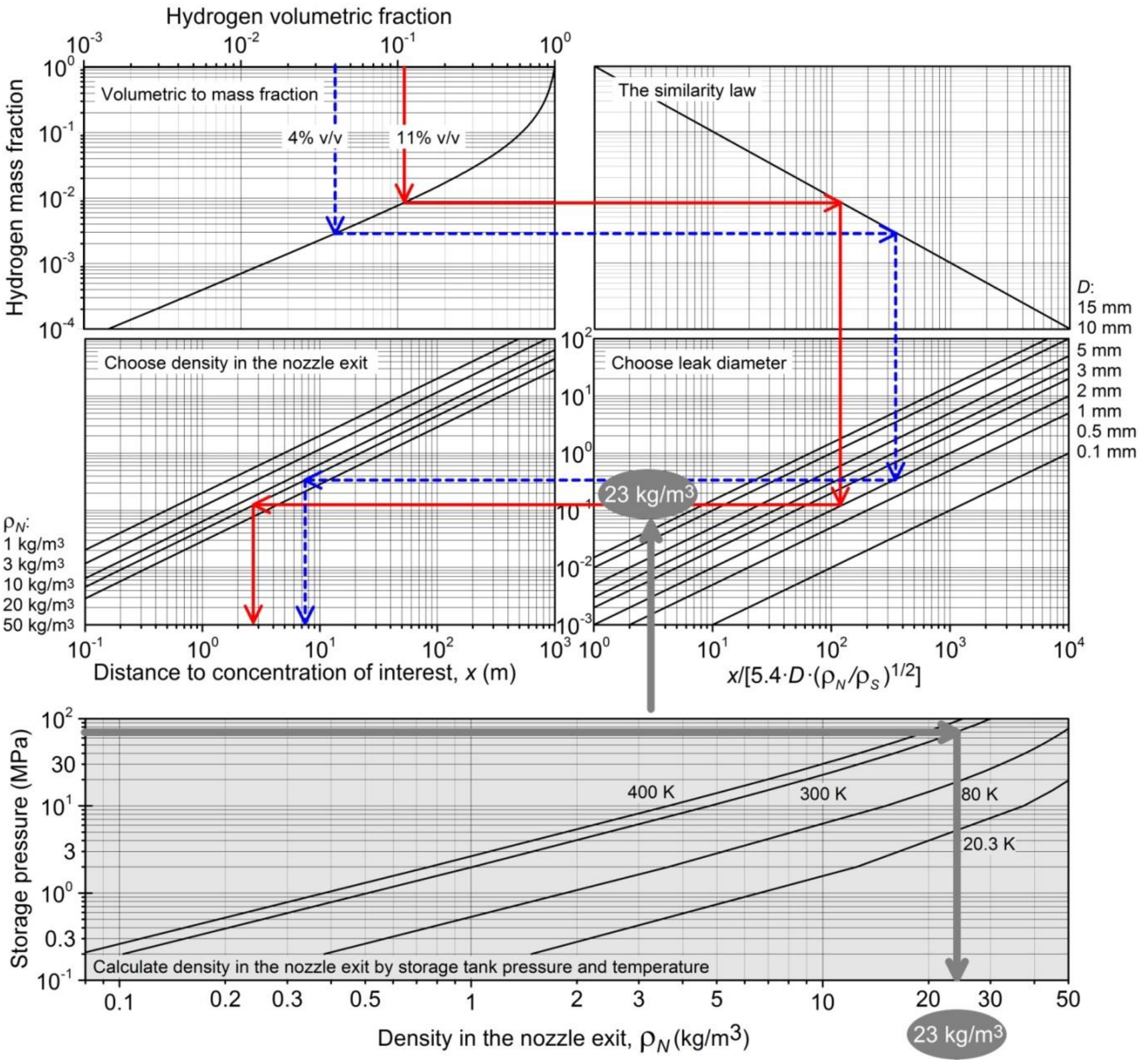


Figure 7. The nomogram for concentration decay calculation in unignited jets [2].

The use of the equation (2) for the similarity law with the more accurate value of hydrogen density at the nozzle calculated by the under-expanded jet theory (23.95 kg/m^3) and air density of 1.205 kg/m^3 (NTP) gives a distance of 8.36 m for 4 vol. % of hydrogen in air. The error of graphical calculations is at the acceptable level and below 10%.

Task for trainees: using the nomogram in Figure 7 evaluate the distance to 11 vol. % of hydrogen concentration in air assuming the same storage pressure 70 MPa, storage temperature 300 K and physical nozzle diameter 1 mm (corresponds to an average flame tip location).

H2FC Cyber laboratory tool 'Hydrogen jet parameters' provides quick and simple way to evaluate the density of the gas in the nozzle by entering the following data: pressure in the reservoir, temperature in the tank, orifice diameter and ambient pressure http://h2fc.eu/sageserver.

The similarity law for under-expanded jets and the nomogram are performance-based tools for calculation of hazard distances for unignited releases. They are the alternative to the prescriptive codes. For instance, the International Fire Code, (2006) contains a table of prescribed distances between a hydrogen system and various potential targets, including an air intake to a building [15]. However, this code does not provide or require any information either on the hydrogen storage parameters (pressure and temperature) and a leak size from the system. This code is an example of an archaic prescriptive approach that contradicts the modern requirements to codes and standards to be performance-based [2].

The standard NFPA 55, 2010 [16] moved one step further, compared to the prescriptive International Fire Code, 2010 [15], by presenting a set of 4 equations to calculate distances to the axial concentration of 4 vol. % of hydrogen in air. Molkov, 2012 [2] indicated two weak points in this standard. To "simplify" the use of the methodology by practitioners each of 4 equations is assigned to a quite wide range of pressures. This is resulted in a "programmed" over-prediction and under-prediction of the distance depending on the storage pressure. However, the most serious disadvantage in the calculation of the distance by NFPA 55, 2010 [16] is the use of a leak size of only 3% of the flow area of the pipe (this choice is based on leak frequencies of other gases available to gas industry) [2]. Indeed, the similarity law states that for the same density of hydrogen in the nozzle exit ρ_N, i.e. for the same storage pressure, the hazard distance is directly proportional to the leak diameter. Thus, the questionable choice of a leak size as 3% of cross-section area of the pipe in NFPA 55 (2010) results in the "prescribed" decrease of the distance by reciprocal to square root from 0.03, i.e. by 5.77 times. It is clear that in the case of full bore rupture of a hydrogen pipe the consequences could be catastrophic if this "3%" approach is widely applied and enforced by the regulators. The risk-informed approaches cannot compromise the science-informed engineering design. The alternatives to this "forced" decrease of the hazard distance is safety engineering design of hydrogen systems, e.g. reduction of pressure in the pipe when possible and the decrease of the pipe diameter to the minimum size required by the technological reasons and/or substitution of one large pipe by a number of smaller pipes, use of PRD with enhanced safety characteristics, etc. [2].

The conclusion can be drawn that the similarity law may be used to calculate the hazards distance more accurately compared to currently available standards and codes. This methodology is scientifically underpinned and can account for friction and minor losses in a leak pathway when/if necessary. Last but not least, the hydrogen safety engineering guarantees the freedom to consider worst-credible scenario of full bore rupture rather than the questionable 3% of cross section area of pipe approach as suggested by some codes and standards [2].

Reduction of a hazard distance from a hydrogen release

The equation (4) demonstrates that the hazard distance for unignited jets, *x*, is proportional to the diameter of the release, *D*, and grows as a square root from the storage pressure (term density ρ_N). With this in mind, the key safety requirement for unignited hydrogen release can be formulated as: *reduce the diameter of piping (which is a leak diameter for a credible worst-case scenario) to the technologically affordable minimum.* The same can be applied to the diameter of the Pressure Relief Devices (PRDs) or Temperature Activated Pressure Release Devices (TPRDs) [3].

When a jet becomes buoyant?

Depending on the buoyancy effect the jets can be momentum-controlled, transitional or buoyancy controlled as demonstrated in Figure 3. The hazard distance for unignited hydrogen release is higher for a horizontally-oriented leak as opposed to the diagonal or vertical. In many cases vertical, unignited jet, which happens outdoors will not pose any hazard to people or cause damage to buildings and structures. For First Responders, however, it is important to know whether a leak is originally momentum- or buoyancy-controlled, or at what hydrogen concentration the flow regime changes from momentum to buoyant for the same jet (for example, in the case of vertical downward directed leaks).

The technique presented below, allowing distinguishing between momentum- and buoyancy-controlled flow in expanded and under-expanded jets, is based on the work of Shevyakov et al. [17, 18] that was carried out with the expanded jets only. Figure 8 shows, in logarithmic coordinates, the dependence of the ratio of distance to nozzle diameter *x/D* (ordinate) for a particular volumetric concentration of hydrogen in air on the *Froude number Fr* (abscissa) in its classical form:

$$Fr=U^2/gD, \quad (5)$$

where *U* is the velocity at the nozzle exit (notional nozzle exit for under-expanded jets), m/s,
g is the gravitational acceleration (standard acceleration of gravity on Earth is 9.80665 m/s^2),
D is the nozzle diameter (notional nozzle exit diameter for under-expanded jet), m.

For under-expanded jets in Figure 8 parameters to be used in (5) - the notional nozzle exit diameter *D* and the velocity at the notional nozzle exit *U* - were calculated by the under-expanded jet theory [12]. Both expanded and under-expanded jets obey the same functional dependence with accuracy of 20% acceptable for engineering applications.

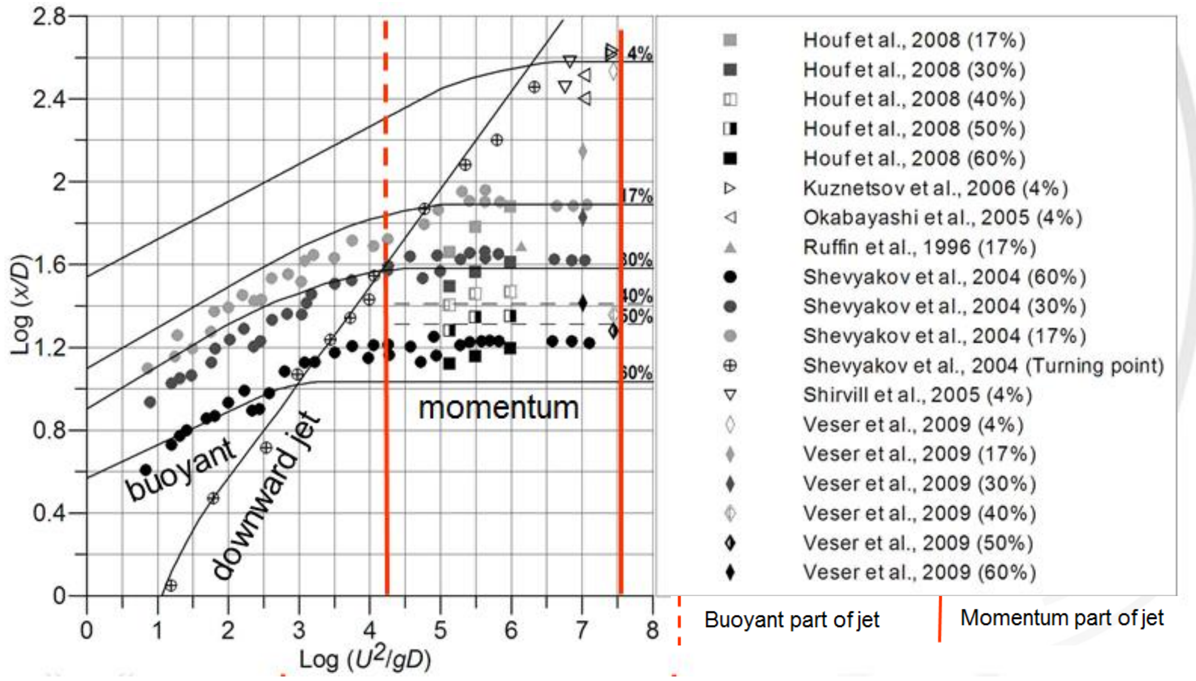


Figure 8. The dependence of the distance to nozzle diameter ratio for particular concentration of hydrogen in air on the Froude number [17, 18].

Figure 8 shows five theoretical curves (solid lines) plotted by Shevyakov et al., 1980, 2004, the experimental data by Shevyakov and co-authors for expanded jets [17, 18], and the data by other researchers for under-expanded jets. Practically all under-expanded jets in hydrogen-related incidents/accidents will be in the momentum-controlled regime as follows from the available tests applied to validate the correlation in Figure 8. Four of five theoretical curves in the graph are related to hydrogen concentrations of 4 vol. %, 17 vol. %, 30 vol. %, and 60 vol. % respectively. Each of these four curves has an ascending buoyant part and a momentum "plateau" part [2].

It is important to stress that the Froude number at the transition from the buoyant part of the curve to the momentum one depends on the concentration of hydrogen under consideration. For example, at the axial concentration of hydrogen equal to 60 vol. % the jet stays in momentum-controlled regime until the *Log* (*Fr*)>3.5, while for the jet to be in the momentum-controlled regime at the axial location where hydrogen concentration drops to 4 vol. % (LFL) the nozzle exit Froude number has to be much higher, i.e. *Log* (*Fr*)>6.5 (i.e. three orders of magnitude higher) [2].

The fifth curve on Figure 8 labelled as the "Downward jets" is of a special interest for those who will make decisions at the scene of an accident. It gives for a jet directed vertically downward a dimensionless distance from the nozzle to the turning point, where the jet changes its direction of flow from downward to upward. To calculate the distance to the turning point only knowledge of the Froude number at the nozzle (notional nozzle) is required. The fifth curve intersects each of the four other curves in Figure 8 in the region of *transition from momentum-dominated to buoyancy-controlled flow* as expected [2]. In order to use the correlation in Figure 8 the following steps should be applied:

1. Calculate the nozzle exit Froude number, *Fr*, and its logarithm. Apply the under-expanded theory to calculate the notional nozzle exit diameter and the velocity in the notional nozzle exit for under-expanded jets.

2. Draw a vertical line upward from the point on the abscissa (horizontal) axis equal to the calculated Froude number logarithm. The intersection of this vertical line with the line marked as “Downward jets” on the graph indicates the concentration, above which the jet is qualified as momentum-dominated (solid red line), and below which the jet is qualified as buoyancy-controlled (dash red line).

For example, if a jet exit Froude number is *Log* (*Fr*)=4.25 the intersection of the vertical line with the line “Downward jets” is at the location of the theoretical curve corresponding to 30 vol. %. Thus the jet is in the momentum-dominated regime when the concentration in the jet is above 30 vol. % and it becomes buoyant when the concentration on the jet axis is below 30 vol. % (further downstream of the axial concentration of 30% by volume).

This technique is quite simple to apply and at the same time can be very useful for First Responders. For instance, the hazard distance for a horizontal jet release can be essentially reduced as only a length of the momentum-dominated part of the jet can be taken as an indication of the hazard distance rather than aggregated (both momentum- and buoyancy-controlled parts of the jet) distance to 4% by volume (LFL) [2].

What is a safe PRD diameter?

The similarity law (2) is a simple and a thoroughly validated tool for hydrogen safety engineering for both expanded and under-expanded round jets. Let us consider the following scenario: a FC forklift is parked in a warehouse. The forklift is equipped with a hydrogen storage tank fitted with a pressure relief device (PRD). Let us calculate what diameter the PRD should have in order to provide a safe upward release of hydrogen from the on-board storage at 35 MPa. In this case we would like to exclude the formation of a flammable layer under a warehouse ceiling, which is 10 m above the PRD. To realize this safety strategy the concentration on the jet axis at a distance of 10 m should be equal to or less than 4 vol. % (corresponding mass fraction of hydrogen is 0.00288). The density of hydrogen in the nozzle exit, calculated by the under-expanded jet theory for the storage pressure of 35 MPa, is ρ_N=14.4 kg/m^3. Thus, the diameter of the PRD can be calculated from the similarity law (2) as equal or less than 1.5 mm:

$$D = \frac{C_{ax}^{m}}{5.4}\sqrt{\frac{\rho_S}{\rho_N}}x = \frac{0.00288}{5.4}\sqrt{\frac{1.205}{14.4}}10 = 0.0015m\,, \quad (6)$$

To finalize this safety strategy for the use of hydrogen-powered forklifts in the warehouse a requirement to fire-resistance rating of the on-board storage tank must be formulated and testing carried out. Indeed, the fire-resistance rating should be greater than the blow-down time (i.e. the time needed to empty the storage vessel) of the storage tank to exclude its catastrophic failure in the case of external fire. It is clear that the use of a PRD with a larger diameter would create either a flammable cloud or a jet flame with higher hazards, e.g. dangerous overpressure during “delayed ignition” or deflagration of initial cloud, and associated risks [2]. The ignited hydrogen release (or jet fires) will be discussed in a subsequent lecture.

Blow-down of a compressed hydrogen storage tank

A blow-down is a process associated with the emptying of storage tank content through an orifice of a TPRD/vent/leak. The blow-down time will depend on the mass of hydrogen stored, volume of the tank, the pressure, and the orifice diameter.

For example, Tables 2 and 3 indicate volumes, pressures, weights and blow-down times to atmospheric pressure (in s) of hydrogen for on-board storage of selected demonstration or prototype FC vehicles. For a vehicle with the highest volume of storage tank (vehicle 3, 156 L, 70 MPa) the blow-down time is the highest. Although for typical orifice diameters of leaks, between 4 and 6 mm, the blow-down time ranges from 124 s (just over 2 minutes) to 54 s (slightly less than 1 minute), implying that this is a very rapid process.

Table 2. The examples of the on-board hydrogen storage parameters for different FC vehicles.

Vehicles	Manufacturer	Model	Pressure (MPa)	Volume (L)	Weight (kg)	Status
1	Hyundai	Tucson Hybrid FCEV	35	152	3.6	Demonstration
2	VW	Touran HyMotion	35	81	1.9	Prototype
3	Toyota	FCHV-adv (2008)	70	156	6.2	Prototype
4	VW	Tiguan HyMotion	70	81	3.2	Vehicle Testing

Table 3. Adiabatic blow-down times calculated for different leak diameters for on-board storage tanks of vehicles 1 - 4.

Leakage diameter [mm]	Blow-down time vehicle 1 (s)	Blow-down time vehicle 2 (s)	Blow-down time vehicle 3 (s)	Blow-down time vehicle 4 [s]
2	427	226	502	260
3	189	100	222	115
4	105	56	124	64
5	67	35	79	41
6	46	24	54	28

Figure 9 demonstrates how the pressure reduces inside the storage tanks during the blow-down. As you can see the drop in the pressure is significant: it reduces to atmospheric values rapidly.

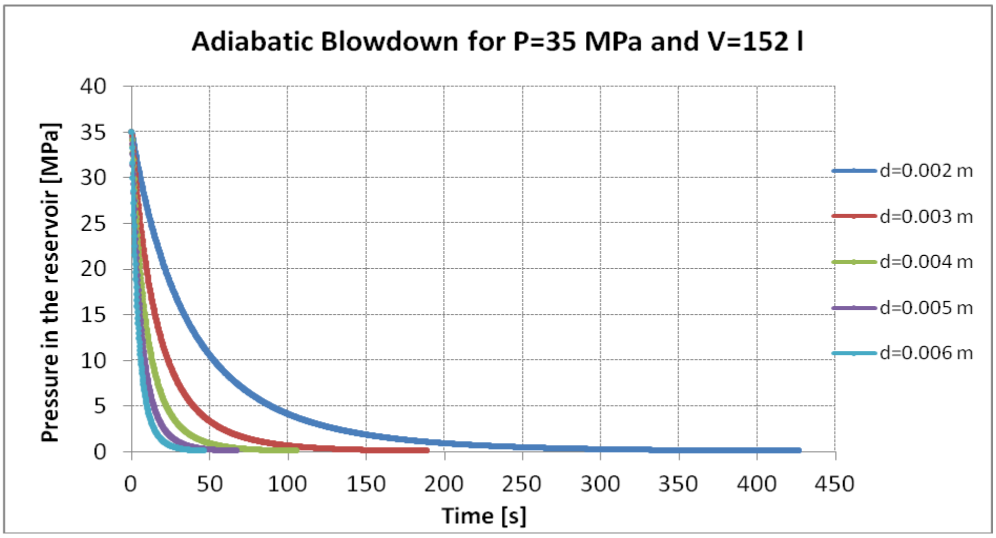


Figure 9. A pressure drop inside a hydrogen storage tank as a function of time for different leak diameters (vehicle 1).

Recently, a CFD study of unignited hydrogen releases from on-board hydrogen storage of a FC car was carried out at HySAFER centre of Ulster University [19]. Li et al., 2015 considered an accident scenario involving a vertical downward release of hydrogen from a thermally-activated pressure relief device (TPRD) under a FC car located outdoors (i.e. in the open atmosphere). An unignited release of hydrogen may occur due to an unexpected initiation a faulty TPRD, for example following a severe car crash. TPRDs are usually located underneath the FC vehicle (Figure 9), and their vents orientated vertically downwards, therefore the release of hydrogen will impinge the ground [19]. The released hydrogen can form a flammable cloud that has the potential to result in a flash fire.

The dimensions of a typical salon car used in [19] are shown in Figure 10. The authors assumed that the on-board hydrogen tank with a volume of 171 litres, adopted from the Honda FCX specification [20], is full. Two storage pressures were considered: 35 and 70 MPa. The TPRD is assumed to be located near the rear wheel under the vehicle as shown in Figure 10 and its orifice diameter is 4.2 mm [21]. Other assumptions include: the ambient pressure and temperature at 1 atm and 20 °C, respectively; no wind in the environment [19].

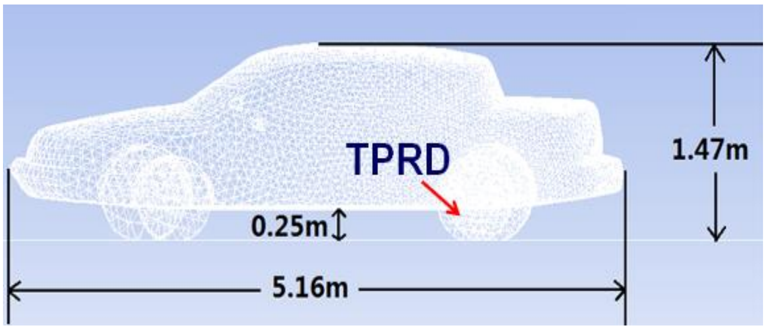
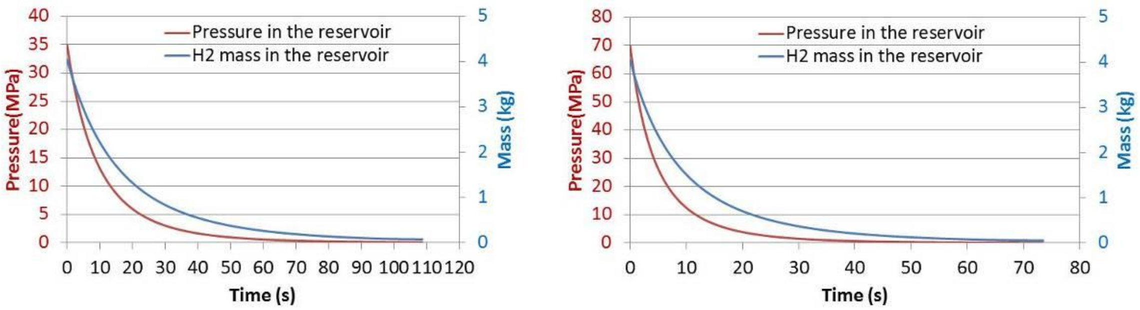


Figure 10. A side view of a FC car geometry and a position of a TPRD [19].

In this study, the conservative value of hydrogen concentration equal to 4 vol. % is applied as the harm criterion for the general public, while 8 vol. % - as the harm criterion for those first responders who are not equipped with thermal protective clothing, such as policemen and emergency medical personnel. For the firefighters having a bunker gear, the hydrogen flammable cloud will be harmless

as the gear will protect them from the potential hydrogen flash fire. In addition to the harm criteria to people, 4 vol. % hydrogen concentration was selected as the damage criterion to the air intake of buildings. If the flammable envelope of 4 vol. % hydrogen concentration reaches the location of an air intake into a high-rise building, then the consequences for both the occupants and the structure of the building could be catastrophic [19].

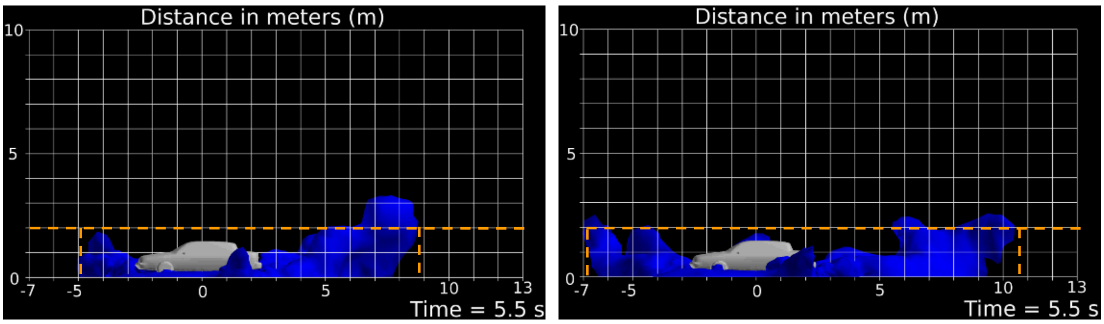
In real-world conditions, a hydrogen release from a high pressure tank is not a steady-state release but a blow-down process with pressure reducing in the reservoir until the tank is empty. The notional nozzle model mentioned earlier can be applied to simulate the pressure dynamics in the hydrogen storage tank during an under-expanded jet. The Cyber Laboratory tool 'Adiabatic blow-down of storage tank' was used. The obtained results are shown in Figure 11. For the release from the 4.2 mm orifice, 171 L tank at 35 MPa, the total blow-down time is less than 110 seconds (< 2 minutes), and the transition from an under-expanded to an expanded jet occurs at 85 s. For the release from the 4.2 mm orifice, at 70 MPa with identical mass, the total blow-down time is less than 75 s, with the transition from an under-expanded to an expanded jet occurring at 58 s [19].



(a) (b)

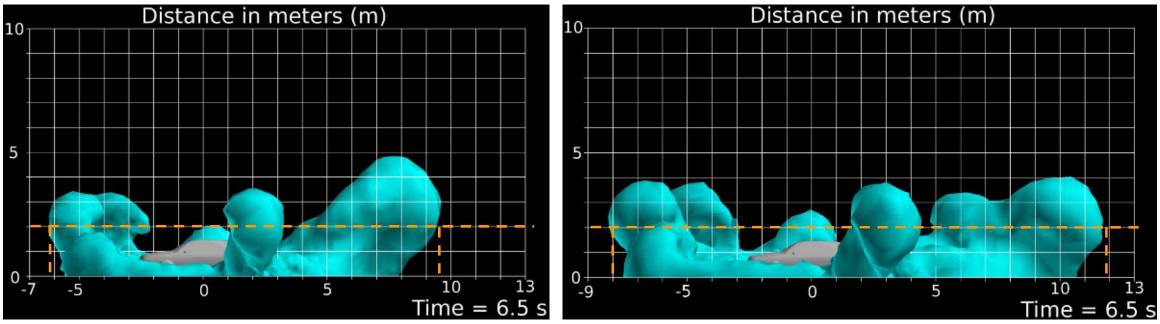
Figure 11. Adiabatic blow-downs (reduction of pressure and hydrogen mass) of storage tanks at 35 MPa (a) and 70 MPa (b) (orifice diameter - 4.2 mm) [19].

As you can see from Figure 12 for the first responder without thermal protective clothing, the longest hazard distance from the point of the release is 8.8 m and 10.5 m, for 35 MPa and 70 MPa storage pressures, respectively. The hazard distance for the release from hydrogen storage at 70 MPa is nearly 20% higher compared to 35 MPa storage pressure. In both cases the largest sizes of 8 vol. % hydrogen envelopes near the ground were formed at 5.5 s after the opening of the TPRD. Afterwards, the envelopes will shrink and the hazard distances decrease.



(a) (b)

Figure 12. 8 vol. % hydrogen envelopes registered at 5.5 s after start of release: a) for 35 MPa storage pressure, b) for 70 MPa storage pressure (longest hazard distance extend assuming first responder height cut-off at 2 m) [19].

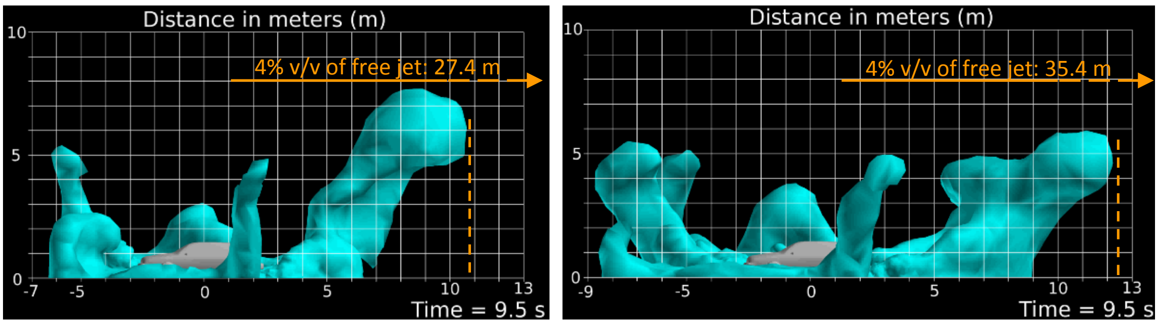


(a) (b)

Figure 13. 4 vol. % hydrogen envelopes registered at 6.5 s after start of release: a) for 35 MPa storage pressure, b) for 70 MPa storage pressure (longest hazard distance extend assuming first responder height cut-off at 2 m) [19].

As it shown in Figure 13 for the general public on the ground, the longest hazard distances for 35 and 70 MPa releases are 9.4 and 11.8 m, respectively. In both cases the largest 4 vol. % hydrogen envelopes near the ground were registered at 6.5 seconds after the initiation of the TPRD. Afterwards, the envelopes as well as the hazard distances will reduce. Figure 13 only represents 4 vol. % envelopes for the height lower than 2 m (yellow cut-off lines). The largest flammable envelopes for the total domain are shown in Figure 14, from which the hazard distances for the surroundings can be evaluated [19].

It can be seen from Figure 14 that for a building air intake, the longest hazard distances are equal to 10.7 m and 12.3 m, for 35 MPa and 70 MPa releases respectively. The hazard distance for the 70 MPa release is increased by 15% compared to the 35 MPa release. In both cases the largest 4 vol. % hydrogen envelopes occur at 9.5 seconds after the opening of the TPRD. Afterwards, the envelopes will shrink and the hazard distances will decrease. If the hazard distances from these impinged jets are compared with the hazard distances calculated for free jets (27.4 m for 35 MPa storage pressure and 35.4 m for 70 MPa storage pressures) , the results show a significant reduction of more than 60% and 65%, for the 35 MPa and 70 MPa releases respectively, as shown in Figure 14.



(a) (b)

Figure 14. The extent of 4 vol. % hydrogen envelopes for unignited releases from storage tanks: a) pressurised to 35 MPa, b) pressurised to 70 MPa [19].

Thus to sum up, the CFD study carried out by Li et al., 2015 [19] demonstrated that:

- for unignited hydrogen releases from storage tanks pressurised to 35 MPa and 70 MPa, the longest hazard distances occur within 10 s after the opening of the TPRD and the duration of the hazards associated with the release of hydrogen is less than 2 min;
- the deterministic hazard distances for unignited hydrogen releases from a TPRD, orientated vertically downwards under a FC car, are significantly shorter than those of free jets;
- for both the members of the general public and first responders not equipped with the thermal protective clothing maximum hazard distance from unignited release ranges from 8 to 12 m depending on storage pressure;
- to ensure that the concentration of hydrogen is always less than LFL (4 vol. %) at the location of the air intake of buildings, the hazard distance should be at least 11 m for 35 MPa releases and 13 m for 70 MPa releases [19].

Hydrogen unignited releases indoors will be discussed later in the lecture 'Hazards of hydrogen use indoors'.

Generally, the main safety strategy how to deal with a hydrogen leak is to minimize its mass flow rate, for example by reducing the size of any potential leak by keeping the pipe diameters as small as possible and to 'let it go' to prevent hydrogen accumulation to a hazardous level when a flammable hydrogen-air mixture represents unacceptable risks [2]. The prevention and mitigation of unignited hydrogen leaks are discussed below.

Prevention of hydrogen leaks

The initial steps, prior to detection and mitigation of hydrogen releases, are the preventive measures to control the associated risks. Prevention measures are the safety measures that can act on the combination of causes of a hazardous event to prevent it from happening. These measures reduce the likelihood of the event. They aim to prevent a loss of tightness and an equipment failure. They include but not limited to the following measures:

- Prevent the formation of flammable atmospheres through an inherently safer design of FCH systems;
- Carefully select the materials for FCH systems to avoid hydrogen embrittlement;
- Minimize the quantity of hydrogen (and potentially oxygen) that is stored and involved in an operation;
- Equipment validation;
- Physical protection;
- Periodic leak checks;
- Elimination of ignition sources;
- Periodic equipment inspection.

Prevention measures related to the mechanical integrity of hydrogen systems involve: 1) validating equipment design through performance testing and 2) periodical checks of the equipment once it has been installed. The equipment can be removed from service in the end of the specified life-time [22]. Design testing and validation aim to prove that the equipment suits the application, for which it is going to be used. Resistance and endurance tests can also be applied. Resistance tests are basic tests, when all the relevant characteristics of the system are tested (e.g. hydraulic pressure test). Endurance tests are more elaborate, when the system being subjected to cyclic loading, and the time until it fails

characterises it endurance. A factor is applied to establish the service life, for example a requirement to withstand 50,000 test cycles for a specified service life of 10,000 cycles [22].

The equipment subjected to mechanical integrity testing is listed below:

- Gaseous hydrogen container
- Container valves
- Flexible hoses
- Quick connection devices.

Inherently safer design is an approach that focuses on reducing or eliminating hazards associated with the product or the process. Let us consider how safety of a fuel cell (FC) system could be improved by reducing hazards without the interfering the technology itself. Unfortunately, current FC systems are often designed using piping diameters of 5-15 mm and pressures of 0.5-1.5 MPa without consideration of hazards. The mass flow through a 5 mm diameter orifice at storage pressure of 0.5 MPa can be calculated using the under-expanded jet theory, and is about 6 g/s. For a pipe of 15 mm diameter and pressure 1.5 MPa the mass flow rate is 170 g/s [2].

Now let us estimate the mass flow rate for a 50 kW FC system, which provides energy to large facilities such as hotels, hospitals, office buildings, and multi-family dwellings. Assuming that an electrical efficiency of a FC is 45%, and the upper heat of reaction (combustion) of hydrogen with air is [(286.1 kJ/mol)/(2.016 g/mol)] = 141.92 kJ/g, the mass flow rate for the FC functioning at maximum power can be calculated as (50 kW)/0.45/(141.92 kJ/g)=0.78 g/s. For example, this mass flow rate can be provided at a pressure 0.5 MPa through a restrictor in the storage or piping system with an orifice diameter of only about 1.8 mm, or at pressure 0.2 MPa through a diameter orifice of about 2.9 mm [2].

As it is shown earlier in this lecture, the hazard distance for an unignited release is proportional to a nozzle diameter and square root from a storage pressure. Thus, the decrease of a pipe diameter from 15 to 2.9 mm and reduction of pressure from 1.5 to 0.2 MPa could decrease the hazard distance by more than 14 times [2].

Further analysis can be performed to compare hazard distances for these two options: option 1 – pressure 0.5 MPa and pipe diameter 1.8 mm; option 2 - 0.2 MPa and 2.9 mm. The ratio of hazard distances for unignited releases in option 1 and 2 in assumption of full bore rupture can be estimated as 0.98, i.e. they are practically the same. These examples clearly demonstrate advantages of the science-informed safety design of hydrogen and fuel cell systems to essentially reduce hazard distances without affecting the performance parameters of FC [2].

Mitigation measures for unignited releases

Once the prevention steps have been taken thought can be given to detection and mitigation measures. The safety measures aimed at mitigating or reducing the severity of the consequences of the hazardous event are called mitigation measures [22]. In terms of mitigating the risk the number of people at risk should be reduced as much as possible and an explosion relief, suppression or containment can be provided. For detection of a leak gas sensors may be used if applicable. Flow meters, IR detectors, etc. are also relevant. Some mitigations measures are listed below [22, 23]:

- reduce the size of a leak, for example through the use of hydrogen flow restrictors;
- isolate hydrogen from oxidizers, hazardous materials and dangerous equipment;
- use of alarms and/or warning devices (including hydrogen sensors and fire detectors);
- use of shut-down devices and systems;
- identify and, if possible, separate or eliminate potential ignition sources;
- prevention flammable atmospheres forming, e.g. by ventilation (natural and active);
- elevation of hydrogen systems, use of flow meters, etc.;
- use outdoor location when possible;
- avoid congestion;
- implement hazard distances;
- practice good housekeeping, such as keeping access and evacuation routes clear and keeping weeds and other debris away from hydrogen systems;
- provision of the emergency response.

Detection of hydrogen leaks

Because hydrogen is colourless and odourless, sensors will be key safety equipment for safe refuelling stations and other hydrogen facilities. The addition of an odorant to hydrogen would ease the detection of small leaks. However, this is not practicable in most situations, e.g. this would poison an expensive catalyst in the fuel cells. Detectors/sensors can be used to detect hydrogen releases, to automatically shut down systems, to activate the alarms, and to notify First Responders. Hydrogen sensors are the subject of ongoing research worldwide.

The following criteria are applied to the selection of hydrogen sensors:

- durability and reliability;
- sensitivity to cross-contamination from e.g. hydrocarbons;
- sensitivity to humidity;
- response time;
- whether they will give false positive readings;
- sensitivity to temperature extremes;
- maintenance requirements;
- measurement range;
- an accuracy.

The US DoE published the targets for hydrogen sensors [www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/safety.pdf] as shown in Figure 15.

- Measurement Range: 0.1%-10%
- Operating Temperature: -30 to 80°C
- Response Time: under one second
- Accuracy: 5% of full scale
- Gas environment: ambient air, 10%-98% relative humidity range
- Lifetime: 10 years
- Interference resistant (e.g., hydrocarbons)

Figure 15. Targets for hydrogen sensors outline by US DoE [24].

It is also important to know that in hydrogen safety technologies sensors do not provide a complete detection strategy due to the buoyancy and diffusivity of hydrogen. For example, a hydrogen sensor will be of little use in a large enclosure or outdoors. The placement of sensors should be carefully considered and tools such as CFD may be used to simulate leak scenarios to provide insight into sensor positioning. Both fixed location and personal/hand-held monitors are necessary for protection of personnel and facilities.

The suggested positioning of hydrogen sensors are detailed below:

- locations where hydrogen leaks or spills are possible;
- at hydrogen connections that are routinely separated (for example, hydrogen refuelling ports);
- locations where hydrogen could accumulate;
- in building air intake ducts, if hydrogen could be carried into the building;
- in building exhaust ducts, if hydrogen could be released inside the building.

There are also requirements to fit hydrogen sensors on FC vehicles to warn about potential leaks. Hydrogen detectors locations for Fuel Cell Electric Vehicle (FCEV) are marked as blue dots on Figure 16 and include:

- exhaust pipe (process control) ;
- passenger cabin (safety) ;
- engine (safety) ;
- fuel Cell stack (safety) [25].

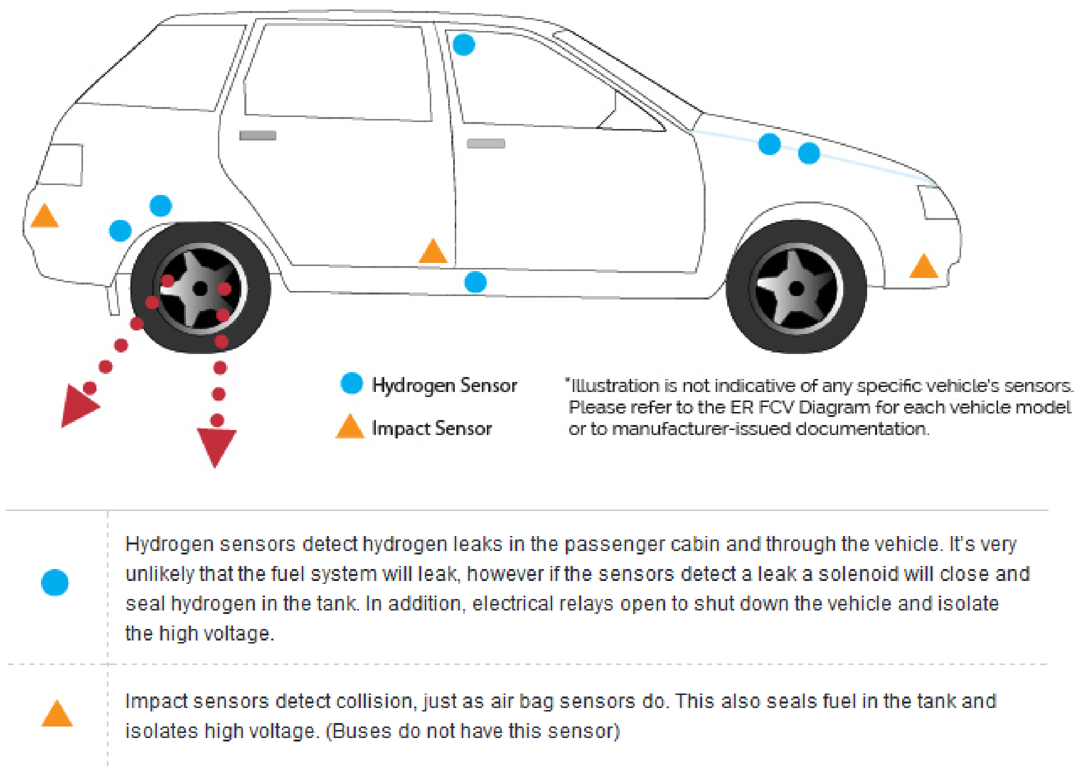


Figure 16. Possible location of hydrogen sensors in a FCEV [25].

A commonly used concentration level for main alarm is 1 vol. % of hydrogen in air, which is equivalent to 25% of the LFL. This level normally should provide an adequate time to respond in an appropriate

manner, such as system shutdown, evacuation of personnel, or other measures as necessary. A warning may be given earlier. More than one sensor platform necessary to reach all target specifications and a combination of sensor platforms shows the best results.

The types of commercially available hydrogen sensors/detectors are:

- electrochemical detectors;
- metal oxides detectors;
- thermal conductivity detectors ;
- field effect gas detectors (FED);
- resistance-based palladium thin film;
- catalytic detectors;
- micro Electro Mechanic Systems (MEMS);
- optical devices;
- research is on-going.

The following factors should be considered while selecting the detectors:

- accuracy (1-10%);
- reliability;
- maintainability;
- calibration;
- detection limits (high and low);
- response time (<10 s);
- recovering or non-recovering in time;
- long life time (more than 5 years);
- low energy consumption (<10MW);
- simple system integration [26].

In 2009 INERIS (France) conducted a test programme within the HYPER project, 2008 [27] based on the international standard parts IEC 61779-1&4, 1998 [28] and aimed at assessing the performance of commercially available hydrogen detectors. These devices were of electrochemical and catalytic types, i.e. the two types most often used in industry. The catalytic sensor was 5 times faster than the electrochemical one to respond to a sudden exposure to hydrogen. However, the response time was approximately 10 s for the catalytic sensor and 50 s for the electrochemical sensor. These figures also apply for the recovery time. In many practical scenarios this long time is hardly acceptable [2].

Catalytic detectors studied within the HYPER project were also prone to loss the sensitivity and drift of zero after a prolonged exposure to hydrogen. This emphasizes the need to regularly calibrate these devices. Higher humidity tended to increase the reading of the catalytic detector for constant hydrogen content. The catalytic detector was very sensitive to the presence of carbon monoxide but the interfering was only temporary, i.e. when the CO exposure ceases the detector behaves in an ordinary way [2].

Research carried out at the Joint Research Centre, Institute for Energy, The European Commission within the HYPER project demonstrated that the time required by the electrochemical sensor to respond to hydrogen exposure of known concentration becomes longer when the gas flow rate is reduced, i.e. it could be twice longer by solely reducing the flow rate from 100 to 30 ml/min. This

finding is particularly important when the sensor is intended to control the formation of an explosive atmosphere within a FC cabinet [2].

There is another issue related to faster catalytic sensors that is not yet sufficiently addressed in the literature. This is a potential to ignite hydrogen-air mixture with high concentrations of hydrogen by the sensor. The ignition of hydrogen-air mixtures with high content of hydrogen by recombiners was already observed [29].

A variety of methods and sensors types are commercially available to detect the presence of hydrogen [23]. Many of these detectors are suitable for the use in automatic warning and operating systems, see for example ISO 26142:2010 [30] for details concerning stationary systems.

Summary

Unwanted hydrogen releases are followed by the mixing of escaped gas with air, thus establishing the initial conditions for fire and explosion hazards. The unignited releases involve the escape of compressed gaseous hydrogen stored at high pressures at FCH systems and infrastructure. Accidental releases of compressed gaseous hydrogen fall into two main categories: permeation leaks and high pressure jets. One of the important questions for First Responders is whether a release of gaseous hydrogen will lead to the formation of a flammable mixture with air. By using similarity law and under-expanded jet theory First Responders will be able to evaluated the size of the flammable hydrogen envelope and to calculate hydrogen concentration decay along the jet axis. Additionally, First Responders will learn how to calculate the blow-down time and to assess the pressure dynamics in a storage tank of known capacity. Finally, this lecture introduces First Responders to the means of reducing the hazard distance from the point of the release as well as to prevention/mitigation/detection measures of unignited hydrogen releases.

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