

HyResponse

BASICS OF HYDROGEN SAFETY FOR FIRST RESPONDERS

Lecture. Unignited hydrogen releases, their prevention and mitigation



Content

- Compressed hydrogen leaks
 - Expanded and under-expanded jets
 - Sub-sonic, sonic and super-sonic jets
 - Momentum- and buoyancy-controlled jets
- Hydrogen concentration decay
- When a jet becomes buoyant?
- What is a safe PRD diameter?
- Blow-down of a compressed hydrogen storage tank
- Prevention of hydrogen leaks
- Mitigation measures for unignited releases
- Detection of hydrogen leaks



Objectives of the lecture

- Classify unignited hydrogen releases (leaks/jets) and to 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 a 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.



Hydrogen releases

- FC vehicles have on-board hydrogen storage tanks at pressures up to 70 MPa, and a refuelling infrastructure operates at pressures up to 100 MPa.
- Due to the small size of its molecules hydrogen is prone to leak, e.g. permeation.
- The releases may originate from: valves, connections, pinholes in pipes, a full-bore pipe rupture (worst-case scenarios); cylinders, pumps, regulators, etc. Example: [an experiment carried out at SINTEF](#) (Norway).
- A release of hydrogen either through a PRD or from a pipe rupture will result in a high-pressure jet.
- The releases can be unignited (non-reacting) or ignited (reacting).
- Catastrophic release of hydrogen during high-pressure tank rupture, e.g. in a fire.
- Hydrogen releases may occur both indoors and outdoors.

Typical flow rates for hydrogen releases

- **Permeation** of hydrogen, diffusion through the walls or interstices of a vessel, pipes or interface materials (SAE J2578, 2009).
- The **safe permeation rate** for FC vehicles at 20°C is limited to 6 mL/hr per L of a storage tank capacity (The European Regulation for type approval of hydrogen-powered vehicles, 2010). For 170 L capacity – **25.3×10^{-6} g/s.**
- A leak from a broken pipe (150 kW FC): about **3 g/s.**
- A release via PRD (diameter 5.08 mm) from a storage tank at 35 MPa: **390 g/s.**
- A release from an industrial pipeline (diameter 30 cm) at p=2.5 MPa: **100 kg/s.**



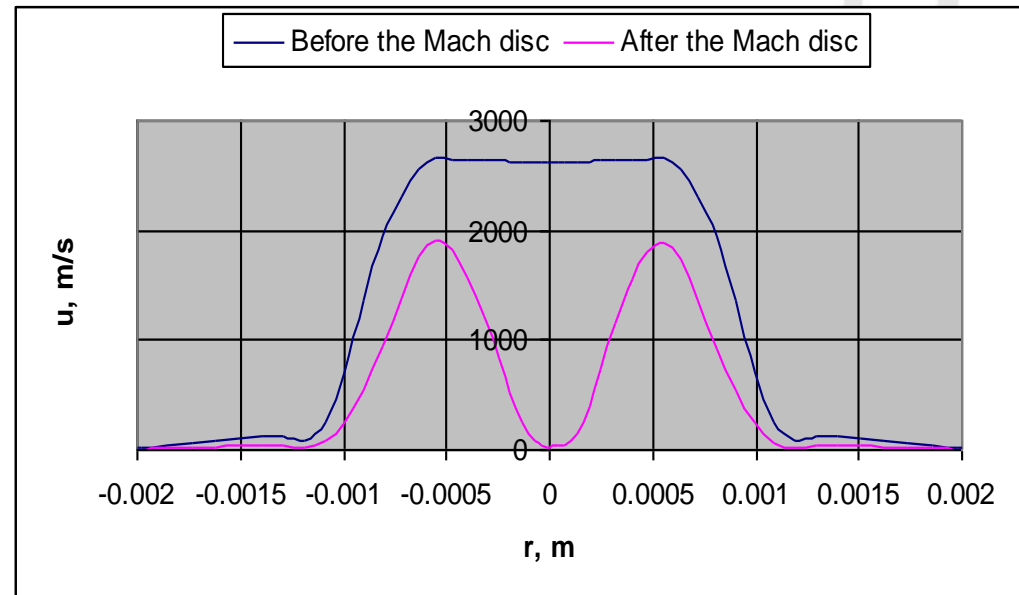
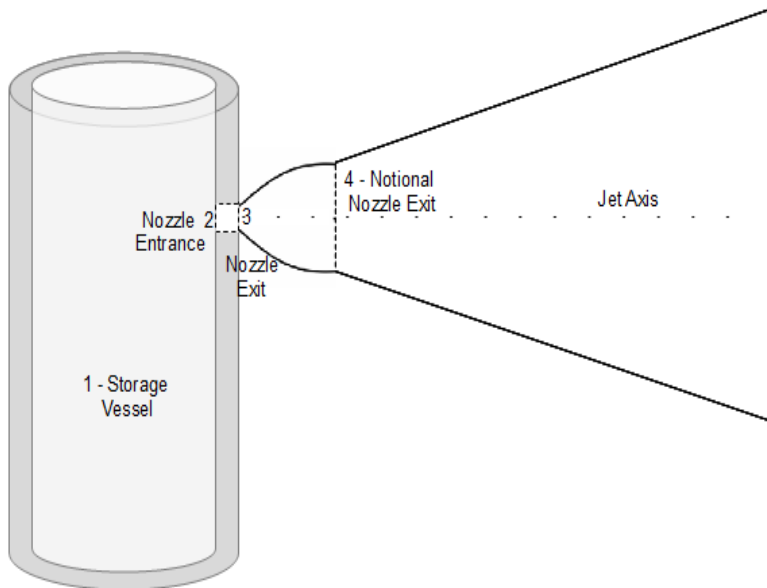
Permeation and dispersion

- The **rate of hydrogen permeation** through a particular material depends on **temperature, internal pressure and the membrane thickness**. The higher is the storage pressure the higher is the permeation rate (refer to Lecture 'Safety of hydrogen storage').
- Three main phenomena drive the dispersion of permeated hydrogen: **buoyancy, diffusion, and natural ventilation**.
- 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.
- Permeated hydrogen is distributed homogeneously in a garage-type enclosure.
- Maximum allowable permeation rate at 20°C for a **passenger car** is **8 mL/hr/L** and for a **FC-bus** **5 mL/hr/L** in a garage-type enclosure. **UU simulations demonstrated that with this level of permeation rate the hydrogen dispersion in a typical garage is not a problem.**



Expanded and under-expanded jets

- **Expanded jet** is a jet with a pressure at the nozzle exit equal to atmospheric pressure.
- **Under-expanded jet** is a jet with a pressure at the nozzle exit above the atmospheric pressure. The exit velocity remains locally sonic (**choked flow**). **Non-uniform velocity!**
- An unscheduled release from a high-pressure storage tank creates a **highly under-expanded jet**.

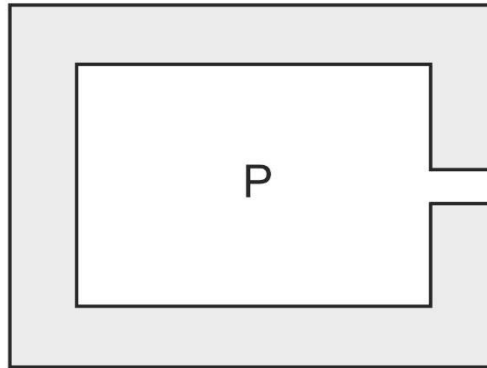


Sub-sonic, sonic and supersonic flows

- Speed of sound: $C = \sqrt{\gamma \frac{P}{\rho}} = \sqrt{\gamma \frac{RT}{M}}$

- Subsonic** flow: velocity $U < C$, $M < 1$

$$\frac{P_s}{P} \geq \left(\frac{2}{\gamma + 1} \right)^{\gamma/(\gamma-1)} = \frac{1}{1.89}$$



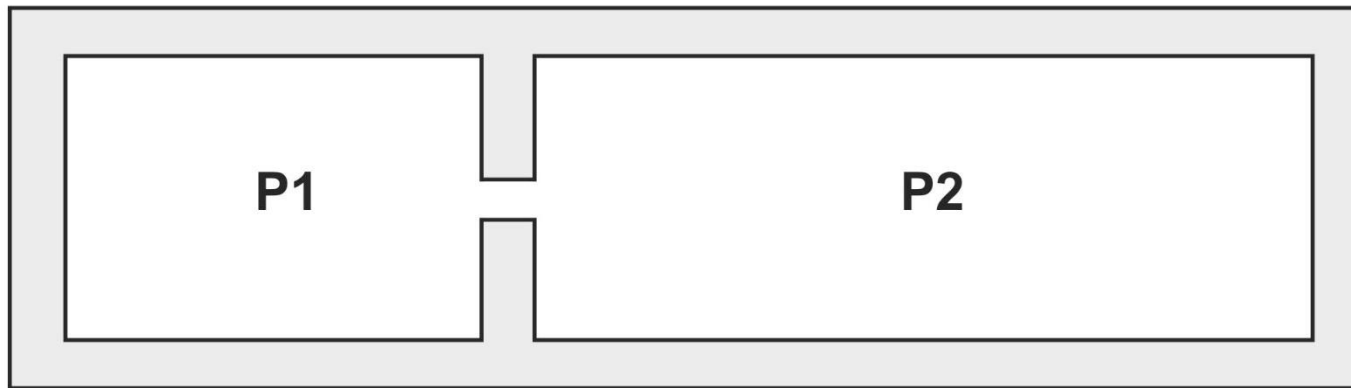
The Mach number (M) of the jet is a dimensionless number equal to a ratio of local flow velocity to the local speed of sound. It is an important parameter in determining its behaviour.

- Sonic** flow: velocity $U = C$ (choked flow at the exit, $M = U/C = 1$)
- Super-sonic** flow: velocity is larger than the speed of sound ($U > C$)

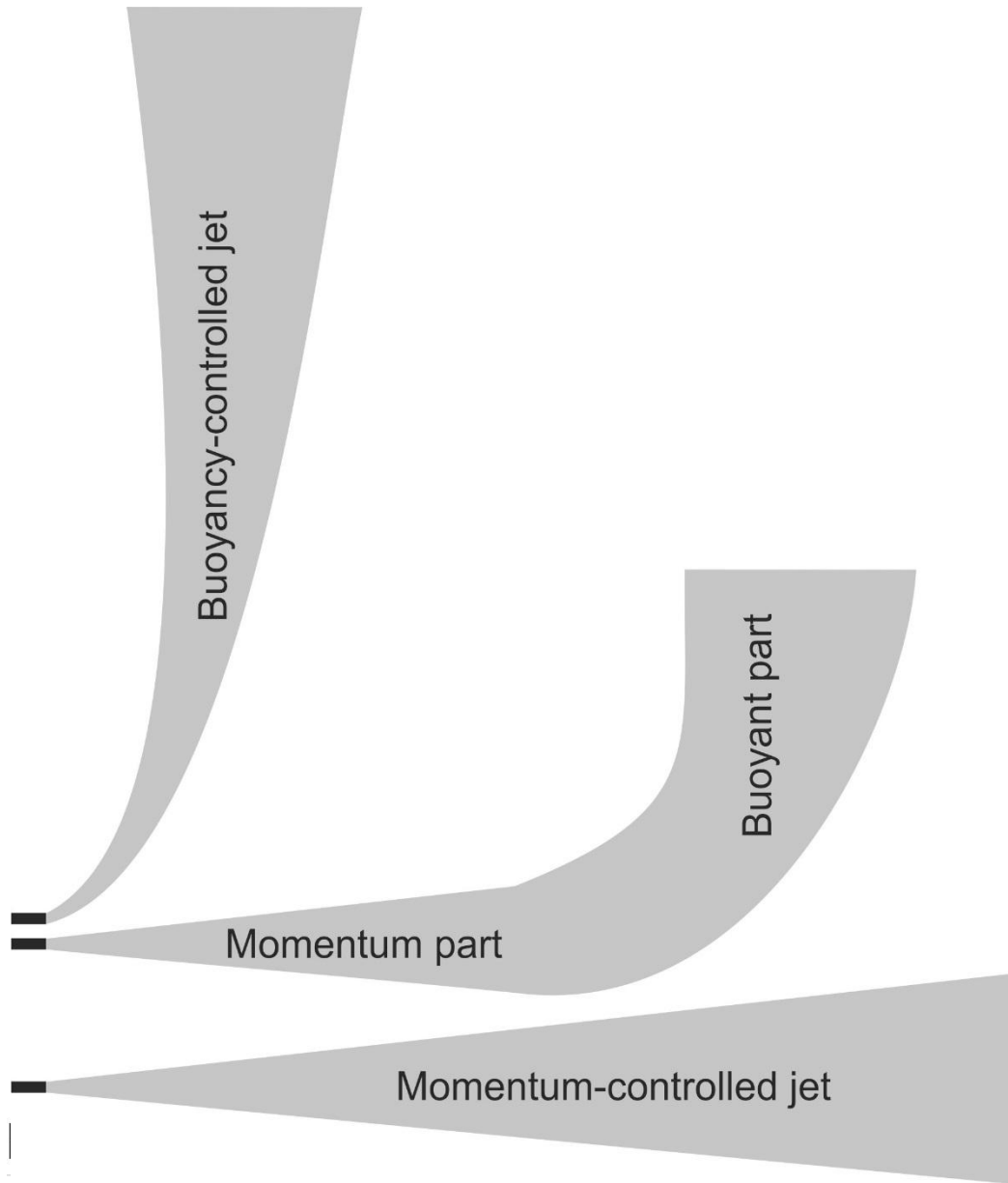


Sub-sonic, sonic and supersonic jets

- **Subsonic matched jets:** ratios of pressure in high-pressure and low-pressure chambers is $P_1/P_2=1-4.1$ (theoretical ratio $P_1/P_2=1.89!$... $P_1/P_N=2$ and $P_N/P_2=2$...)
- **Sonic under-expanded jets:** $P_1/P_2=4.1-41.2$
- **Supersonic under-expanded jets:** $P_1/P_2>41.2$



Momentum vs. buoyancy-controlled jets



- Fully momentum-dominated jet
- Fully buoyancy-controlled jet
- Momentum jet transits to buoyant

Hazard distance (horizontal) strongly depends on a type of jet (effect of buoyancy).

Buoyant jets decay faster than momentum jets (vertical).

The similarity law is a conservative approach

Under-expanded jets: simulations

- Tank pressure **16.1 MPa**
- Nozzle diameter **0.25 mm**
- Mass flow rate **0.46 g/s**

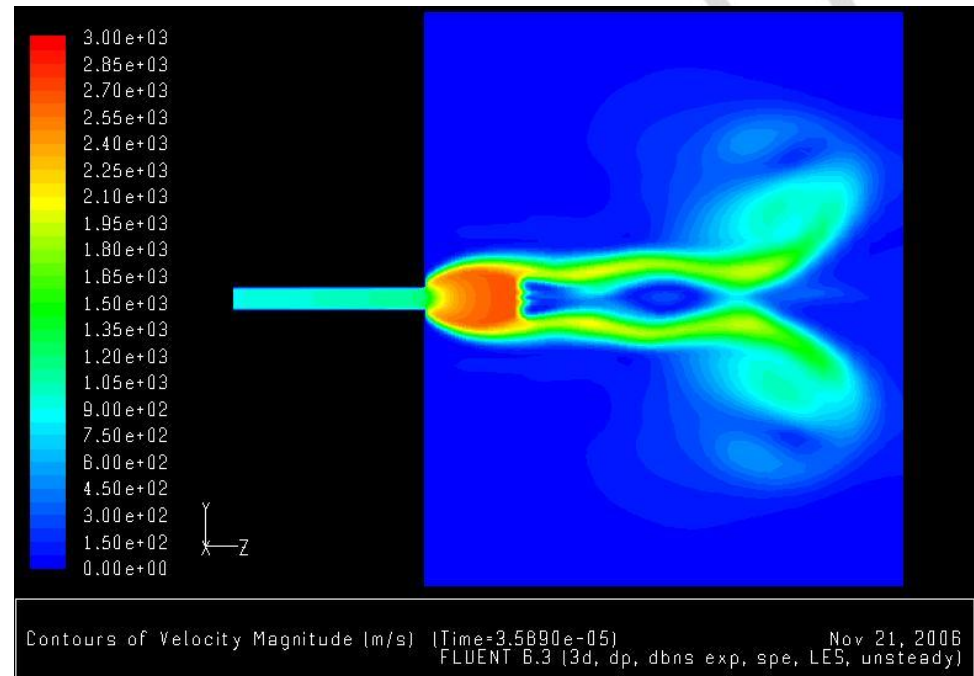
- **Simulations videos:**

[Velocity](#)

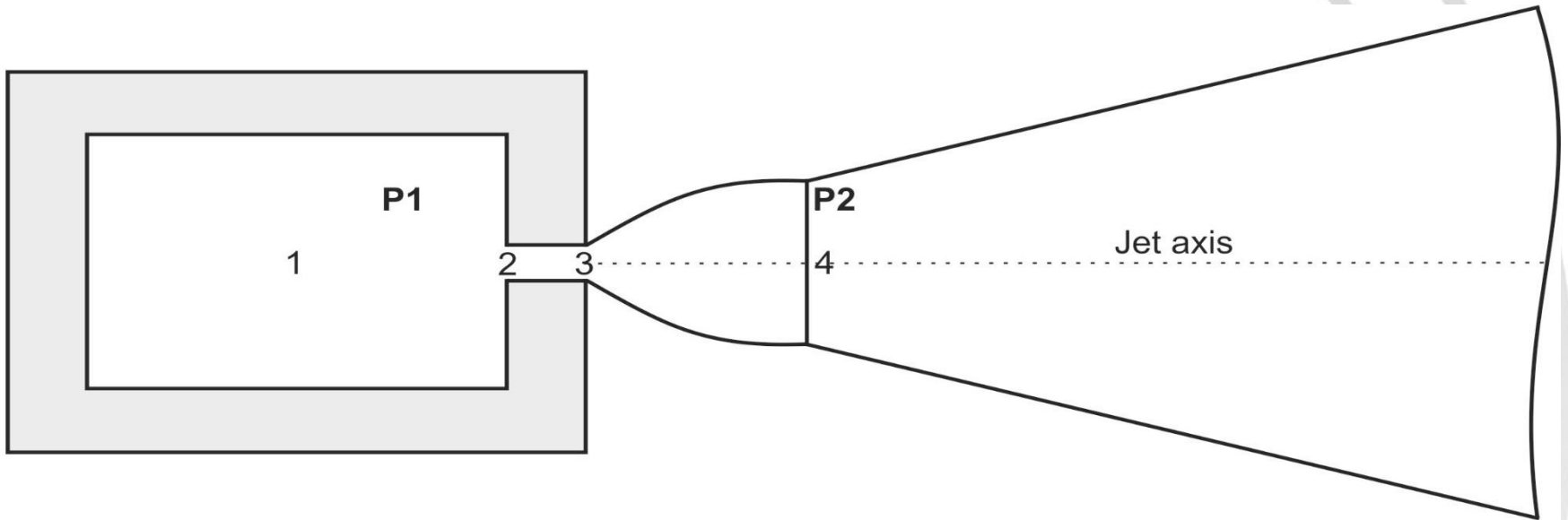
[Hydrogen mole fraction](#)

[Temperature](#)

- Concentration of hydrogen in a jet decays from 100% at the nozzle (point of leak) to the lower values along the jet axis.



The under-expanded jet scheme



1- High pressure vessel

2- Nozzle entrance

3- Nozzle exit (= notional nozzle entrance)

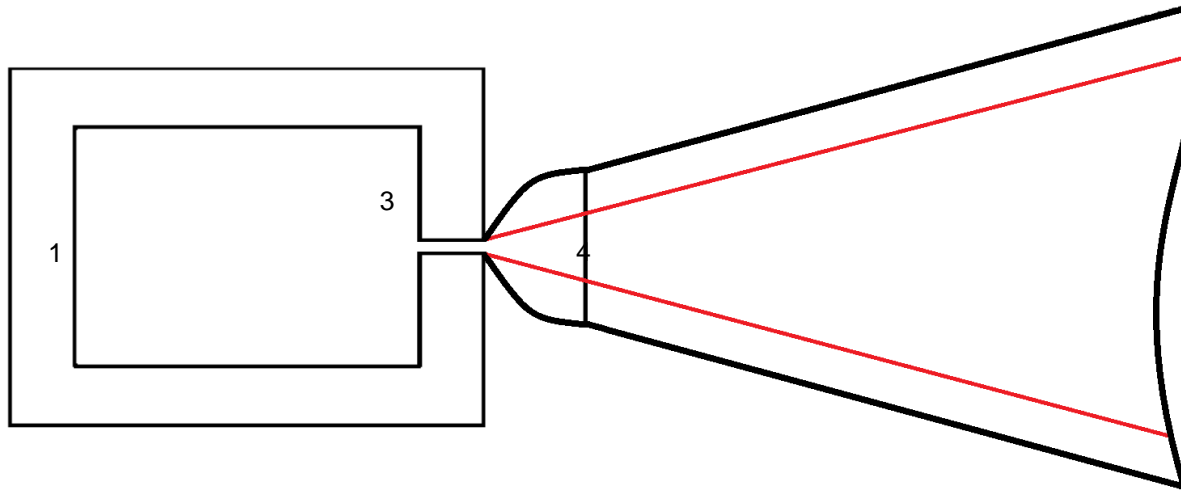
4- Notional (effective) nozzle exit (3-4: no entrainment)

The notional nozzle exit, 4, parameters correspond to fully expanded jet with the pressure equal to ambient and uniform flow velocity equal to local speed of sound. In some cases there can be essential minor and friction losses in the flow pathway 2-3 that cannot be neglected, e.g. the case of very narrow crack.

P_1 Storage pressure

P_2 Atmospheric pressure (after jet expansion)

The expanded and under-expanded jet scheme



Red line – expanded jets; black line - under-expanded jets

1 – reservoir

3 – nozzle

4 – **effective nozzle diameter**, pressure is equal to ambient; velocity is equal to the speed of sound; only for under-expanded jets.

Flammable envelope

- As discussed previously **combustion** is generally of a primary concern when considering harm criteria. In the event of an unscheduled hydrogen release, a **flammable jet** may result. In the event of its subsequent ignition people, structures, equipment and environment may be involved in a fire.
- 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 content 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 of the leak.**



What is a hazard distance?

- As per draft definition, ISO TC197 **hazard distance** is a distance from the (source of) hazard to a determined (by physical or numerical modeling, 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.
- 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**.

Sources: LaChance, J (2009). Risk-informed separation distances for hydrogen refuelling stations. International Journal of Hydrogen Energy, Vol. 34, pp. 5838-5845.

EIGA Determination of safety distances, IGC Doc 75/07/E, Revision of Doc 75/07/rev.



Hydrogen concentration decay

- In order to define where the flammable hydrogen-air mixture is formed it is important to know how the concentration decays, from a 100 vol. % at the nozzle to a concentration of interest at a distance x .
- The original form of the **similarity law** (expanded jets) by Chen and Rodi (1980):

$$C_{ax,m} = 5.4 \sqrt{\frac{\rho_N}{\rho_S}} \frac{D}{x}$$

The mass fraction of leaking gas $\rightarrow C_{ax,m}$

ρ_N \rightarrow Density of the surrounding gas (i.e. air = 1.205 kg/m³)

ρ_S \rightarrow Density of the surrounding gas (i.e. air = 1.205 kg/m³)

D \rightarrow The nozzle diameter

x \rightarrow Distance from the nozzle

with **the only** one **unknown** parameter for under-expanded jets ρ_N - **density in the nozzle** (actual nozzle size is applied here).

The “unknown” density is calculated by the **under-expanded jet theory** developed at Ulster University (ρ_N affects the flammable envelope size of 4 vol. % i.e. 0.00288 mass fraction).



A simple estimate of density in the nozzle: $\rho_N = \left(\frac{p_1}{2} \times \rho_{H_2}^{NTP}\right)$

Useful information

- ❖ The mass fraction (C_m) calculated based on the volumetric (mole) fraction (C_V):

$$1/C_m = 1 + (1/C_V - 1)M_S/M_N,$$

where M_S and M_N are molecular masses of surrounding gas (air) and nozzle gas, respectively.

- ❖ The mass fraction of **0.0282** corresponds to the volumetric fraction of **0.295** (*stoichiometric mixture hydrogen-air*); the mass fraction of **0.044365** corresponds to the volumetric fraction of **0.401** (*maximum burning velocity*), **0.013037** – **0.16**, **0.008498** – **0.11**, **0.005994** – **0.08**, **0.00288** – **0.04** (*LFL*), **0.00141** – **0.02** (*1/2 of LFL*), **0.0007** – **0.01** (*1/4 LFL*).



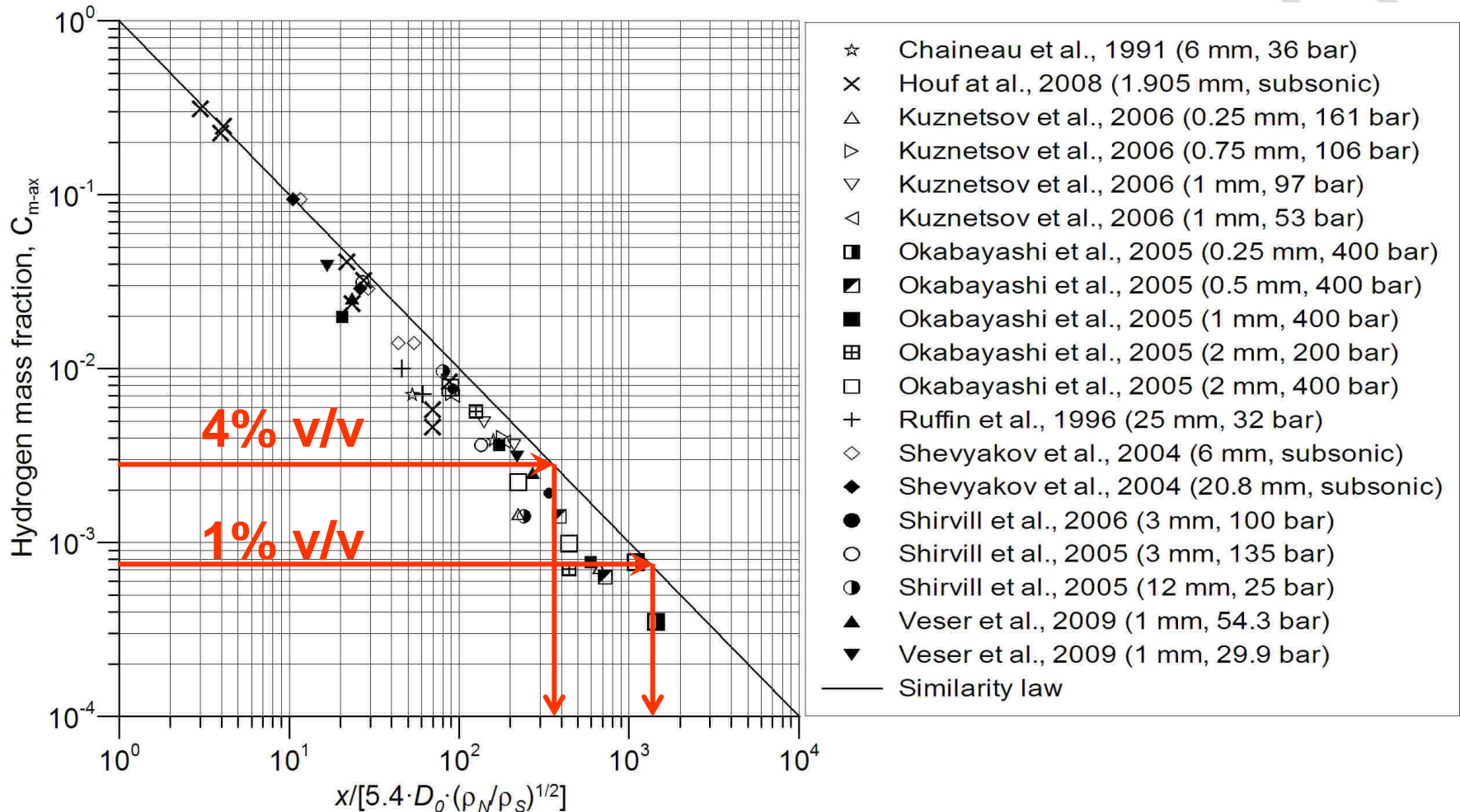
What is axial concentration of interest?

- The ratio of distance x to a concentration of interest to a nozzle diameter D (x/D): (with $\rho_S/\rho_N=14.38$, because $\rho_N=0.0838 \text{ kg/m}^3$, $\rho_S=1.205 \text{ kg/m}^3$ **in the case of fully expanded flow in a real nozzle**):
- $x/D_{30\%}=49.1$; $x/D_{4\%}=491$; $x/D_{2\%}=1003$; $x/D_{1\%}=2019$
- 30 vol. % stoichiometric hydrogen-air mixture
- 4 vol. % is LFL of hydrogen in air
- 2 vol. % - UK regulator applies 50% of LFL (alarm)
- 1 vol. % - shut-down systems.



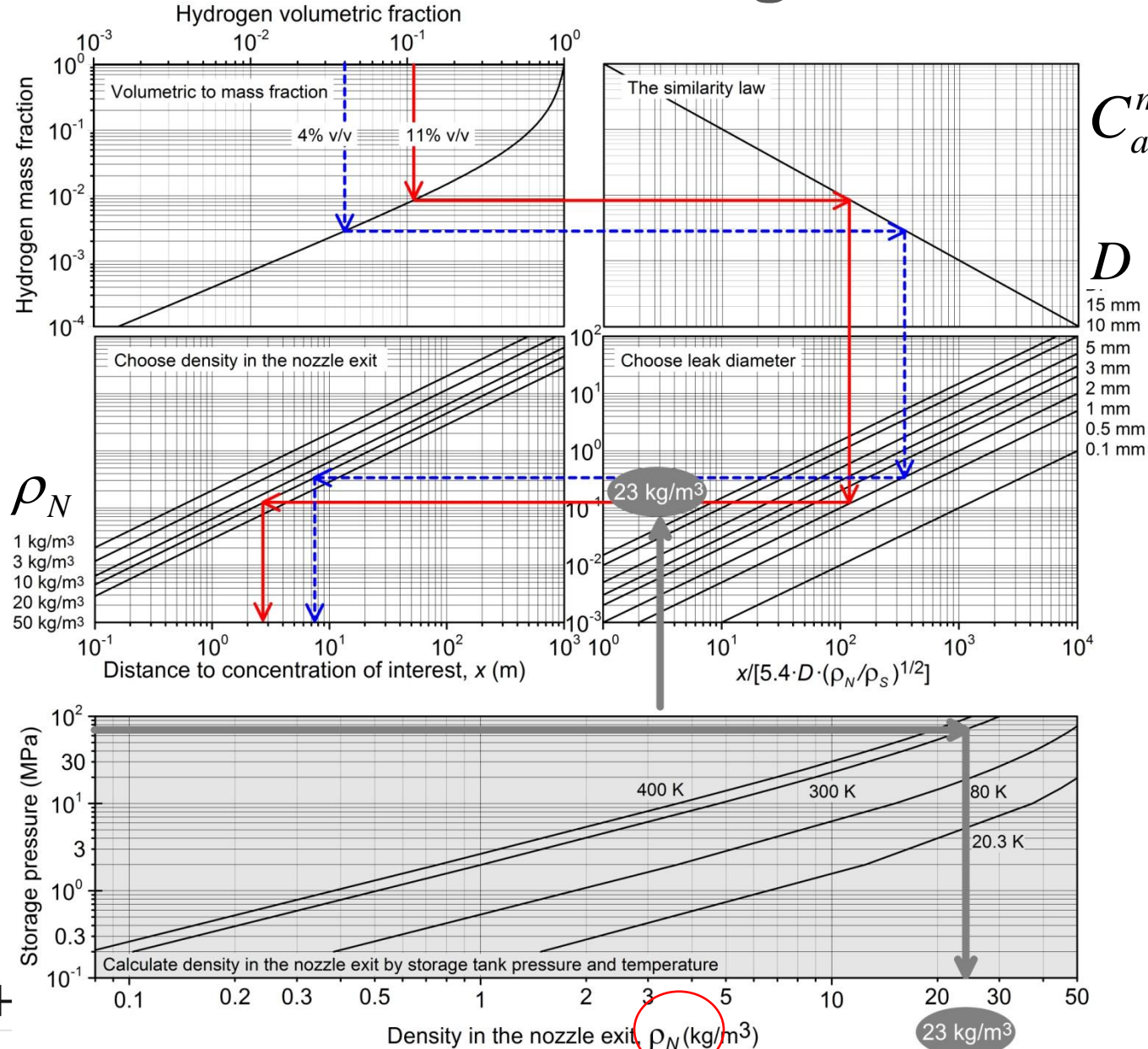
How to calculate jet concentration decay?

The similarity law is conservative to tests - effect of losses



Distance to 4 vol. %: $x_{4\%} = 1708 \cdot \sqrt{\rho_N} \cdot D$

Concentration decay in unignited jets: nomogram



$$C_{ax}^m = 5.4 \sqrt{\frac{\rho_N}{\rho_S}} \frac{D}{x}$$

D

15 mm
10 mm
5 mm
3 mm
2 mm
1 mm
0.5 mm
0.1 mm

23 kg/m³

$x/[5.4 \cdot D \cdot (\rho_N/\rho_S)^{1/2}]$

Density in the nozzle exit, ρ_N (kg/m³)

23 kg/m³

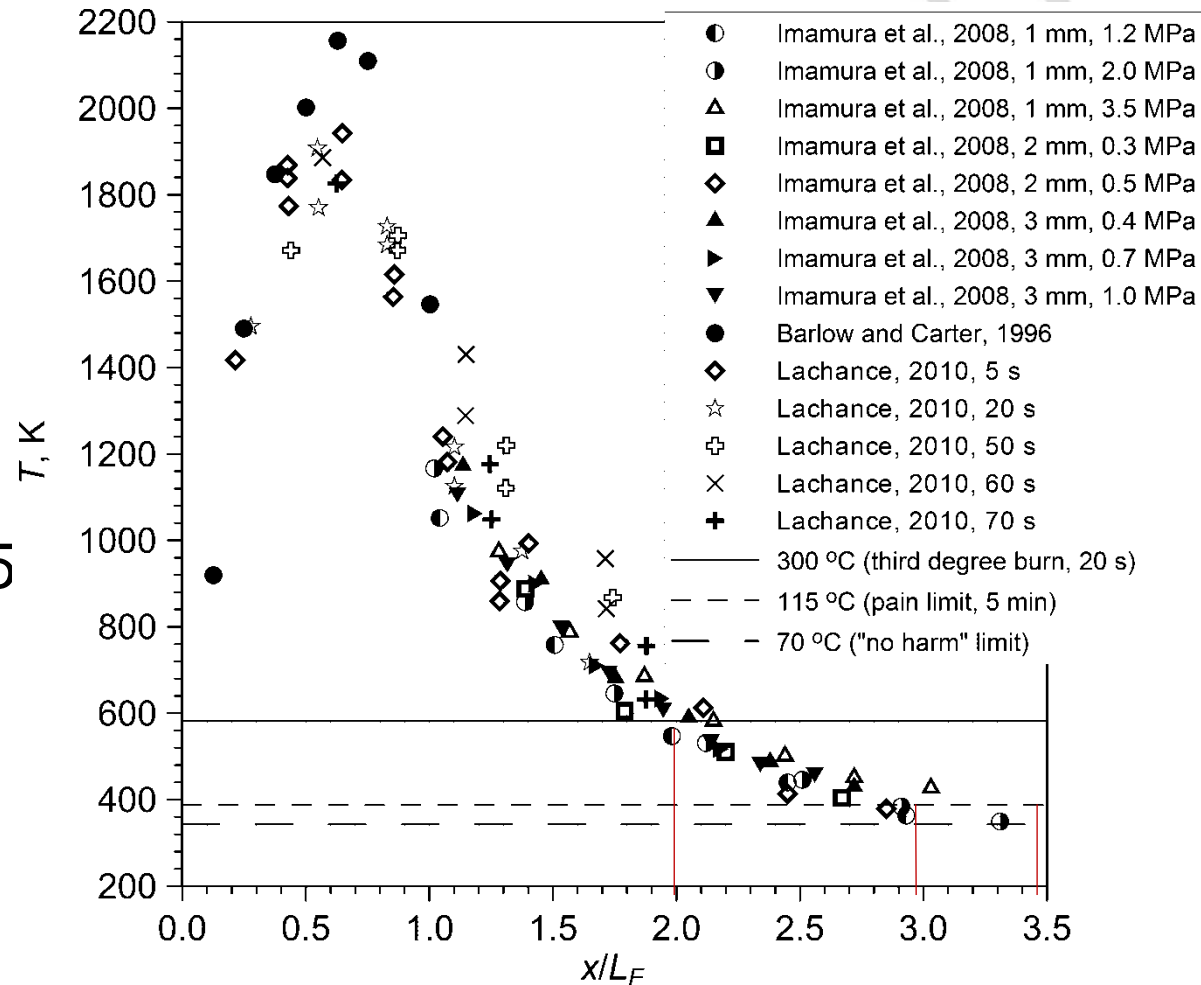
Temperature decay along jet fire axis

- Momentum-dominated leak
- Jet fires (three hazard distances):

$x=3.5L_F$ for “no harm”
(70 °C)

$x=3L_F$ for pain limit (115 °C, 5 min)

$x=2L_F$ for third degree
burns (309°C, 20 s)



Unignited versus ignited jets

$$x_{4\%} = 1708 \cdot \sqrt{\rho_N} \cdot D$$

- The ratios of a hazard distance to *LFL* (non-reacting jet) to three hazard distances based on the choice of harm criteria for jet fire are (**average flame tip location 11 vol. %** in non-reacting jet):

$$x_{4\%}/x_{T=70C} = x_{4\%}/(3.5 \cdot x_{11\%}) = 2.95/3.5 = 0.84 \text{ ("no harm")};$$

$$x_{4\%}/x_{T=115C} = 2.95/3 = 0.98 \text{ ("pain limit")};$$

$$x_{4\%}/x_{T=309C} = 2.95/2 = 1.48 \text{ ("death limit" – unprotected).}$$

- In the conservative case (**flame tip location 8 vol. %**) these ratios:

$$x_{4\%}/x_{T=70C(8\%)} = 2.08/3.5 = 0.59 \text{ ("no harm")};$$

$$x_{4\%}/x_{T=115C(8\%)} = 2.08/3 = 0.69 \text{ ("pain limit")};$$

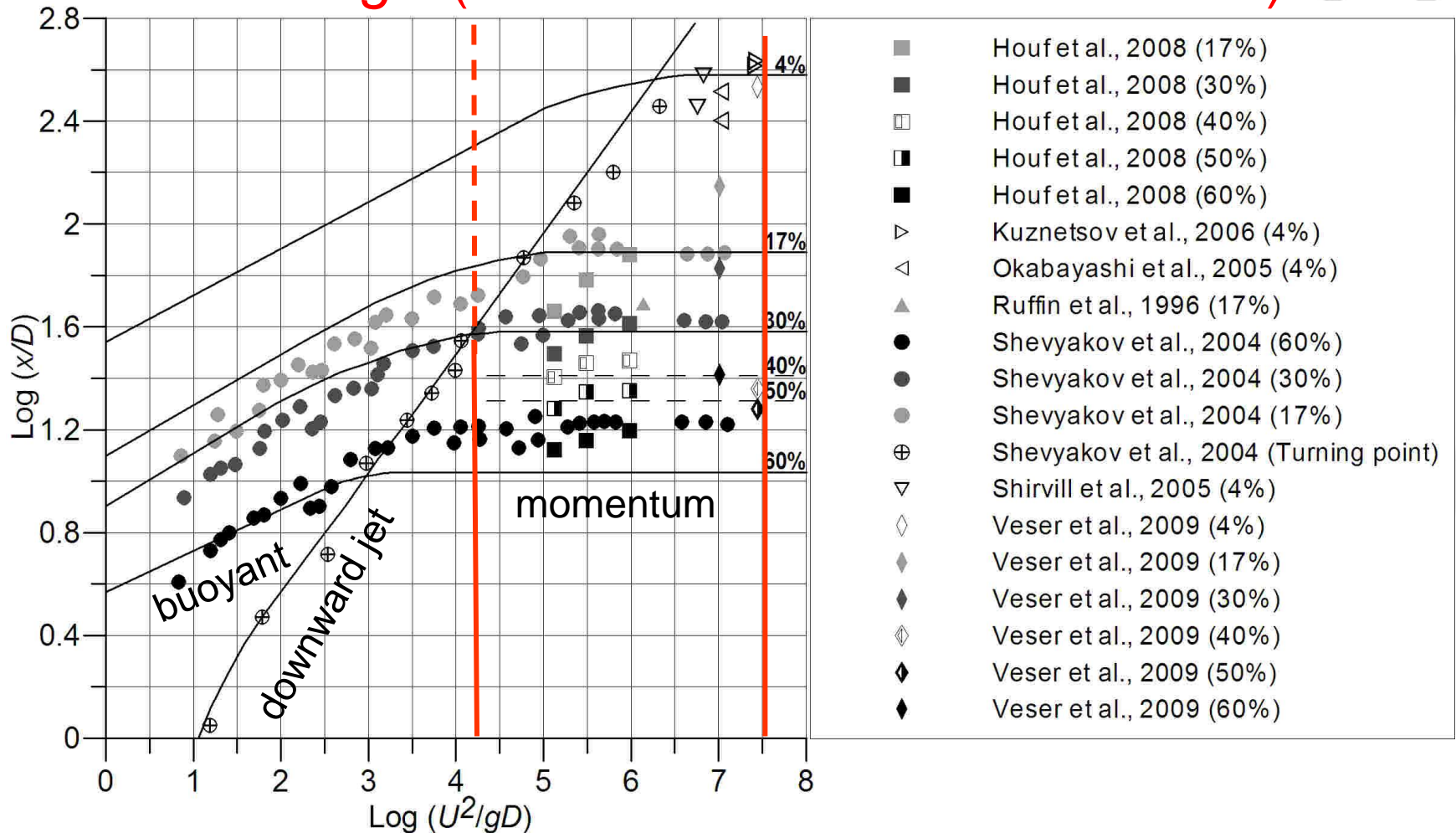
$$x_{4\%}/x_{T=309C(8\%)} = 2.08/2 = 1.04 \text{ ("death limit" – unprotected).}$$

- **“Unexpected” conclusion** - in the conservative case all three distances for jet fire are either longer or equal to the hazard distance based on *LFL* (non-reacting release).

When a jet becomes buoyant?


Start from the Froude number:

$$Fr = U^2 / gD \quad (U \text{ and } D \text{ real or notional nozzle})$$



What is a safe PRD diameter for FC forklifts?

- A forklift in a warehouse
- **Safety strategy:** in a case of upward release from the forklift on-board storage at $p=35 \text{ MPa}$ we would like to exclude formation of a flammable layer under a ceiling (**10 m** above the PRD).
- To realize this strategy the concentration on the jet axis at distance 10 m should be equal or below 4 vol. % (mass fraction $C_{ax}=0.00288$).
- The under-expanded jet theory gives $\rho_N = 14.4 \text{ kg/m}^3$ for storage pressure 35 MPa. Thus, the **PRD diameter** can be calculated straight forward from the similarity law as **1.5 mm**


$$D = \frac{C_{ax}}{5.4} \sqrt{\frac{\rho_s}{\rho_N}} x = \frac{0.00288}{5.4} \sqrt{\frac{1.205}{14.4}} 10 = 0.0015m$$

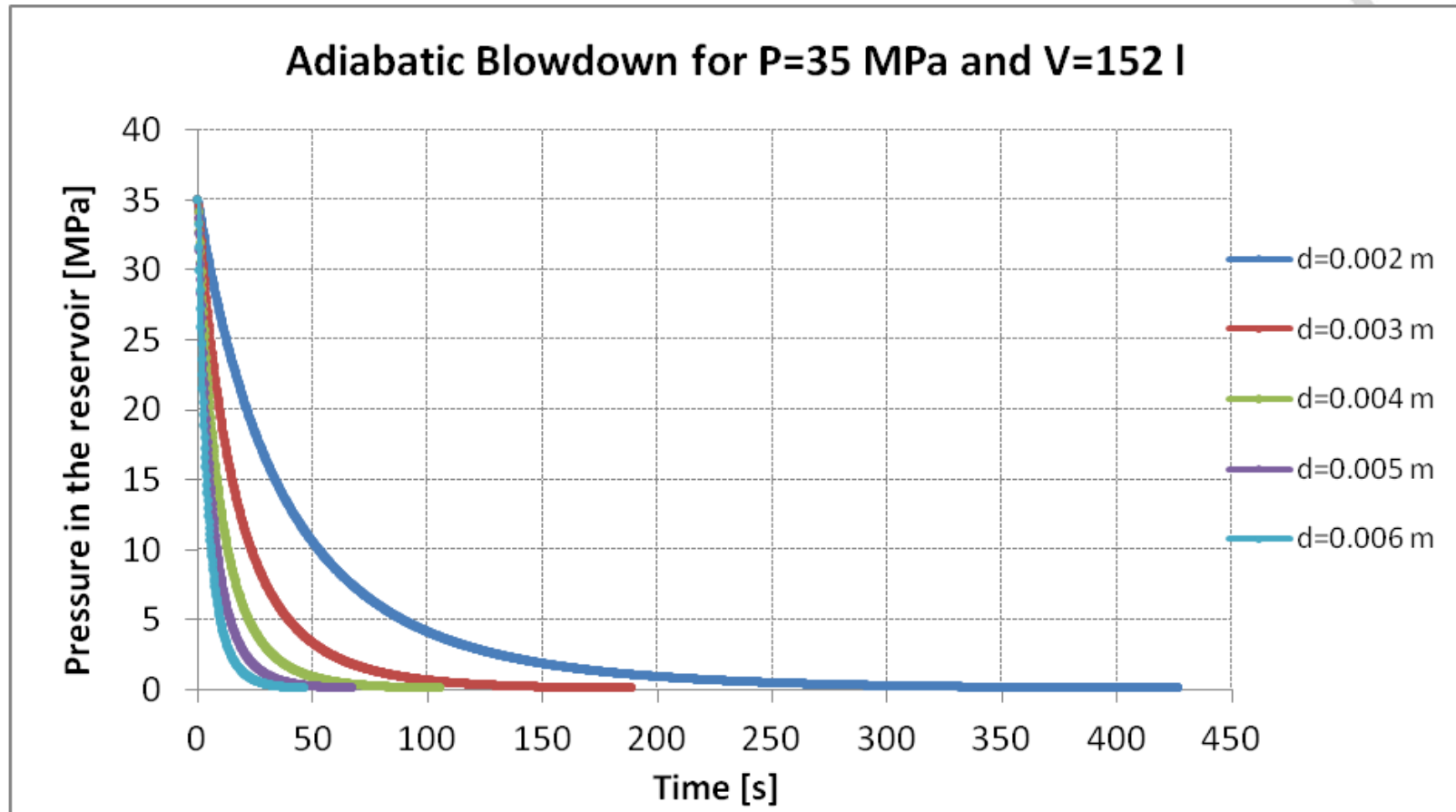
Blow-down of compressed hydrogen storage tank

- An adiabatic blow-down of the on-board storage tank

Veh	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

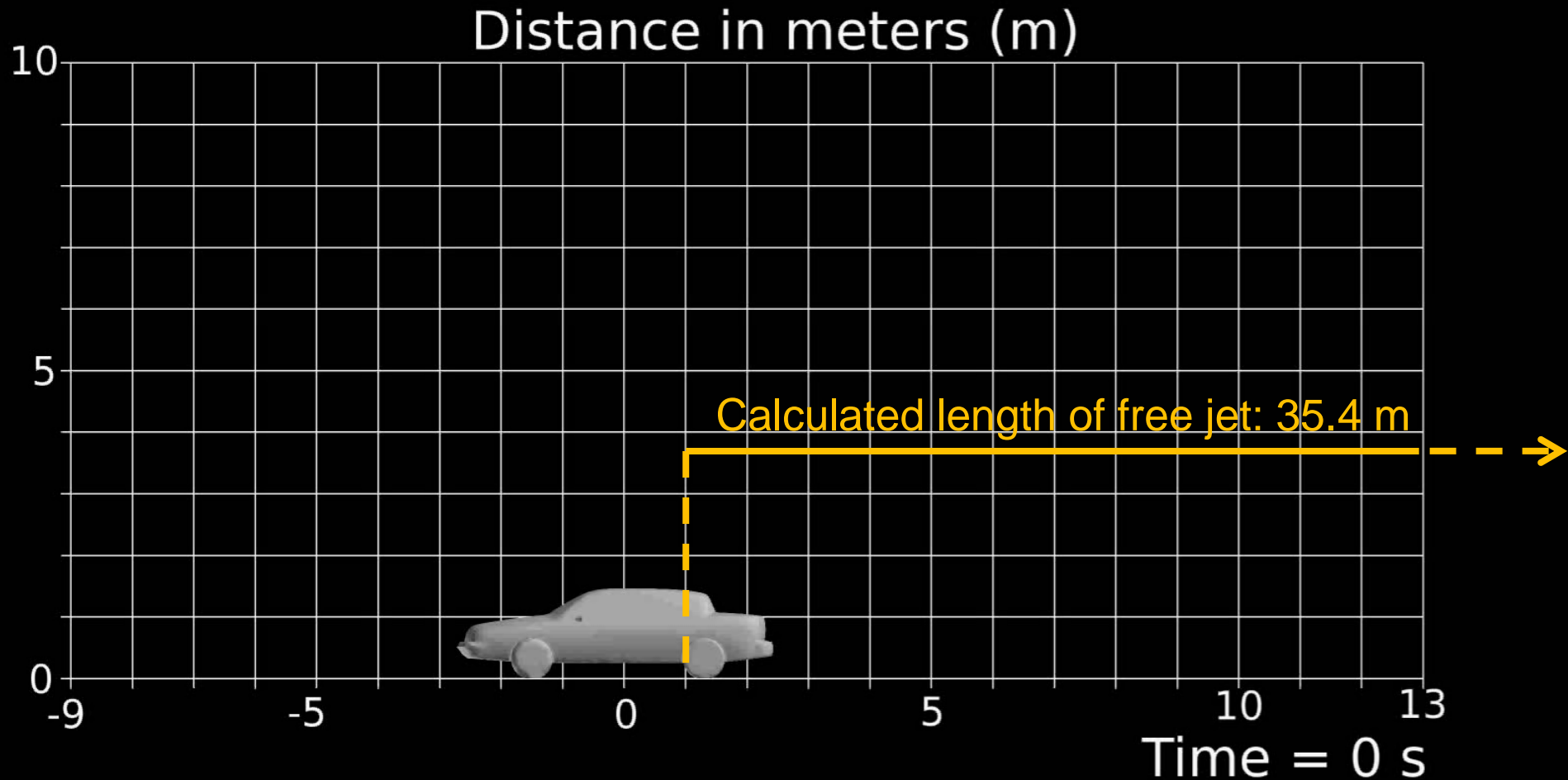
Leakage diameter [mm]	Blowdown time vehicle 1 [s]	Blowdown time vehicle 2 [s]	Blowdown time vehicle 3 [s]	Blowdown time vehicle 4 [s]
2	427	226	502	260
3	189	100	222	115
4	105	56	124	64
5	67	35	79	41
6	46	24	54	28

Pressure drop inside the tanks during the blow-down



Unignited release: 70 MPa

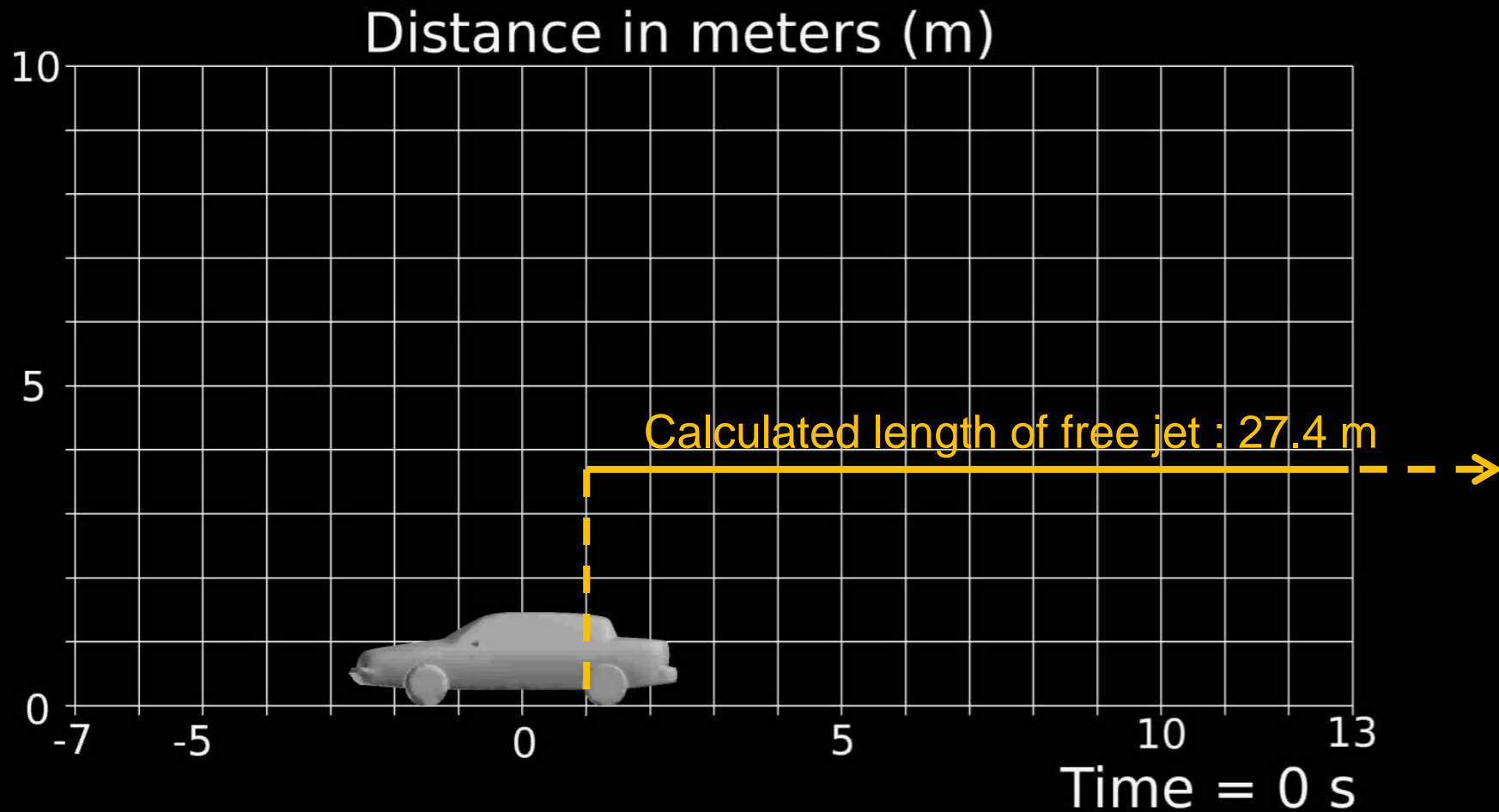
- 4 vol. % envelope
- 4.2 mm release diameter



The largest flammable envelope occurs within 10 s – around **12 m**

Unignited release: 35 MPa

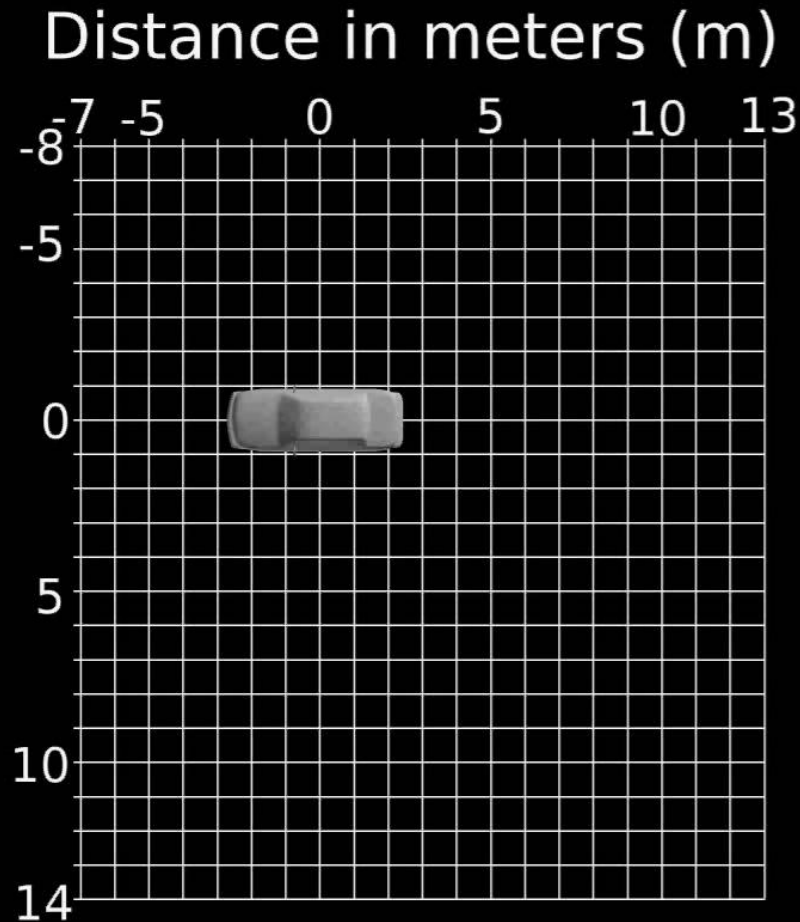
- Side view (4 vol. % envelope)
- 4.2 mm release diameter



The largest flammable envelope occurs within 10 s **from 8 to 11 m**

Unignited release: 35 MPa

- Top view (4 vol. % envelope)

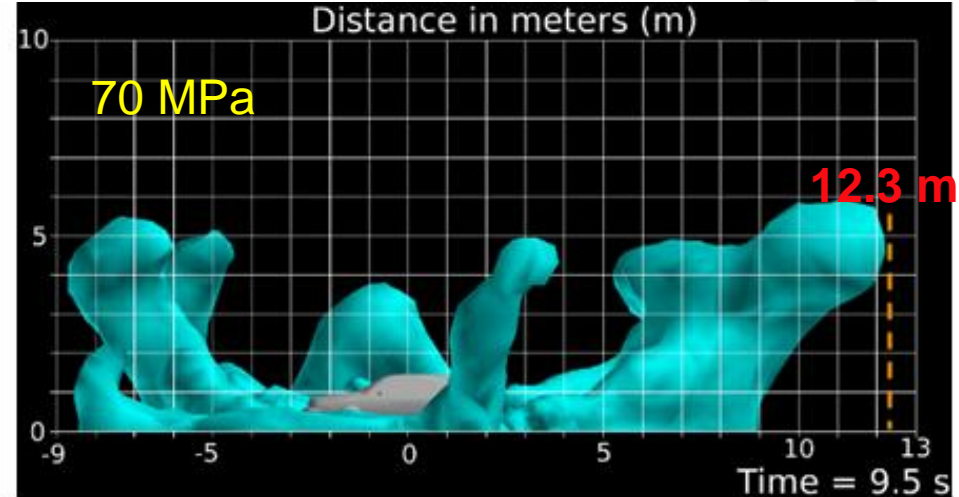
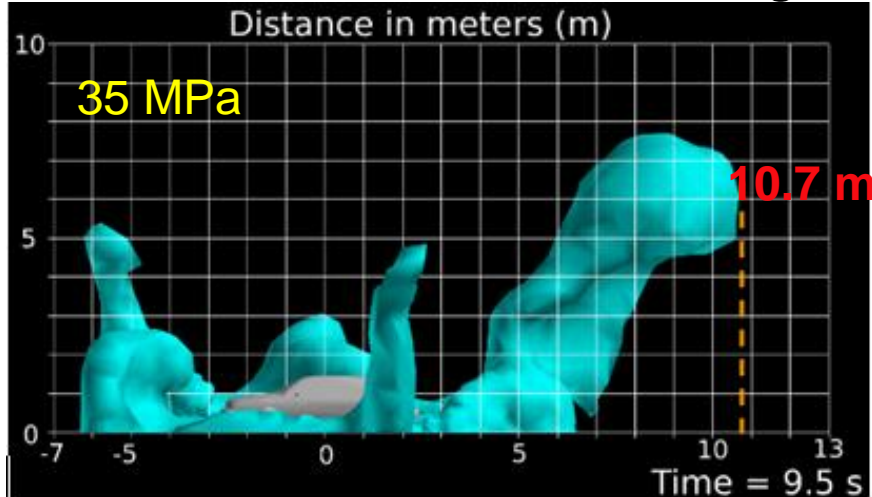


Time = 0 s

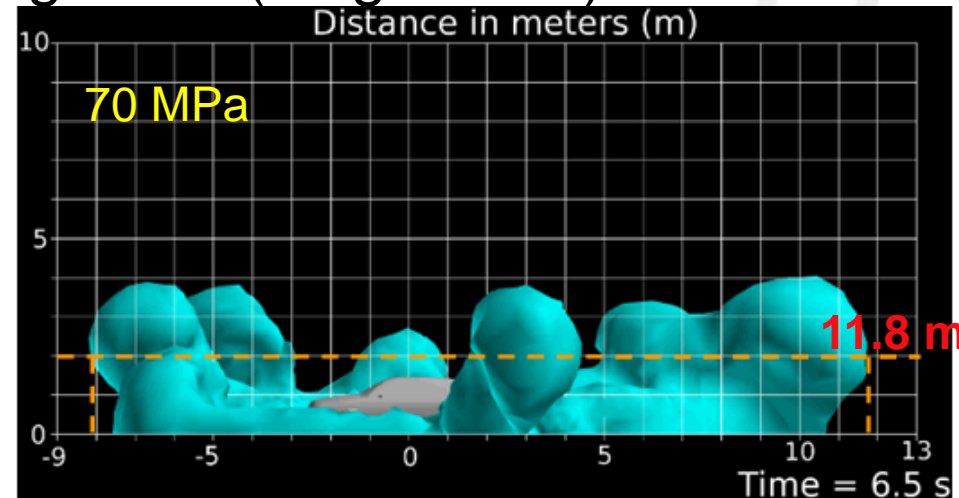
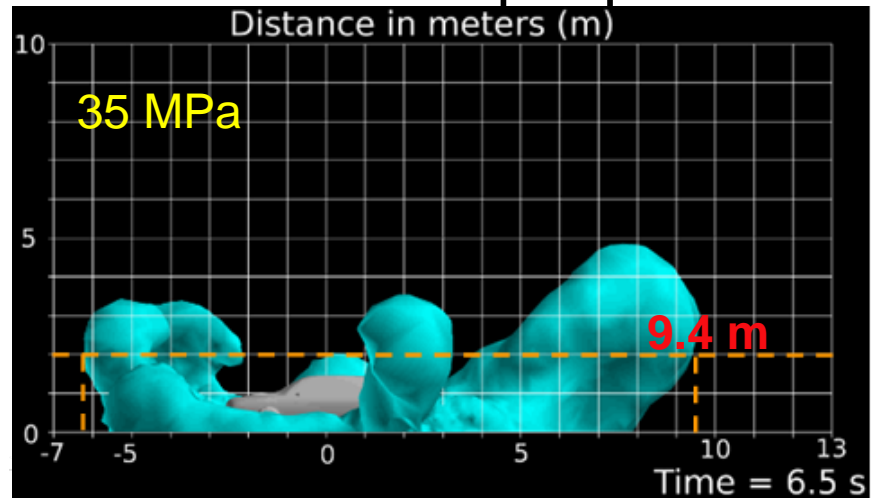
Unignited releases: summary

- Hazard distances

For a building air intake



For people on the ground (height <2m)



Prevention of hydrogen leaks

- Inherently safer design of hydrogen systems.
- Careful materials selection.
- Minimize the quantity of hydrogen that is stored and involved in an operation.
- Equipment design validation.
- Periodic equipment inspection.
- Periodic leak test.

Mitigation of hydrogen leak consequences

- Reduce the size of any potential leak for example by keeping pipe diameters as small as possible, through the use of flow restrictors etc.
- Isolate hydrogen from oxidizers, hazardous materials and dangerous equipment.
- Use of alarms and/or warning devices (including hydrogen and fire detectors).
- Avoid ignition sources.
- Prevention flammable atmospheres forming, e.g. by ventilation.
- Elevation of hydrogen systems, use of flow meters, etc.
- Use outdoor location when possible.
- Avoid congestion.



Detection of hydrogen leaks

Detectors/sensors can be used to detect releases, automatically shut down systems, activate alarms, and notify First Responders.

- Suggested locations:

- 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.

- Hydrogen detectors locations for a Fuel Cell Electric Vehicle (FCEV):

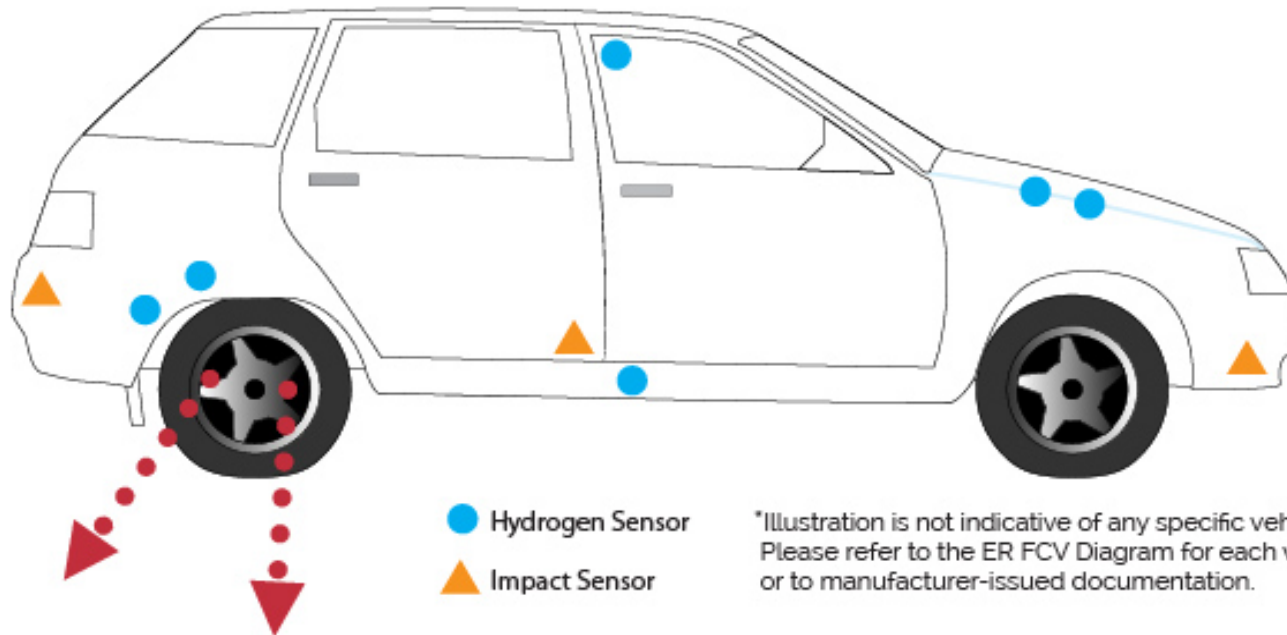
- Exhaust pipe (process control)
- Passenger cabin (safety)
- Engine (safety)



Fuel cell stack (safety)

Source: ISO/TR 15916 (2004). Basic considerations for the safety of hydrogen systems. International Organization for Standardization. ISO Technical Committee 197 Hydrogen Technologies. International Organization for Standardization, Geneva.

Possible locations of hydrogen detectors/sensors in a FC car



*Illustration is not indicative of any specific vehicle's sensors. Please refer to the ER FCV Diagram for each vehicle model or to manufacturer-issued documentation.



Hydrogen sensors detect hydrogen leaks in the passenger cabin and through the vehicle. It's very unlikely that the fuel system will leak, however if the sensors detect a leak a solenoid will close and seal hydrogen in the tank. In addition, electrical relays open to shut down the vehicle and isolate the high voltage.



Impact sensors detect collision, just as air bag sensors do. This also seals fuel in the tank and isolates high voltage. (Buses do not have this sensor)

Source: California Fuel Cell Partnership, http://cafcp.org/toolkits/safety/safety_systems

Hydrogen detectors (1/2)

Apart from the stationary detection system hydrogen system operators should also have a portable hydrogen detector available for their use in and around a hydrogen system. A commonly used concentration level for main alarm is 1 vol. % hydrogen in air, which is equivalent to 25% of the LFL. This level normally should provide an adequate time to respond in appropriate manner, such as system shut-down, evacuation of personnel, or other measures as necessary. A warning may be given earlier.

- 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



- More than one sensor platform necessary to reach all target specifications.
- Combination of sensor platforms shows best results.

Hydrogen detectors (2/2)

Factors to consider while selecting 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
- Temperature, pressure, flow, humidity sensors for monitoring and control are commercially available



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