Introduction to Hydrogen Safety Engineering

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Public perception

The 1937 Hindenburg dirigible disaster

No explosion
Why hydrogen?

- **Fossil Fuel Reserves** (Proven reserves based on current production; source: World Coal Institute):
  - Coal: 200 years
  - Gas: 70 years
  - Oil: 40 years

- **Geopolitical fears**: fossil fuel depletion, potential wars
- **Independence of energy supply**
- **Environment pollution**: green hydrogen (zero emission): renewable energy (wind, tide, solar, hydro) – hydrogen storage – fuel cells – vehicles, stationary and portable applications
- **Climate change**

- **Global market is projected to be $8.5B by 2016.**
Space shuttle Challenger disaster (1986)
At 9:11 am on November 4, 2009, the refinery experienced a catastrophic failure of a **25 cm pipe** off the bottom of a reactor in the Mobil Distillate Dewaxing Unit.

At the time, the unit was undergoing a special operation to regenerate the catalyst. This operation involved circulating **high-pressure hydrogen** inside the piping, at a temperature of 800 F and a pressure of **43 bar**.

There’s a release and almost instantaneously the gas ignites in large fireball estimate to be **35 m high**.

The damage from the explosion in the residential neighborhood east of the facility.

Clearly this explosion had the potential to cause deaths or serious injuries had it occurred even a few moments earlier or later in the day. There were 4 workers near the process unit at the time of the explosion. They were blown to the ground. Another worker had been taking readings next to the pipe that failed just 1-2 minutes before the release.
Fukushima nuclear plant (2011)
Hydrogen safety

- Hydrogen safety studies were initiated decades ago - result of accidents in the process industries, and were supported by safety research for nuclear power and aerospace sector.
- However, the Challenger Space Shuttle (2007) and the Fukushima nuclear (2011) tragedies demonstrated that our knowledge and engineering skills to deal with hydrogen require more investment both intellectual and financial.
- Hydrogen is getting out of hands of trained professionals in industry and become everyday activity for public (700 bar). This implies a new safety culture, innovative safety strategies, breakthrough engineering solutions.
- It is expected that the level of safety at the consumer interface with hydrogen must be similar or exceeds that present with fossil fuel usage.
- Safety parameters of hydrogen and fuel cell products will directly define their competitiveness on the market.
Scope of hydrogen safety engineering

**HSE:** application of scientific and engineering principles to the protection of life, property and environment from adverse effects of incidents involving hydrogen.

World’s first MSc in Hydrogen Safety Engineering

[http://www.ulster.ac.uk/elearning/programmes/view/course/10139](http://www.ulster.ac.uk/elearning/programmes/view/course/10139)
Early “propaganda”

Hydrogen jet fire and gasoline fire: 3 and 60 seconds after car fire initiation

\[ t_1 = 3 \text{ s} \quad \text{and} \quad t_1 = 60 \text{ s} \]
Coming soon…?

HFC Vehicle gasoline pool fire test

Just before PRD initiation

1 s after PRD initiation

10 m fireball
Coming soon…?

The HFCV with initiated PRD (on the left) and the gasoline car (on the right)

No safeguarding by first responders?
External fire tests to initiate PRD

a. Light oil pool fire

b. Cedar wood flame

c. Propane burner

d. Vehicle fire
Upward release from current PRD

Vehicle equipped with two 34 L capacity cylinders at 350 bar and “normal” PRD.

Do we accept 10-15 m flame from a car?
No harm distance is 25-40 m (plus jet noise)!
Downwards release from PRD

Fire was initiated on the instrumentation panel ashtrays. The PRD was actuated 14 min 36 s (upward scenario) and 16 min and 16 s (downward). Blowdown < 5 min (no tank failure, but…).

...what if this car is indoor?
Barriers (free jet 16.5 kPa)

42kPa)

57kPa)
Barrier 60°: 9.5 mm, 800 ms (57 kPa)
High pressure electrolysers

Cell failure mechanism at pressures above 50 bar is under investigation by French-Russian group.
400 bar electrolyser (Japan)

**Titanium** electrolyser before and after the combustion in oxygen

http://www.nsc.go.jp/senmon/shidai/kasai/kasai004/ssiryo4-1.pdf
400 bar electrolyser (Japan)

Titanium electrolyser materials (fluorine from the membrane) were dispersed into surroundings: car windshield before and after (few days) the accident.
Permeation (1/2)

CFD: negligible stratification
(no areas of 100% hydrogen)

Max concentration at 133 min:
tank top - $8.2 \times 10^{-3}$ % by vol.;
ceiling - $3.5 \times 10^{-3}$ % by vol.
Thus, with homogeneously dispersed permeated hydrogen, at reasonable minimum natural ventilation rate of 0.03 ACH, at reasonable maximum prolonged material temperature of 55°C (test temperature factor 4.7 for 15°C), with aging factor 2, the maximum hydrogen concentration will not be above 1% by vol if permeation rate for new tank is below 6 NmL/hr/L (15°C), or 8 NmL/hr/L (20°C).

For comparison:
- JARI: 5 NmL/hr/L (15°C).
- SAE J2579, end of life, 55°C: 150 NmL/min/vehicle (HySafe equivalent figure would be 90 NmL/min/vehicle)
- ISO/TS15869:2009 at end of life (20°C): 75 NmL/min/container

**CFD – contemporary tool for HSE**

UU simulation of UNIPI experiment
**H2 release in a fuel cell**

**Scenario A:**
- H2 flow rate 40 NL/min
- H2 release duration 1200 s
- H2 concentration profiles: 0.5%, 2%, 4%
Indoor: pressure peaking phenomenon!

Small garage LxWxH=4.5x2.6x2.6 m ("brick" vent).
Mass flow rate 390 g/s (H₂: 350 bar, 5.08 mm orifice).

Solution: decrease PRD orifice size and increase fire resistance of onboard storage

\[
\dot{V}_{\text{vent}} = CA \left\{ \frac{2\gamma}{\gamma - 1} \frac{P_S}{\rho_{\text{encl}}} \left[ \left( \frac{P_S}{P_{\text{encl}}} \right)^\frac{2}{\gamma} - \left( \frac{P_S}{P_{\text{encl}}} \right)^\frac{\gamma + 1}{\gamma} \right] \right\}^{1/2}
\]
Microflames: tests and CFD

- **Hazard**: the small leak burns undetected for a long period, damaging the containment system and providing an ignition source.
- **Left flame**: hydrogen downward into air (3.9 $\mu$g/s, 0.46 W). ID=0.15 mm. Exposure 30 s.
- **SAE J2600 permits** hydrogen leak rates below 200 mL/hr (0.46 $\mu$g/s) – no flame!

Sunderland et al. (USA)
Quenching and blow-off limits

Dependence on tube diameter
The open atmosphere – 10 kPa (1/2)
The open atmosphere – 10 kPa (2/2)

Hemisphere 10 m diameter (Fraunhofer ICT)

![Graphs showing flame radius and overpressure over time for different diameters and models, with data points and lines for experiment and models v2.2b with diameters of 2.20 and 2.33 m.](image)
Experiment SRI: open atmosphere

Groethe, M., et al. 1st ICHS: 30% hydrogen-air ($D_{CJ}=1980$ m/s, $H_c=3.2$ MJ/kg) in polyethylene balloon of radius $R=5.23$ m; Direct initiation; Blast wave overpressure was recorded at the radius $R=15.6$ m and the corresponding blast wave impulse was calculated.
LPG car (pressure activated PRD)

T-activated PRD for hydrogen vehicles
Bonfire test (CNG, no PRD)
Bonfire test: Type 4 tank (no PRD)

“Fire resistance” is 1-6 minutes. No combustion contribution to the blast.
“Unsafe” (misleading) statements

(-) Sunavala, Hulse, Thring, 1957: “Calculated flame length may be obtained by substitution the concentration corresponding to the stoichiometric mixture (29.5% of H2 in air) in equation of axial concentration decay for non-reacting jet”

(-) Bilger and Beck, 1975: flame length is defined “for convenience” as the length on the axis to the point having a mean composition which is stoichiometric (H2 concentration is twice of O2).

(-) Bilger, 1976: the calculated flame length may be obtained by substitution the concentration corresponding to the stoichiometric mixture in the equation of axial concentration decay for a non-reacting jet.
Where is a jet flame tip location?

- **Flammable envelope** = 4% v/v (LFL)
- **Flame tip location** = 11% v/v in unignited jet (8-16%)

Flame is from 2.2 times (16%) to 4.7 times (8%) longer than the distance to axial concentration 29.5% (stoichiometric hydrogen-air mixture).!
The switch-of-axes phenomenon

Plane jets (cracks, flanges)

Round jet \( \frac{C_{ax}}{C_N} = 5.4 \sqrt{\frac{\rho_N}{\rho_S}} \frac{D}{x} \)

Plane 2D jet \( \frac{C_{ax}}{C_N} = 2.13 \sqrt{\frac{\rho_N}{\rho_S}} \sqrt{\frac{D}{x}} \)

How it decays compared to axisymmetric jets?
Innovative PRD1 (350 bar)

Flame length reduction: $7.5 \rightarrow 1.8 \text{ m}$
Innovative PRD2 (350 bar)

Flame length reduction: $6.1 \rightarrow 1.8$ m
Innovative short flame PRD

Current PRD

Back view

Current PRD

Side view

Short flame PRD

Short flame PRD
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