Royal Netherlands Navy

Hydrogen Safety

Introduction of hydrogen risk awareness

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RISK AWARENESS HYDROGEN SAFETY

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Delft University of Technology.

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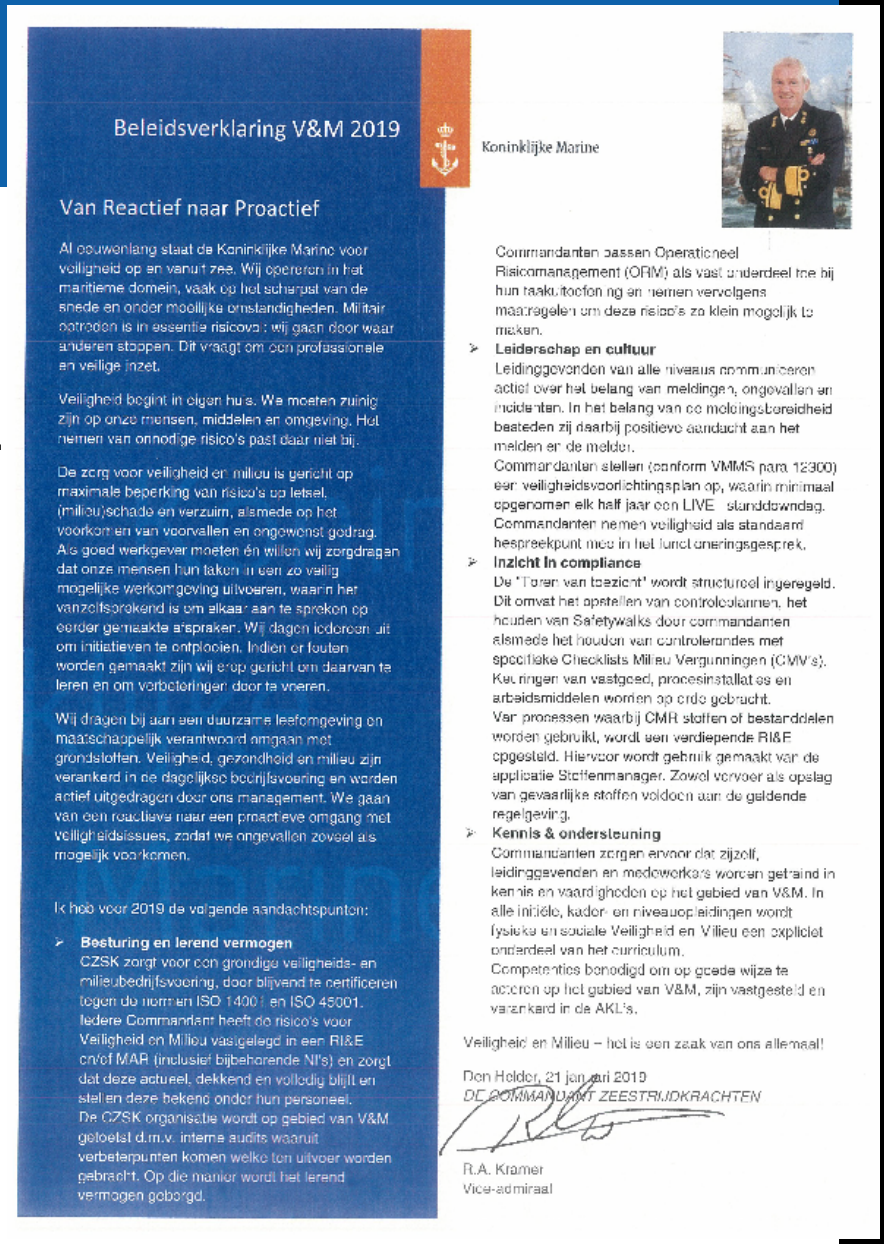
Topics

- Introduction Safety Policy Royal Dutch Navy
- Atomic Structure Hydrogen
- Physical properties Hydrogen
- Hydrogen Hazards
- AtEx requirements
- Hazardous Area classification
- Hazard identification method (Know the hazards, understand the risks)
- Explosion Safety Documentation

Introduction
Safety Aspects of Hydrogen as an Energy Carrier

Policy Safety & Environment Royal Dutch Navy

- **Optimum reduction** of risks to loss of life, injury and property damage.
- Ensure a **SAFE** working environment.
- **Honor** mutual agreement on establishing a safety culture.
- **Learn** from mistakes.
- **Be Pro active.**
- **Be Compliant** with law, legislation and best practices.



Beleidsverklaring V&M 2019

Koninklijke Marine

Van Reactief naar Proactief

Al eeuwenlang staat de Koninklijke Marine voor veiligheid op en vanuit zee. Wij opereren in het maritieme domein, vaak op het scherpst van de snede en onder moeilijke omstandigheden. Militair optreden is in essentie risicovol: wij gaan door waar anderen stoppen. Dit vraagt om een professionele en veilige inzet.

Veiligheid begint in eigen huis. We moeten zuinig zijn op onze mensen, middelen en omgeving. Het nemen van onnodige risico's past daar niet bij.

De zorg voor veiligheid en milieu is gericht op maximale beperking van risico's op letsel, (milieu)schade en verzuim, alsmede op het voorkomen van voorvallen en ongewenst gedrag. Als goed werkgever moeten én willen wij zorgdragen dat onze mensen hun taken in een zo veilig mogelijke werkomgeving uitvoeren, waarin het vanzelfsprekend is om elkaar aan te spreken op eerder gemaakte afspraken. Wij dagen iedereen uit om initiatieven te ontplooien. Indien er fouten worden gemaakt zijn wij erop gericht om daarvan te leren en om verbeteringen door te voeren.

Wij dragen bij aan een duurzame leefomgeving en maatschappelijk verantwoord omgaan met grondstoffen. Veiligheid, gezondheid en milieu zijn verankerd in de dagelijkse bedrijfsvoering en worden actief uitgedragen door ons management. We gaan van een reactieve naar een proactieve omgang met veiligheidsissues, zodat we ongevallen zoveel als mogelijk voorkomen.

Ik heb voor 2019 de volgende aandachtspunten:

- **Besturing en lerend vermogen**
  CZSK zorgt voor een grondige veiligheids- en milieubedrijfsvoering, door blijvend te certificeren tegen de normen ISO 14001 en ISO 45001. Iedere Commandant heeft de risico's voor Veiligheid en Milieu vastgelegd in een RI&E en/of MAR (inclusief bijbehorende NI's) en zorgt dat deze actueel, dekkend en volledig blijft en stellen deze bekend onder hun personeel.
  De CZSK organisatie wordt op gebied van V&M getoetst d.m.v. interne audits waaruit verbeterpunten komen welke ten uitvoer worden gebracht. Op die manier wordt het lerend vermogen geborgd.
  Commandanten passen Operationeel Risicomanagement (ORM) als vast onderdeel toe bij hun taakuitoefening en nemen vervolgens maatregelen om deze risico's zo klein mogelijk te maken.
- **Leiderschap en cultuur**
  Leidinggevenden van alle niveaus communiceren actief over het belang van meldingen, ongevallen en incidenten. In het belang van de meldingsbereidheid besteden zij daarbij positieve aandacht aan het melden en de melder.
  Commandanten stellen (conform VMMS para 12300) een veiligheidsvoorlichtingsplan op, waarin minimaal opgenomen elk half jaar een LIVE standdowndag. Commandanten nemen veiligheid als standaard bespreekpunt mee in het functioneringsgesprek.
- **Inzicht in compliance**
  De 'Toren van toezicht' wordt structureel ingeregeld. Dit omvat het opstellen van controleplannen, het houden van Safetywalks door commandanten alsmede het houden van controlerondes met specifieke Checklists Milieu Vergunningen (CMV's).
  Keuringen van vastgoed, procesinstallaties en arbeidsmiddelen worden op orde gebracht.
  Voor processen waarbij CMR stoffen of bestanddelen worden gebruikt, wordt een verdiepende RI&E opgesteld. Hiervoor wordt gebruik gemaakt van de applicatie Stoffenmanager. Zowel vervoer als opslag van gevaarlijke stoffen voldoen aan de geldende regelgeving.
- **Kennis & ondersteuning**
  Commandanten zorgen ervoor dat zijzelf, leidinggevenden en medewerkers worden getraind in kennis en vaardigheden op het gebied van V&M. In alle initiële, kader- en niveauopleidingen wordt fysieke en sociale Veiligheid en Milieu een expliciet onderdeel van het curriculum.
  Competenties benodigd om op goede wijze te acteren op het gebied van V&M, zijn vastgesteld en verankerd in de AKL's.

Veiligheid en Milieu – het is een zaak van ons allemaal!

Den Helder, 21 januari 2019
DE COMMANDANT ZEESTRIJDKRACHTEN

R.A. Kramer
Vice-admiraal

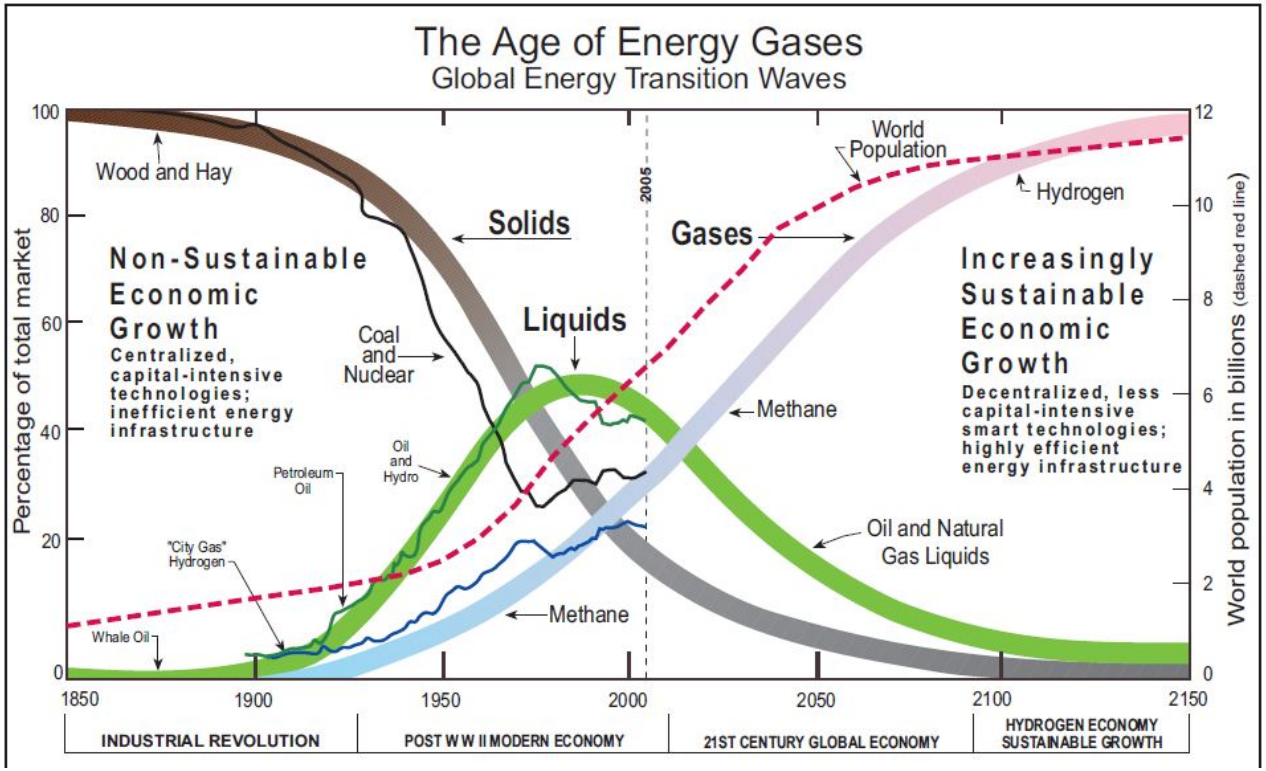
Energy transition

Fossil => Sustainable fuels

OES ambition Department of Defense:

Reduction of fossil fuel consumption with:

- 20% in 2030
- 50% in 2050



Atomic Structure Hydrogen

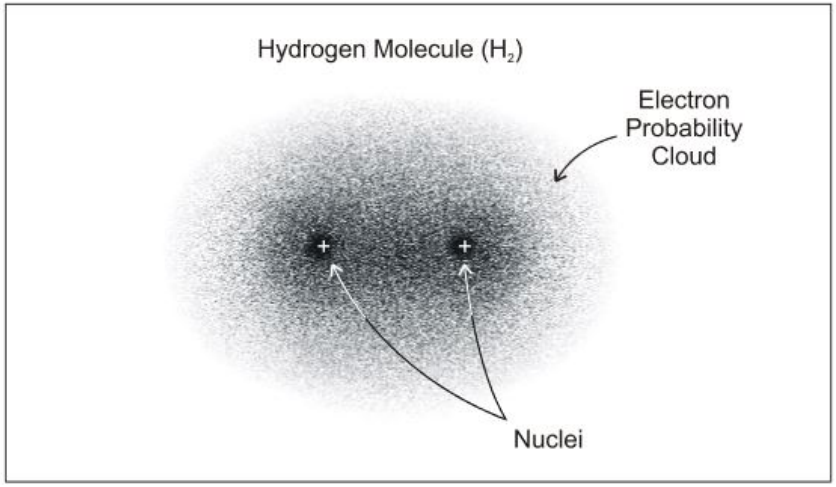
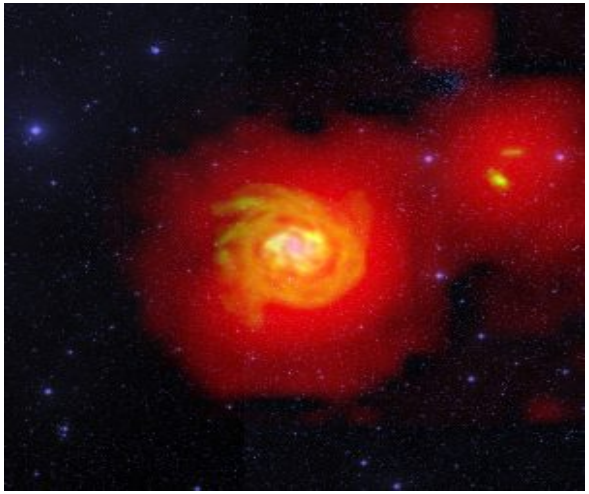


Figure 1-1 Atomic Structure of a Hydrogen Molecule



Hydrogen is the chemical element with the symbol H and atomic number 1. With a standard atomic weight of 1.008, hydrogen is the lightest element in the periodic table. Hydrogen is the most abundant chemical substance in the Universe, constituting roughly 75% of all baryonic mass.[7][note 1] Non-remnant stars are mainly composed of hydrogen in the plasma state.

https://en.wikipedia.org/wiki/Hydrogen

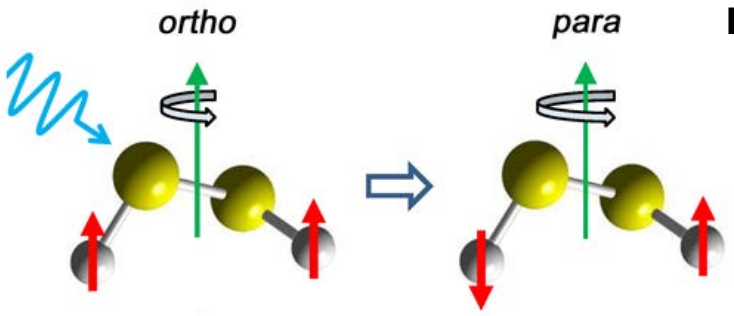
Main isotopes of hydrogen

Isotope	Abundance	Half-life ($t_{1/2}$)	Decay mode	Product
^{1}H	99.98%	stable		
^{2}H	0.02%	stable		
^{3}H	trace	12.32 y	β^-	^{3}He

view · talk · edit | references

The most common isotope of hydrogen, termed protium (name rarely used, symbol 1H), has one proton and no neutrons.
Other forms of isotopes are:

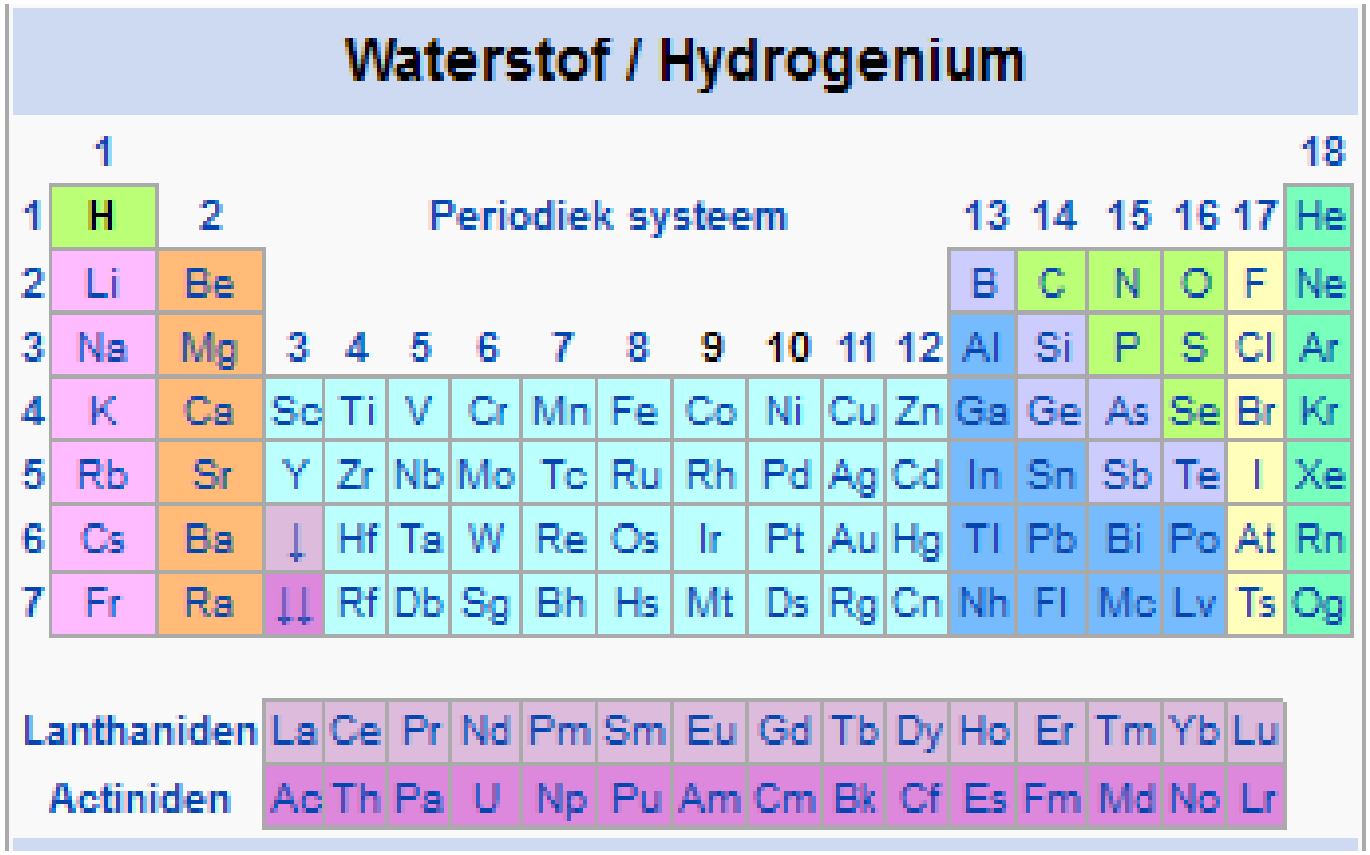
- Deuterium
- Tritium



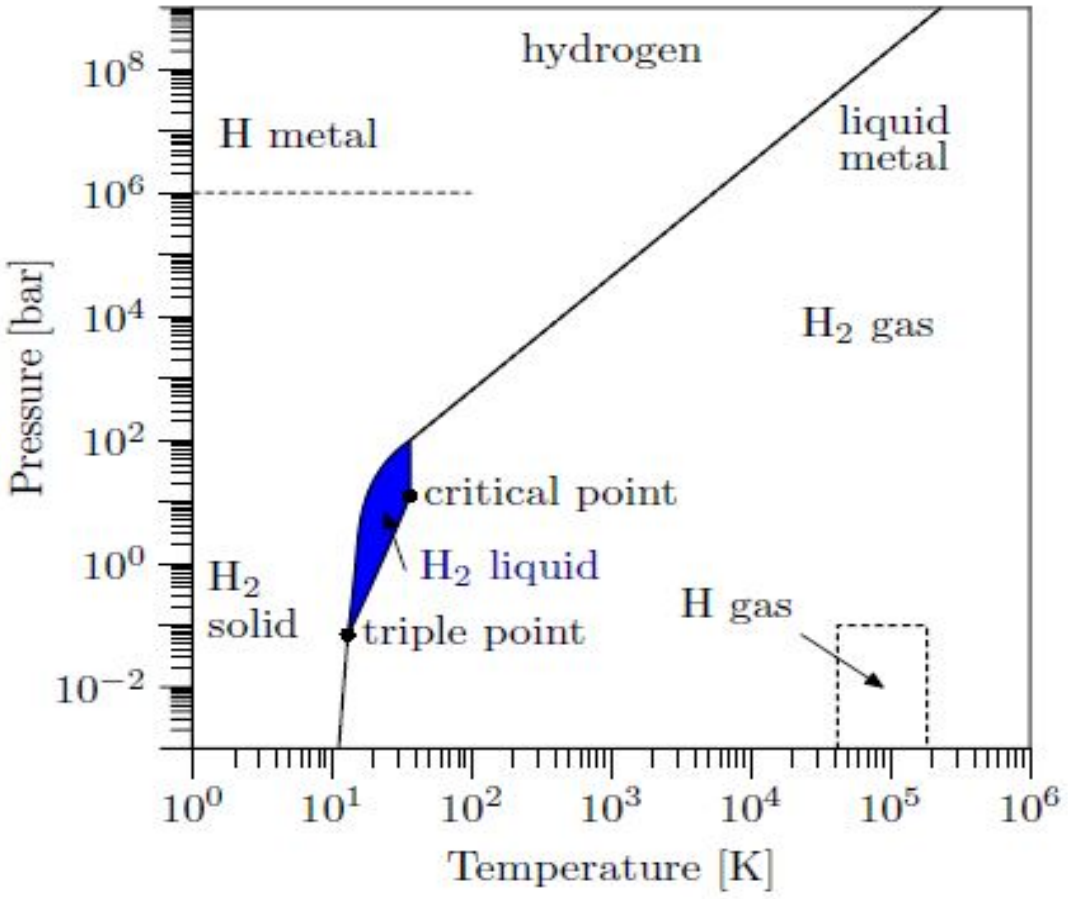
Ref: https://nl.wikipedia.org/wiki/Diwaterstof

Figuur 1 Ortho en Para waterstof

Hydrogen and Periodic Table



Hydrogen Phase envelop





Phenomena, hazards, and risks

Applications and accident scenarios

	Hydrogen release, mixing and distribution	Thermal and pressure and missile effects from fires and explosions	Development and validation of mitigation techniques	Safety assessment and risk analysis	Standards, guidelines, and legal requirements
Production	H2	H2	H2	H2	H2
Transport and distribution, refueling stations	H2	H2	H2	H2	H2
Hydrogen storage (LH2,CGH2)	H2	H2	H2	H2	H2
Tunnels, parking and garages	H2	H2	H2	H2	H2
Utilisation, portable and stationary applications	H2	H2	H2	H2	H2

Physical properties

Ref: H2Tools.org ER training

Hydrogen Properties and Behavior

A gas at ambient conditions

Hydrogen is a cryogen: exists as a liquid at -423°F (-253°C).

- Compressing the gas does not liquefy it
- No liquid phase in a compressed gaseous hydrogen storage tanks

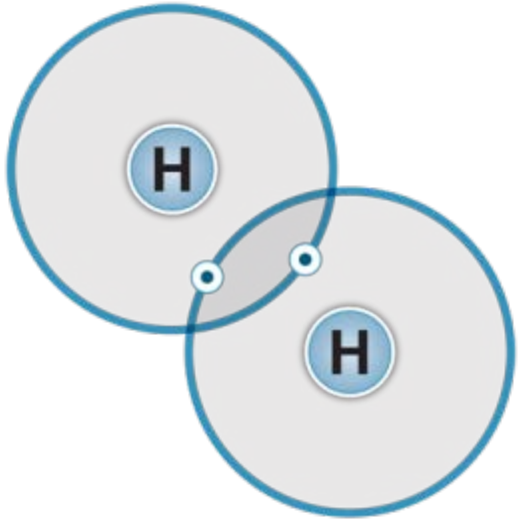
LH2 storage at relatively low pressure (50 psi)

Double walled, vacuum insulated tanks with burst disks, vents, and PRDs

Volumetric ratio of liquid to gas is 1:848

- Compare water to steam (1:1700)

Energy content of 1kg of H_2 is approximately equal to 3.5 ltr of gasoline (in BTUs)



Molecular Hydrogen

Hydrogen Properties: A Comparison

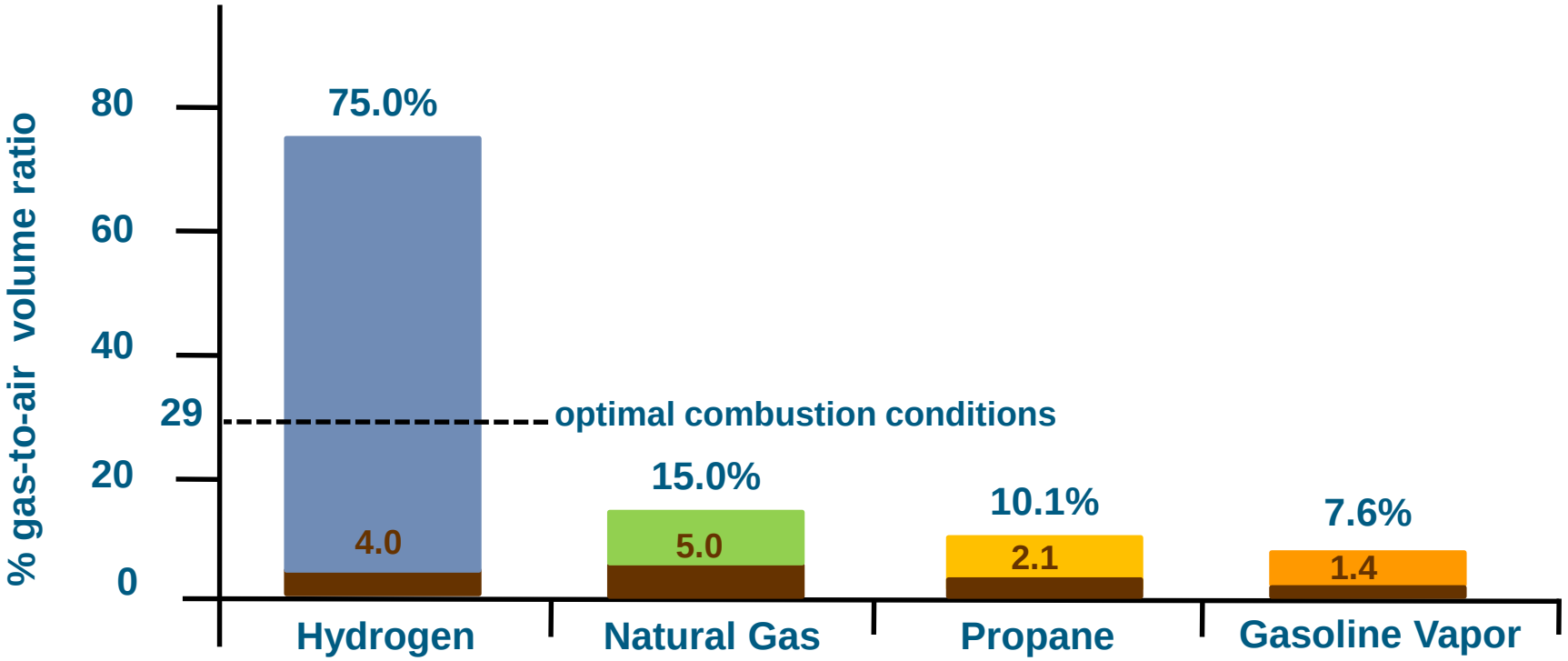
	Hydrogen	Natural Gas	Gasoline
Color	**No**	**No**	**Yes**
Toxicity	**None**	**Some**	**High**
Odor	**Odorless**	**Mercaptan**	**Yes**
Buoyancy Relative to Air	**14X** Lighter	**2X** Lighter	**3.75X** Heavier
Energy by Weight	**2.8X** > Gasoline	**~1.2X** > Gasoline	**43** MJ/kg
Energy by Volume	**4X** < Gasoline	**1.5X** < Gasoline	**120** MJ/Gallon

Source: California Fuel Cell Partnership

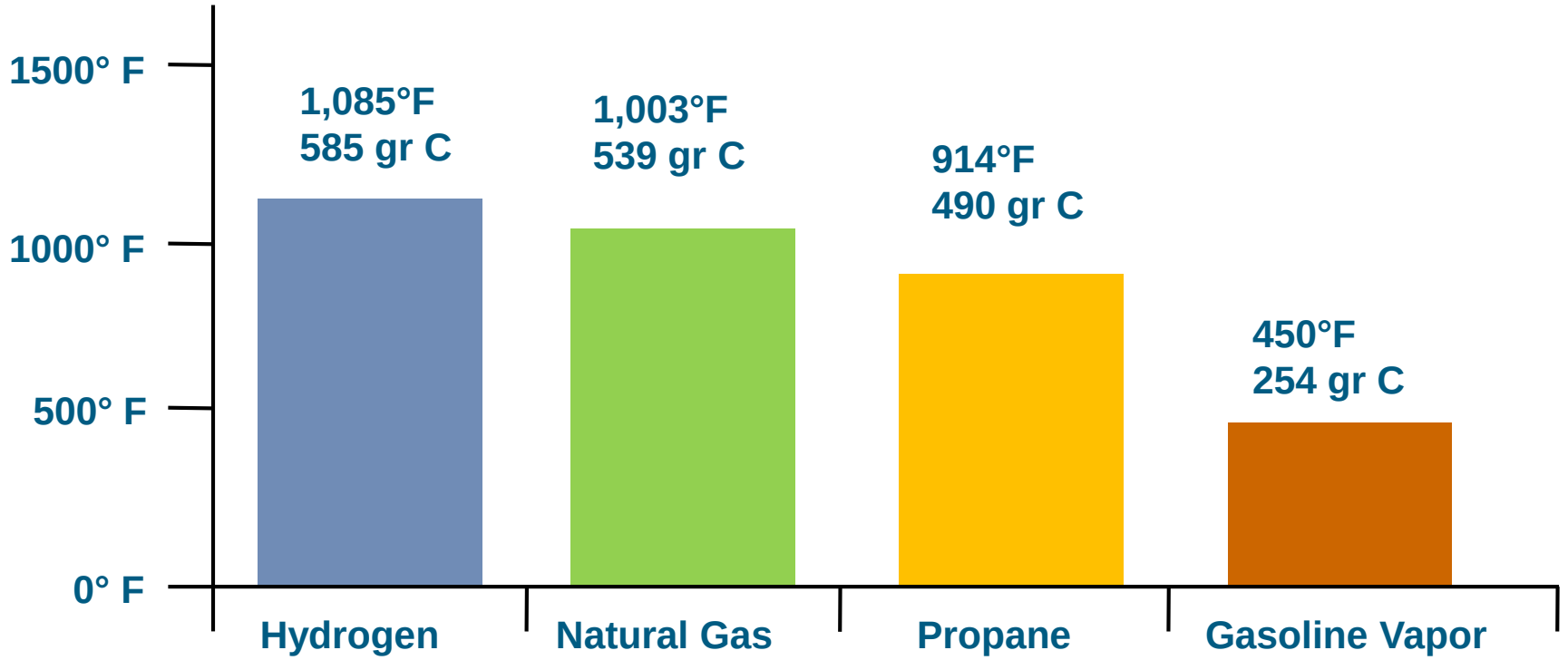
Comparison of Fuel Odorants and Toxicity

Fuels	Odorant Added?	Toxic?
Hydrogen	**No**	**No**
Compressed Natural Gas (CNG)	**Yes**	**No**
Liquefied Natural Gas (LNG)	**No**	**No**
Propane	**Yes**	**No**
Gasoline Vapor	**NOT NEEDED** Naturally Strong Odor	**Yes**

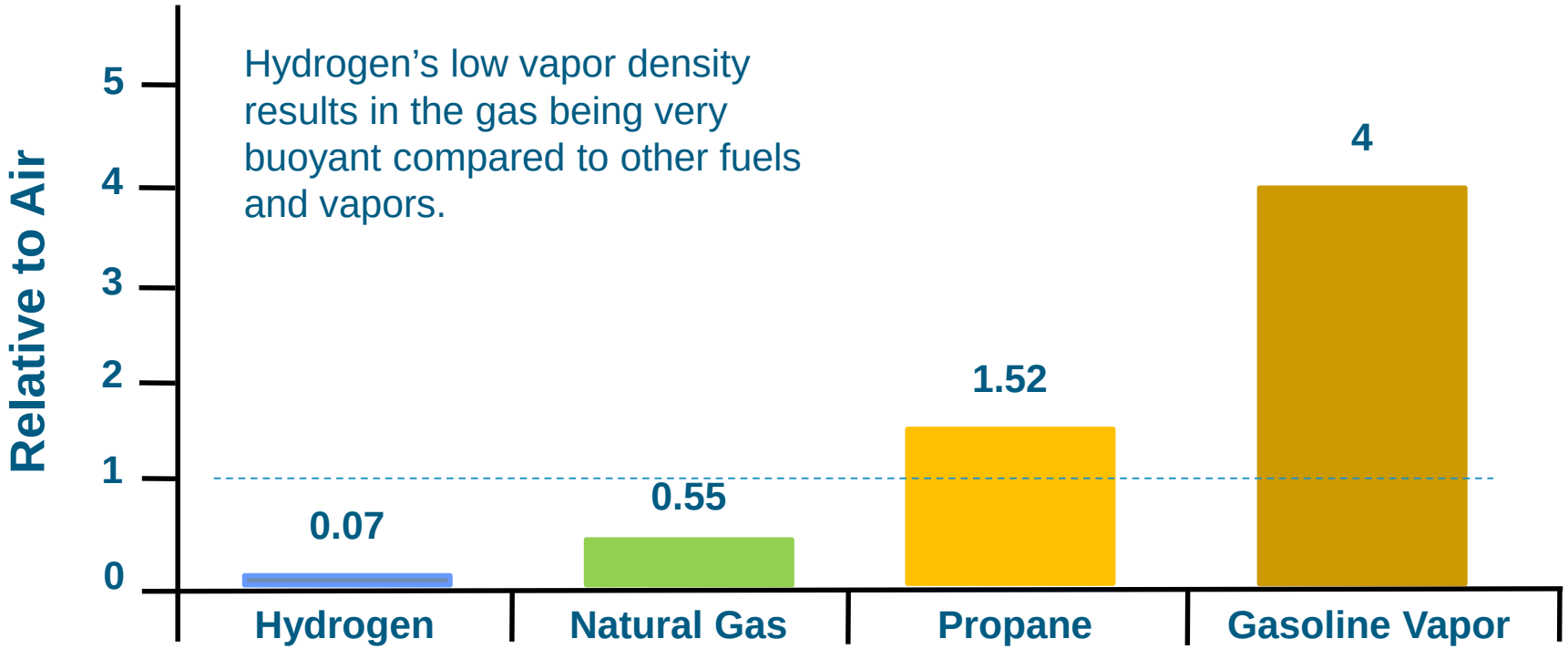
Flammability Range



Auto-ignition Temperature



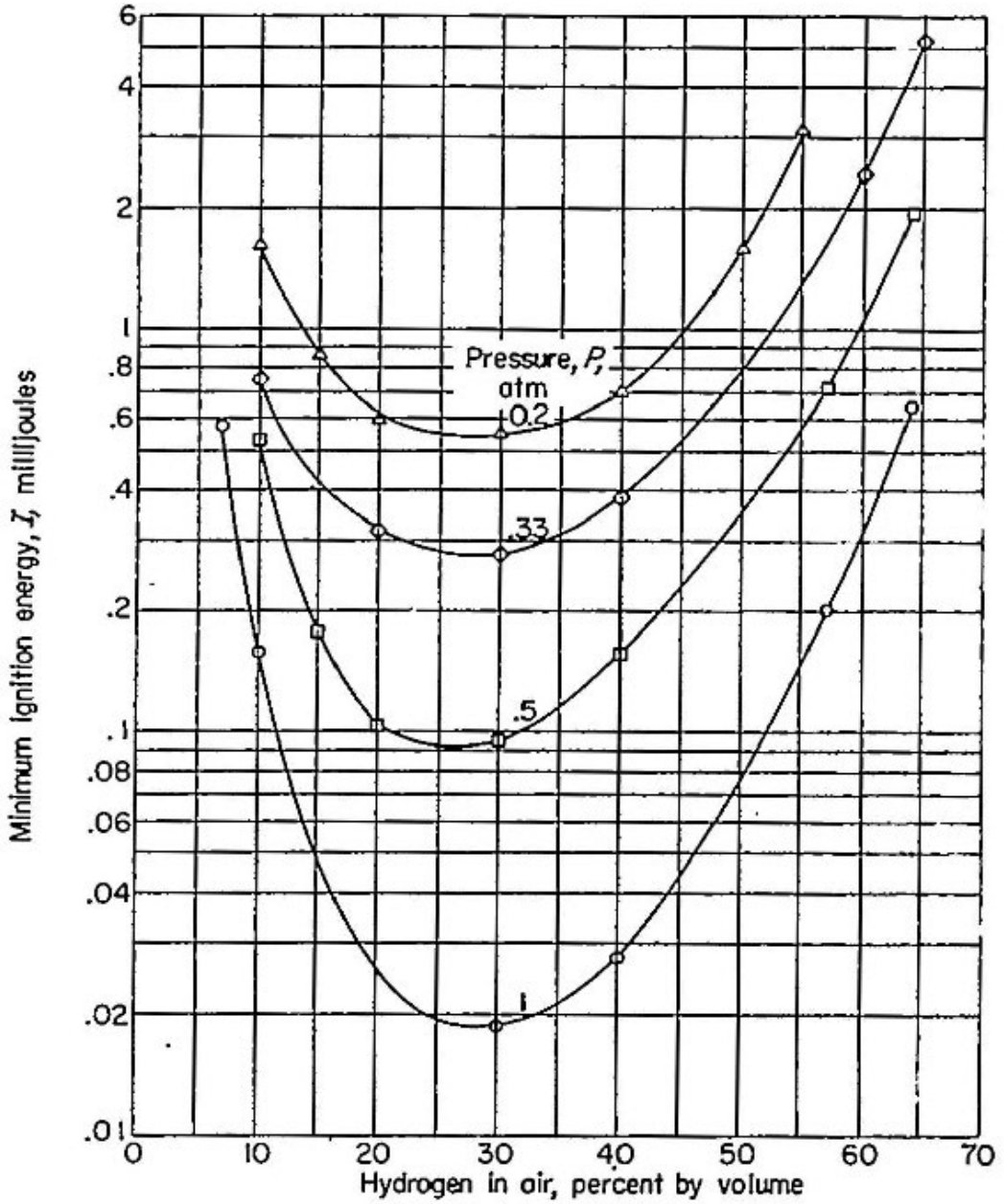
Relative Vapor Density



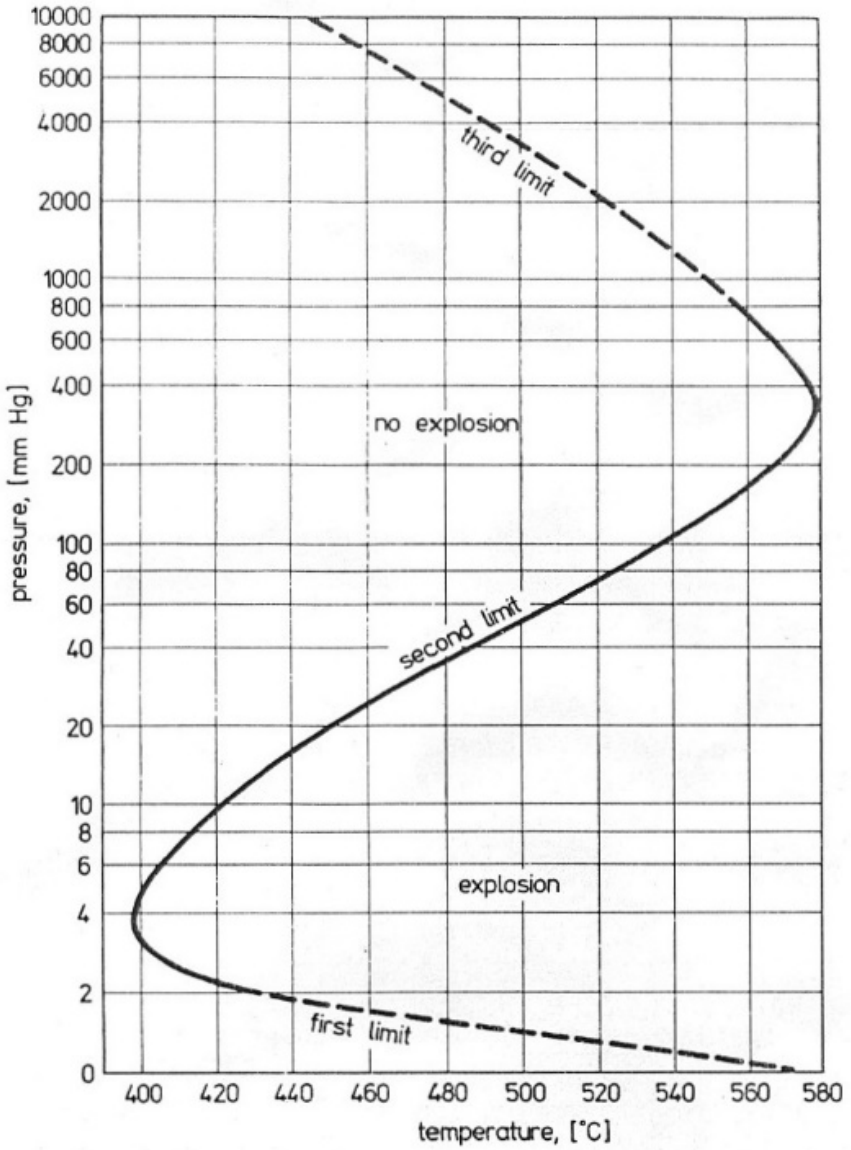
Comparison Flammability limits

Fuel	Lower flamm. limit vol. %	Lower deton. limit vol. %	Stoich. fuel conc. vol. %	Upper deton. limit vol. %	Upper flamm. limit vol. %	Minim. ign. energy mJ	Auto-ign. temp. °C	Lamin. burn. veloc. $cm\,s^{-1}$
Hydrogen (H_2)	4.0	18.3	29.5	59.0	75.0	0.017	585	225
Methanol (CH_3OH)	6.0	-	12.3	-	36.5	0.174	385	48
Methane (CH_4)	5.3	6.3	9.5	13.5	17.0	0.274	537	37
Propane (C_3H_8)	1.7	3.1	4.0	9.2	10.9	0.240	450	47
Gasoline (C_8H_{18})	1.0	1.1	1.9	3.3	6.0	0.240	215	30

Flammability limit



Flammability limits / Explosion limits



Hydrogen Hazards

Ref: ISO 15196

The primary hazards and issues:

Flammability:

- Thermal effects;
- Pressure effects;
- Easy ignitability of some mixtures;

Small size of the molecule:

- Low viscosity;
- High diffusion rate;
- High buoyancy;

The primary hazards and issues (continued):

Interactions with materials (embrittlement of certain metals);

Asphyxiation hazard if oxygen is replaced;

Hazards associated with the storage procedure:

- elevated storage pressure for gas;
- low temperature for cryogenic liquid;
- others for other methods, like metal hydrides.

Designing Safe Systems – Gaseous Hydrogen

Characteristic	Potential Hazard	Control
• Colorless • Odorless • Tasteless	• Impossible for human senses to detect	• Detection sensors
• Low Viscosity • Very small molecule (can be absorbed into materials)	• High leak rate • Embrittles certain materials; can result in structural failure	• Leak detection systems • Ventilation • Material selection
• Low Volumetric Energy Density	• Stored at high pressures	• Storage container design • Pressure-relief devices

Designing Safe Systems – Gaseous Hydrogen

Characteristic	Potential Hazard	Control
• Asphyxiant	• Potential for accumulation in confined spaces (any gas that displaces oxygen in sufficient concentrations will not support life)	• Ventilation • Leak-detection systems
• Wide flammability range (4% – 75%)	• Can ignite or explode over a wide range of concentrations; leaks of all sizes are a concern	• Ventilation • Leak-detection systems

Designing Safe Systems – Gaseous Hydrogen

Characteristic	Potential Hazard	Control
• Low ignition energy	• Minimal energy (small spark) can ignite	• Ventilation • Grounding • System design/removal of possible ignition sources
• Burns with a pale blue flame that is nearly invisible in daylight and does not produce smoke • Low heat emission	• Potential for undetected flame	• Flame detectors

Designing Safe Systems – Liquid Hydrogen

Characteristic	Potential Hazard	Control
• Low liquefying temperature (-423°F/-253°C)	• Cryogenic burns • Lung damage	• System design • Leak-detection systems • Personal protective equipment
• Rapid phase change from liquid to gas	• Over-pressurization	• System design • Pressure-relief devices • Ventilation
• Spill may cause liquid oxygen to form on asphalt surface	• Shock-sensitive surface area	• Ventilation

Risk Assesment

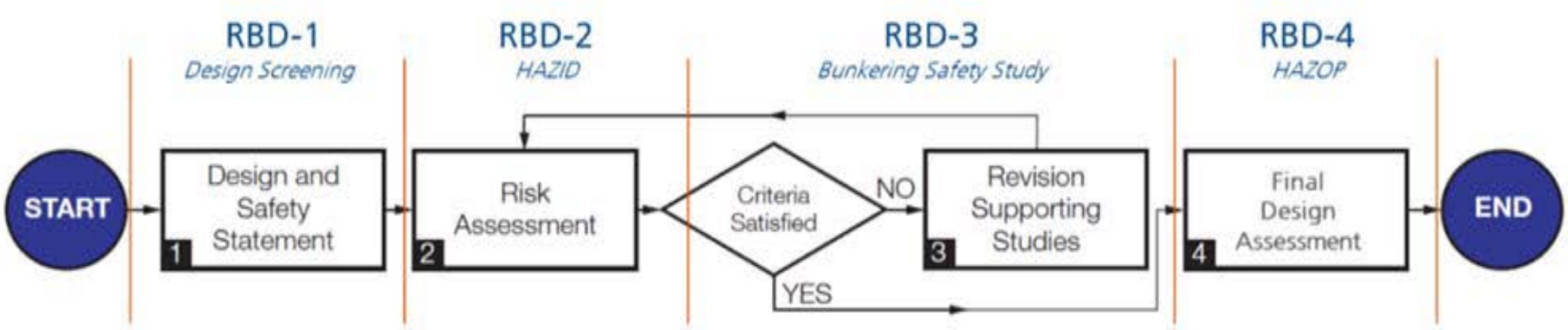
Prevention of ignition sources

Each material design needs to be assessed in its own design as per EU directive 94/9/EC & 2014/34/EU (ATEX 114)
Each system use needs on its work place needs to be assessed in its own use as per EU directive 1999/92/EC (ATEX 153)

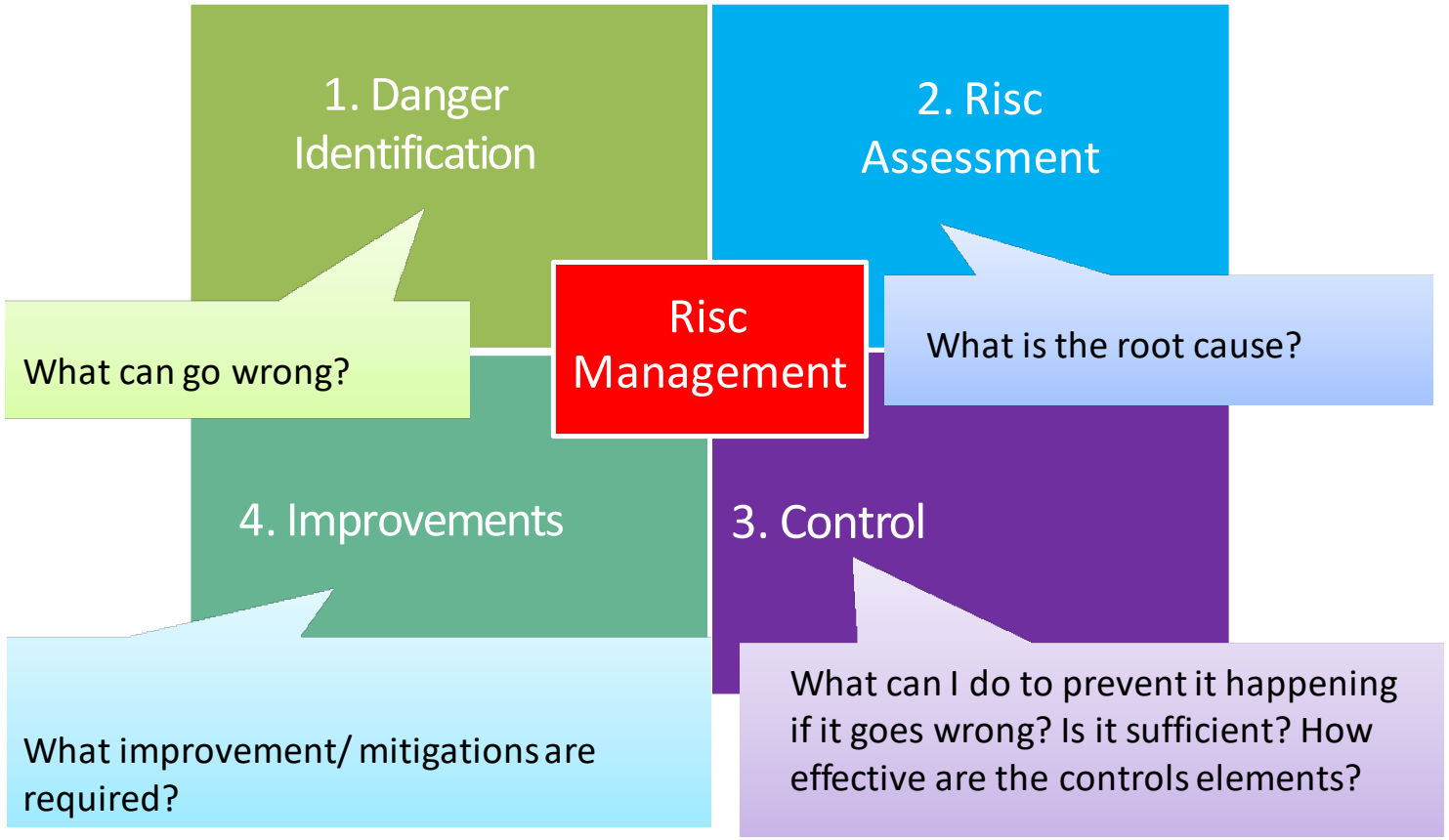
Documented in an Explosion safety document:

- AtEx zoning
- Ignition analysis
- Risk Assesment results
- Action registers

Project risk control

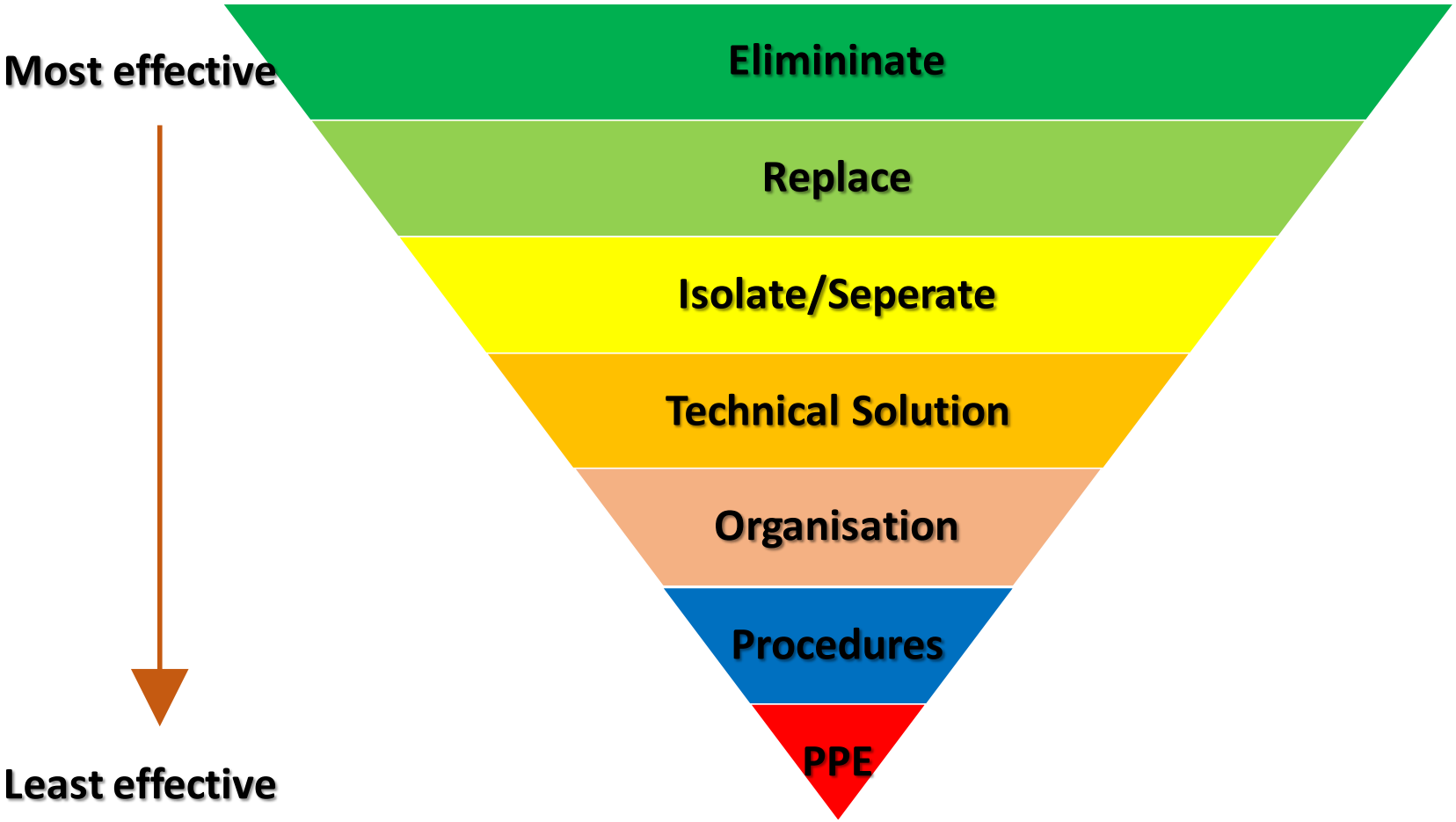


Safety Management System



Risc = Probability x Exposure x effect

Hiërarchal Danger reduction (ALARP)



Prevention of ignition sources

Document into Explosion Safety Document

Use of NPR 7910-1 guideline in 7 step approach:

1. Is a flammable liquid or gas present?
2. Are limited quantities established or is there a basis for zoning useful?
3. Which kind of danger sources are
4. Is ventilation present
5. Apply AtEx zoning
6. Estimate leak quantities
7. Determine zoning distances

AtEx zoning

Meteodata (Ref Den Helder de Kooy)

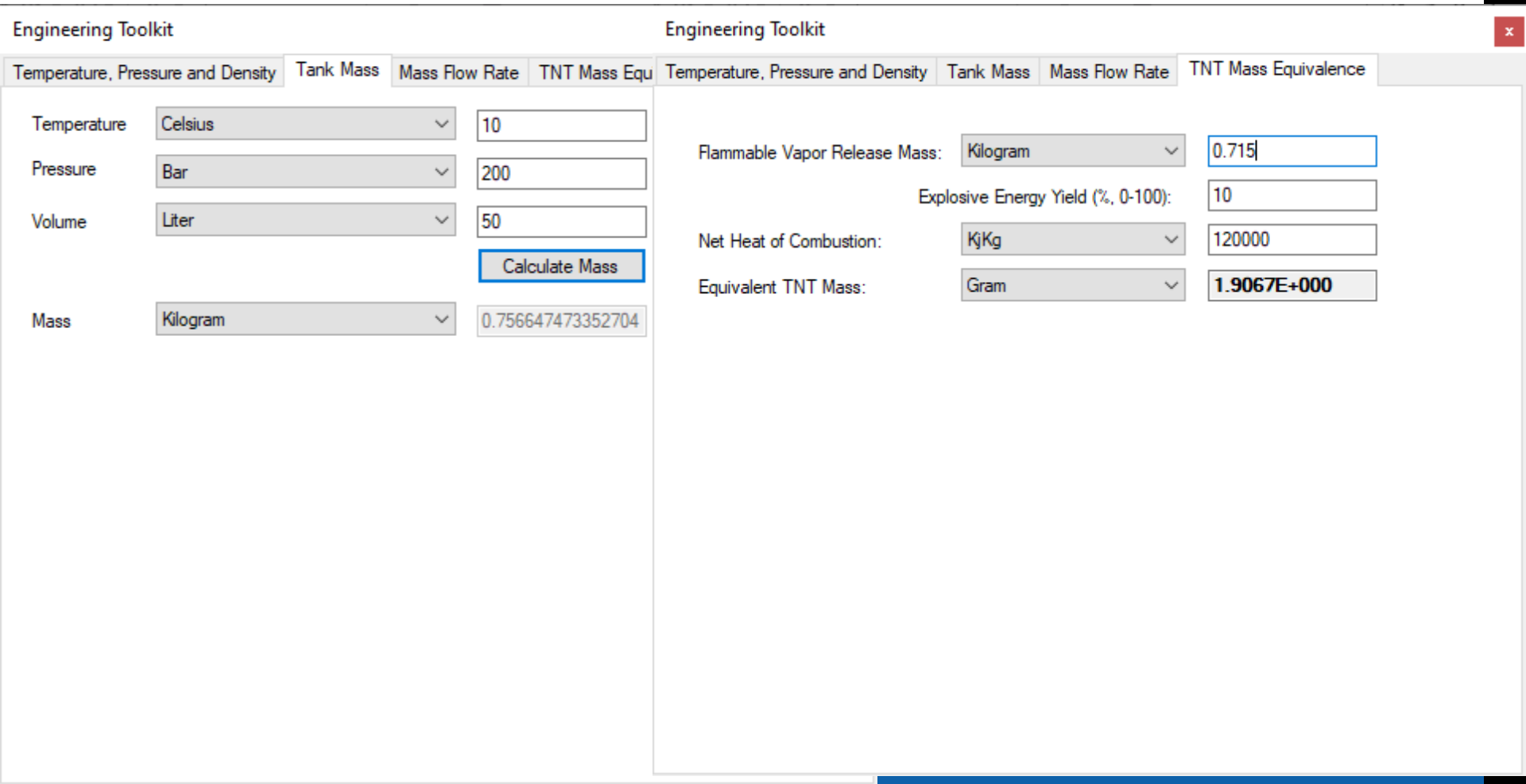
Average year temp. DHR 10 gr C
Airpressure 1014.9 Hpa
Humidity: 78% (12 uur ‘s middags)

Calculations done:
Blow down time,
Max length gasplume with 4% LEL,
Jet Flame,
Heatflux,
Explosion effects

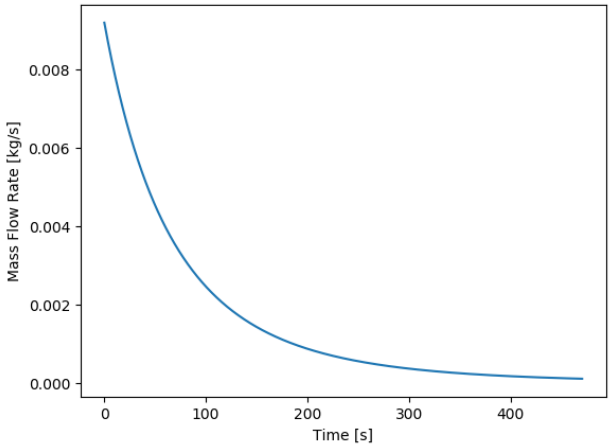
Case 6 (Hydrogen Storage 200 bar, 50 ltr)

Case 1 mm lekkage (pin hole)
Case 3 mm lekkage (line break)

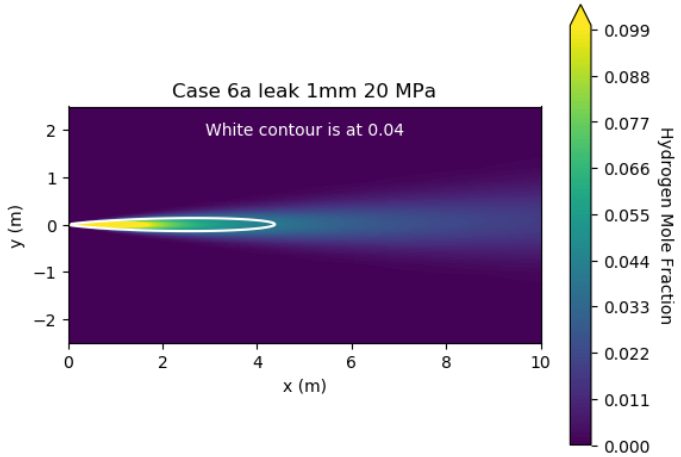
Engineering volume, mass & TNT equivalent for 200 Bar, 50 ltr gas storage



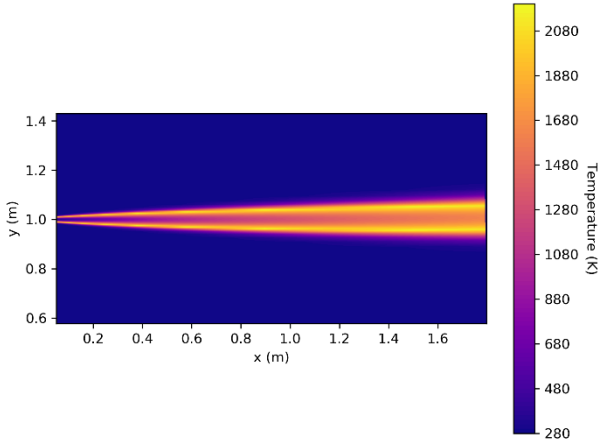
200 Bar 50 ltr 1mm leak Blow downtime



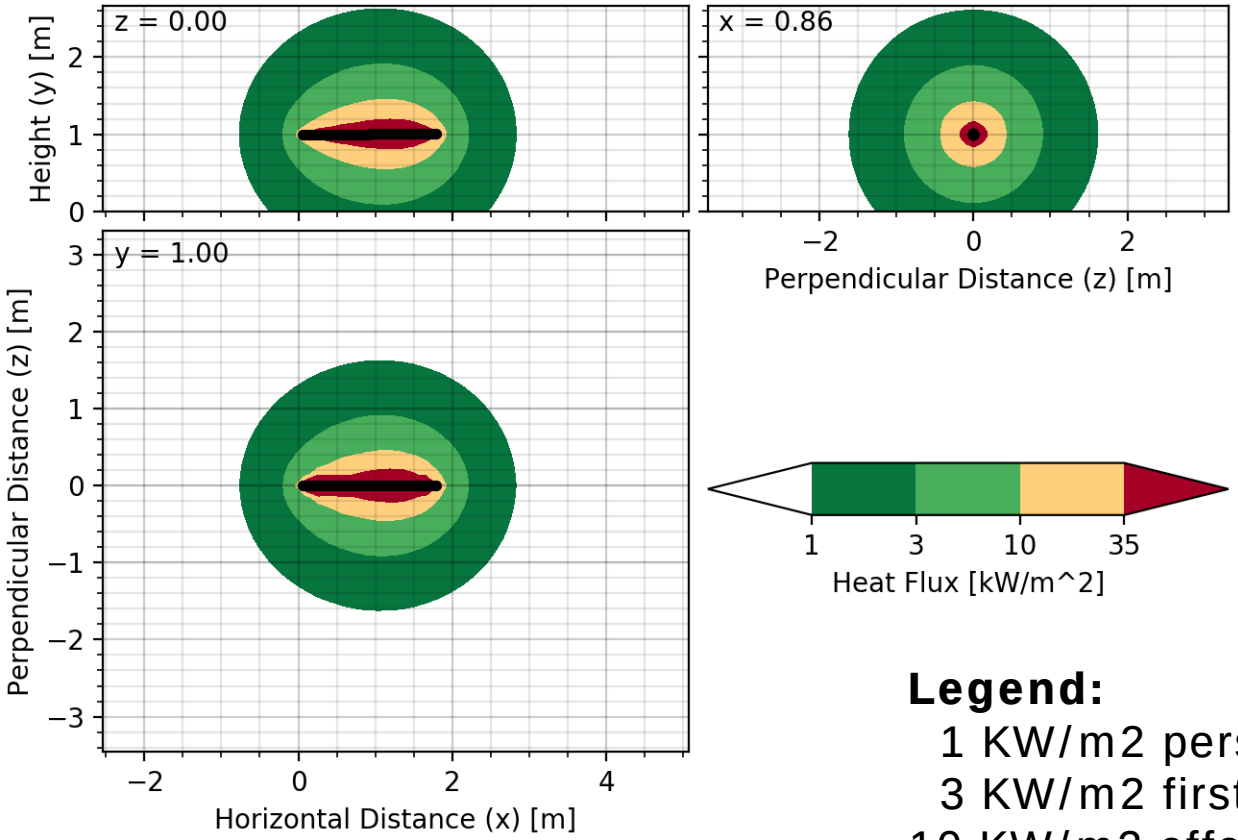
200 Bar 50 ltr 1 mm leak Gasplume



200 Bar 50 ltr 1 mm leak Temperature Jet Flame



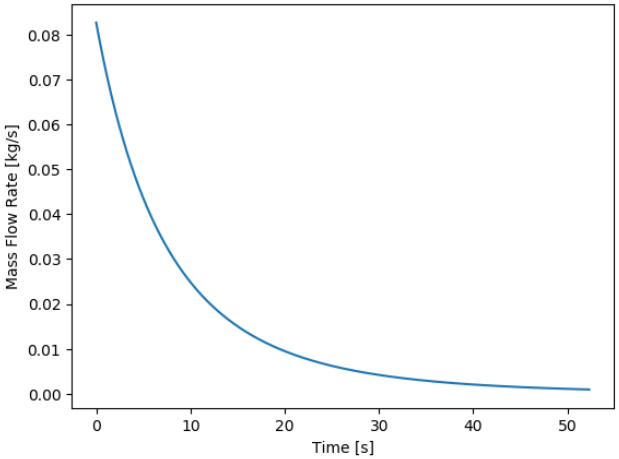
Safety plot Heatflux for jetflame 200 bar 50 ltr tank, 1 mm leak



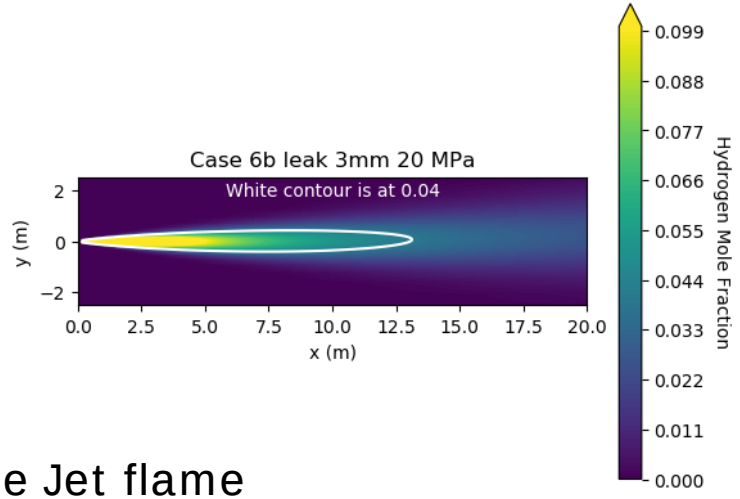
Legend:

1 KW/m2 personnel
3 KW/m2 first aiders
10 KW/m2 effect buildings
35 KW/m2 lethal

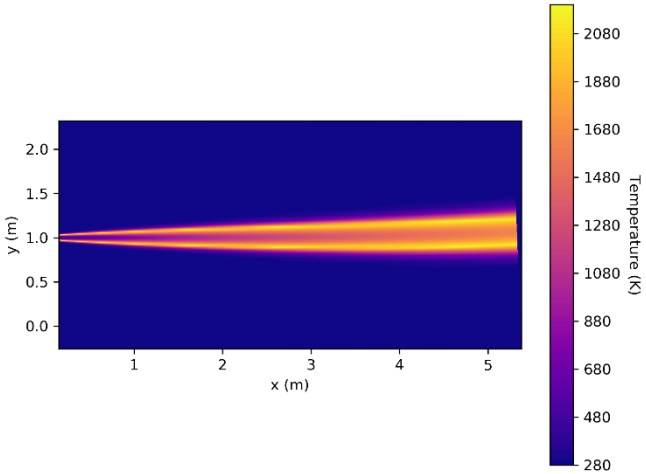
200 Bar 50 ltr 3 mm leak Blow downttime



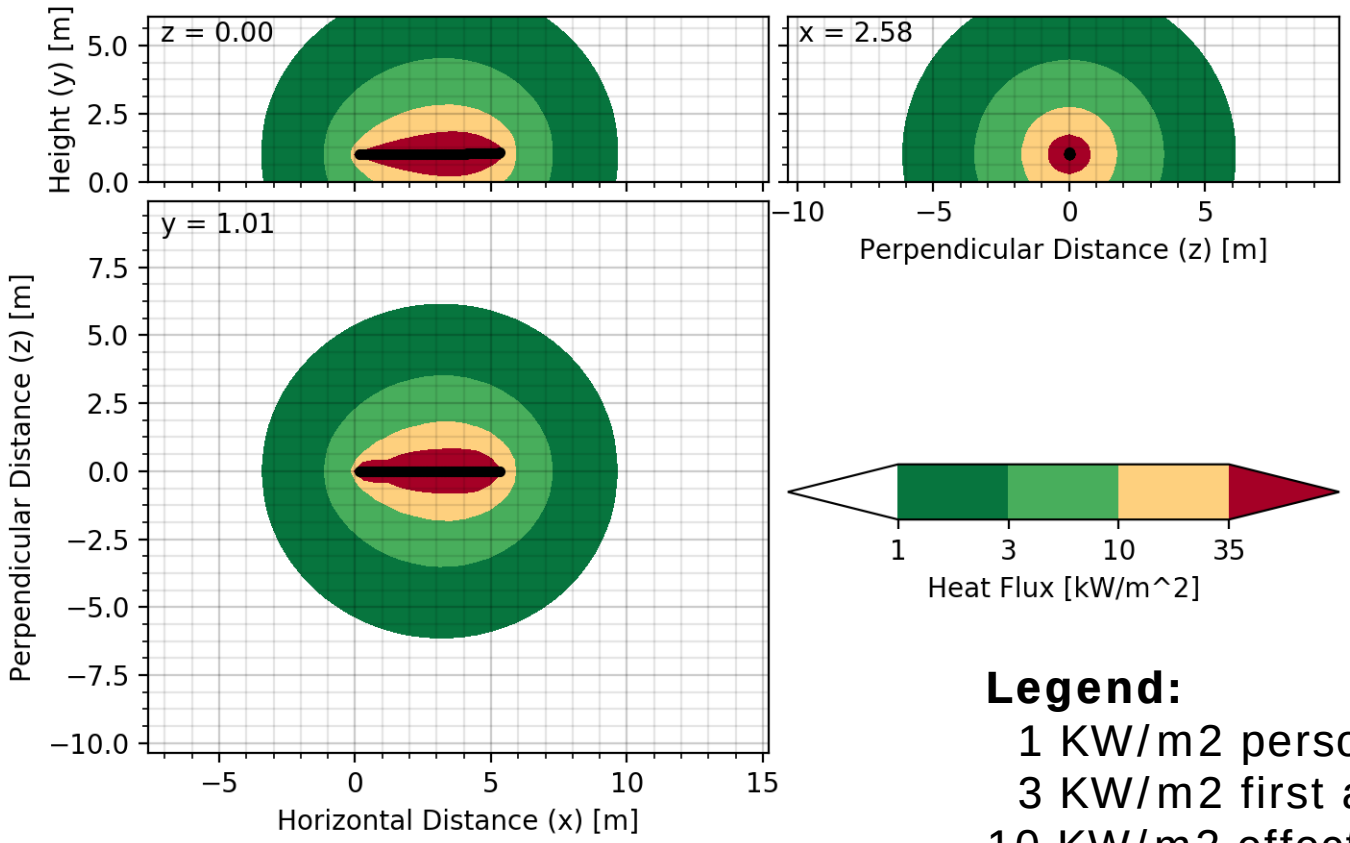
200 Bar 50 ltr 3 mm lek Gasplume



200 Bar 50 ltr 3 mm leak Temperature Jet flame



Safety plot Heatflux for jetflame 200 bar 50 ltr tank, 3 mm leak

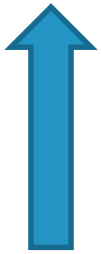


Legend:

1 KW/m2 personnel
3 KW/m2 first aiders
10 KW/m2 effect buildings
35 KW/m2 lethal

Overview Gasplume/ Jetflame effect results 200 Bar, 50 ltr storage

Case 6	Blow down tijd [s]	Leak [mm]	Dist plume [m]	Dist jetflame [m]	Dist lethal [m]	Dist Bldg [m]	Dist First Aider [m]	Dist personel [m]
Pin hole	470	1	4.2	1.8	1.8	1.9	2.2	2.8
Line break	**52**	**3**	**13**	**6**	**6**	**6.5**	**7**	**9.5**



Reference

BST method

Distance applied via Baker-Strehlow-Tang method via interpolation from datatabel en graphics:

(Ref: ProcessSafetyProgress_v18_p235to240 1999 “A New Set of Blast Curves from Vapor Cloud Explosion”

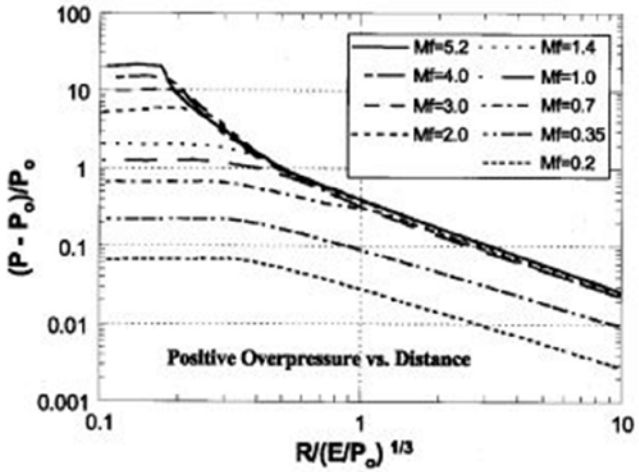


FIGURE 1. Positive Overpressure vs. Distance for Various Flame Speeds

		Massa H_2	Druk	#	Massa per tank	P_0	Δ P over druk in kPa						3 mm	HF Heatflux Ref 3 mm				p	Factor	
Item	Toepassing	kg	Mpa	Aantal tanks	kg	1.0149	100.00	16.50	1.35	34.50	6.90	4.80		35.00	10.00	3.00	1.00			Opmerking
1	0.168 gr H2 @ 300 bar	0.168	30	1	0.168	1.0149	3.3	16.0	96.0	7.0	24.0	36.0	16.0	6.5	7.2	8.9	11.5	6.5	HF	Met beschermde kleding, gehoorbescherming, Ex Gas 2C equipment

AtEx ignition analysis

Ignition analysis EN1127-1 1/3

EN1127-1	Potential ignition source	Equipment	Surrounding
5.1	Hot Surfaces		
5.2	Flames and hot gasses		
5.3	Mechanical cause sparks		
5.4	Electrical Installations		
5.5	Electrical circulation currents, kathodic corrosion protection		
5.6	Static electricity		

Ignition analysis EN1127-1 2/3

EN1127-1	Potential ignition source	Equipment	Surrounding
5.7	Lightning strikes		
5.8	Electric Magnetic fields 9 kHz - 300 GHz		
5.9	Elektromagnetic radiation within the reach of frequency from 300 GHz - 3 x 106 GHz or waves 1000 µm - 0,1 µm (optical spectrum		
5.10	Ionic radiation		
5.11	Ultrasound		
5.12	Adiabatic compression		
5.13	Exo thermal reactions		

Use of equipment within AtEx zone

Used equipment in the field





Flirr thermal imaging camera

Used equipment in the field





Examples

Safety lamp

Learned lessons from incidents

Consequenties van explosies

Older incidents:

- Propane fire and explosions, Dallas
- Explosion at a chemical plant producing rocket fuel, Nevad
- Fire and explosion (domino effect) at a cracking unit on a refinery site (3rd September 2000, Gonfreville l'Orche Havre, France).
- Explosion and fire at a chemical plant (8th Ju 88, Auzouer-en-Touraine, France)
- Massive explosion at a polyethylene action plant (23rd October 1989, Pasedena, Texas
- Pressurized hydrogen tank r e: a tank containing 100m3 of hydrogen at 45 pressure burst without any apparent reason (19 anau, Frankfurt, Germany)

Recent:

- Hydrogen tank explosion kills 2 in Gangneung 23 mei 20
- Hydrogen Gas Explosion and Fire at Air Products and Chemicals, Inc. in Santa Clara 3 Juni 2019 no injuries
- Recent explosions shutdown hydrogen vehicle refueling in NorCal and Norway 11 Juni 2019 No injuries

https://odin.jrc.ec.europa.eu/giada/







Application of the Hazid methodology

What is a Risc?

Risc
=
Probability x Exposure x Effect

Objective of the Hazid

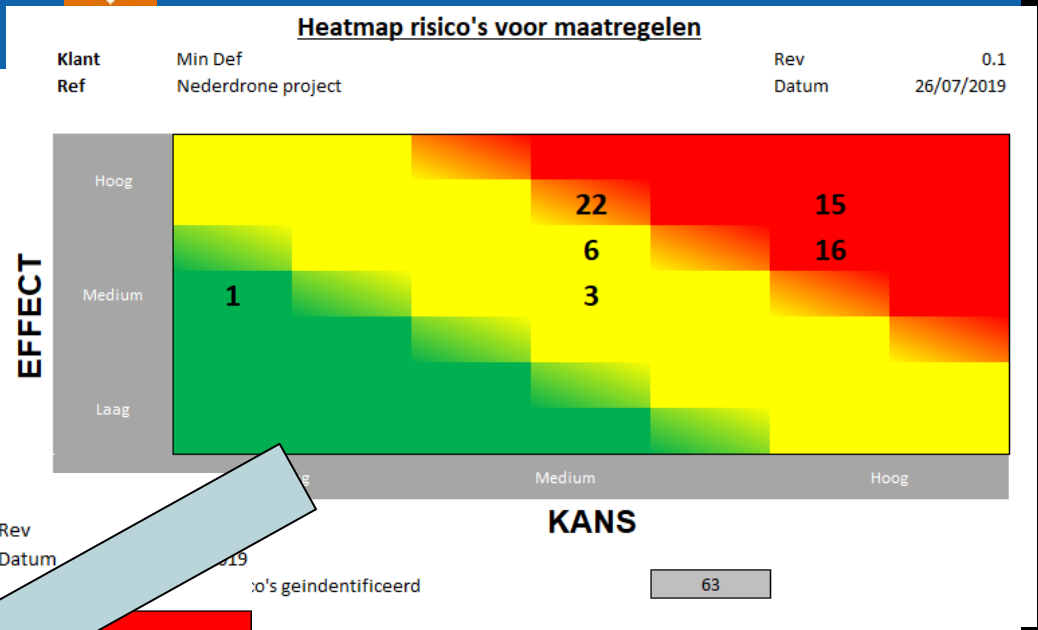
The objectives of the HAZID procedure are to **identify** main **hazards**, to review the **effectiveness** of selected safety measures and, where required, to expand the safety measures in order to achieve a **tolerable** residual **risk**.

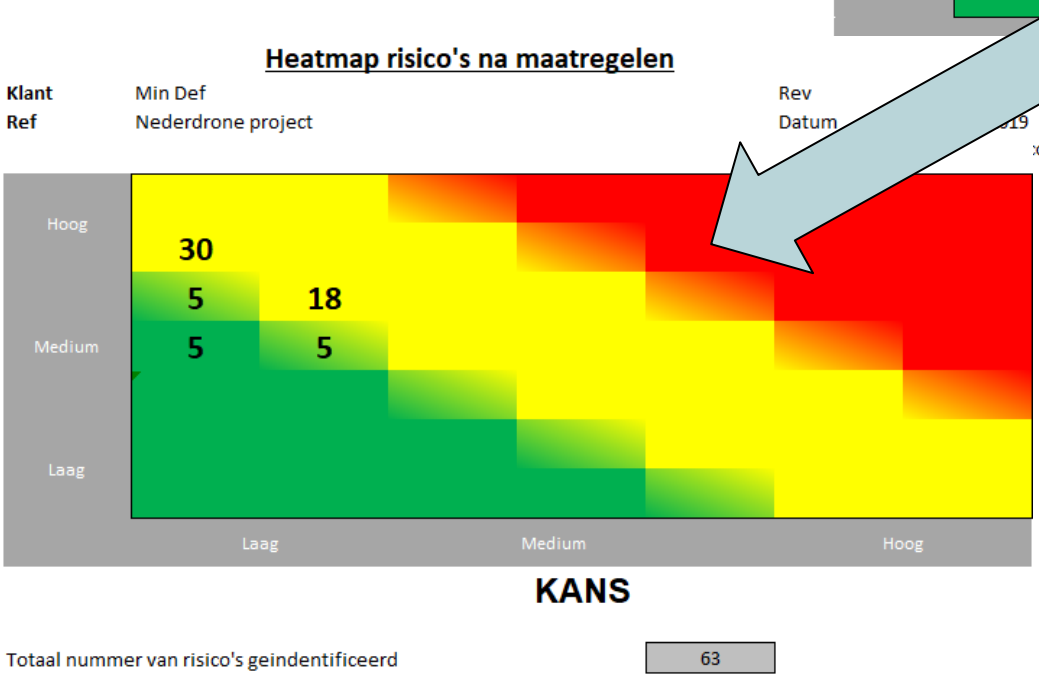
In compliance with the Seveso II Directive, besides facility safety concepts for new installations, also safety concepts for existing operational facilities have to be reviewed.

Brainstorm sessions / Check list guidewords

ALARP Demonstration

Reduce risk before mitigation towards after mitigation

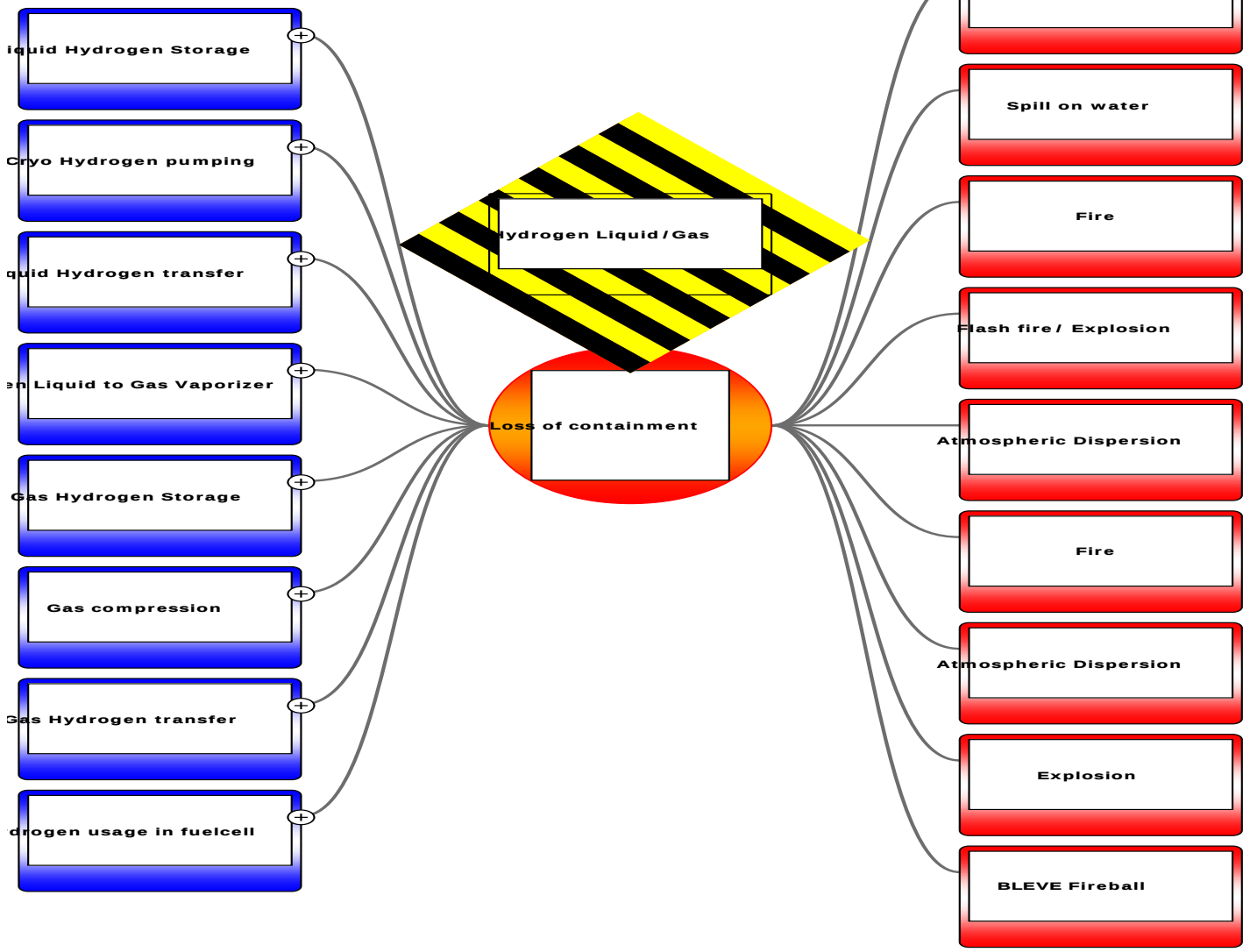




Documentation

Hazid register
RI&E
Action plan/Action register
Hazid report
Explosion Safety document

Bow Tie


iquid Hydrogen Storage
Cryo Hydrogen pumping
quid Hydrogen transfer
en Liquid to Gas Vaporizer
Gas Hydrogen Storage
Gas compression
Gas Hydrogen transfer
drogen usage in fuelcell
ydrogen Liquid / Gas
Loss of containment
Spill onto soil
Spill on water
Fire
Flash fire / Explosion
Atmospheric Dispersion
Fire
Atmospheric Dispersion
Explosion
BLEVE Fireball

Risico matrix

Location: Waterstofdrone op de Guardian

Prepare MAH Sheets for Export to BowTieXP

Code	Hazard	Sources	Threats (separate with ;)	Top Event	Consequences (separate with ;)	Controls (separate with ;)	People		
							Frequency	Severity	
H-01	**Waterstofgas**								
H-01.01	Waterstof onder druk		Overpressure; Dropped Object; Human Error	Loss of Containment	Unignited Release; Fire; Injury/Fatality	Pressure relief valves; Continuous monitoring of well test operations; Restrictions on lifting operations; Permit to work and Well Test Procedures	>1 / year in location	Multiple fatalities	E5

Risk									Comments	
Assets			Environment			Reputation				
Frequency	Severity		Frequency	Severity		Frequency	Severity			
Never heard of	No damage	A1	> 0 in industry	Localised effect	B3	Never heard of	Slight impact	A2		Major Accident Hazard

More course material:

www.h2tools.org

https://www1.eere.energy.gov/hydrogenandfuelcells/

https://www.hydrogen.energy.gov/training/code_official_training/

https://knowhy.eu/

https://hysafe.org