Hazards and Risks of Anhydrous Ammonia

PSR/HSE/RM/SPI©
March 2023

TotalEnergies

Production, Storage and Transport of Anhydrous Ammonia

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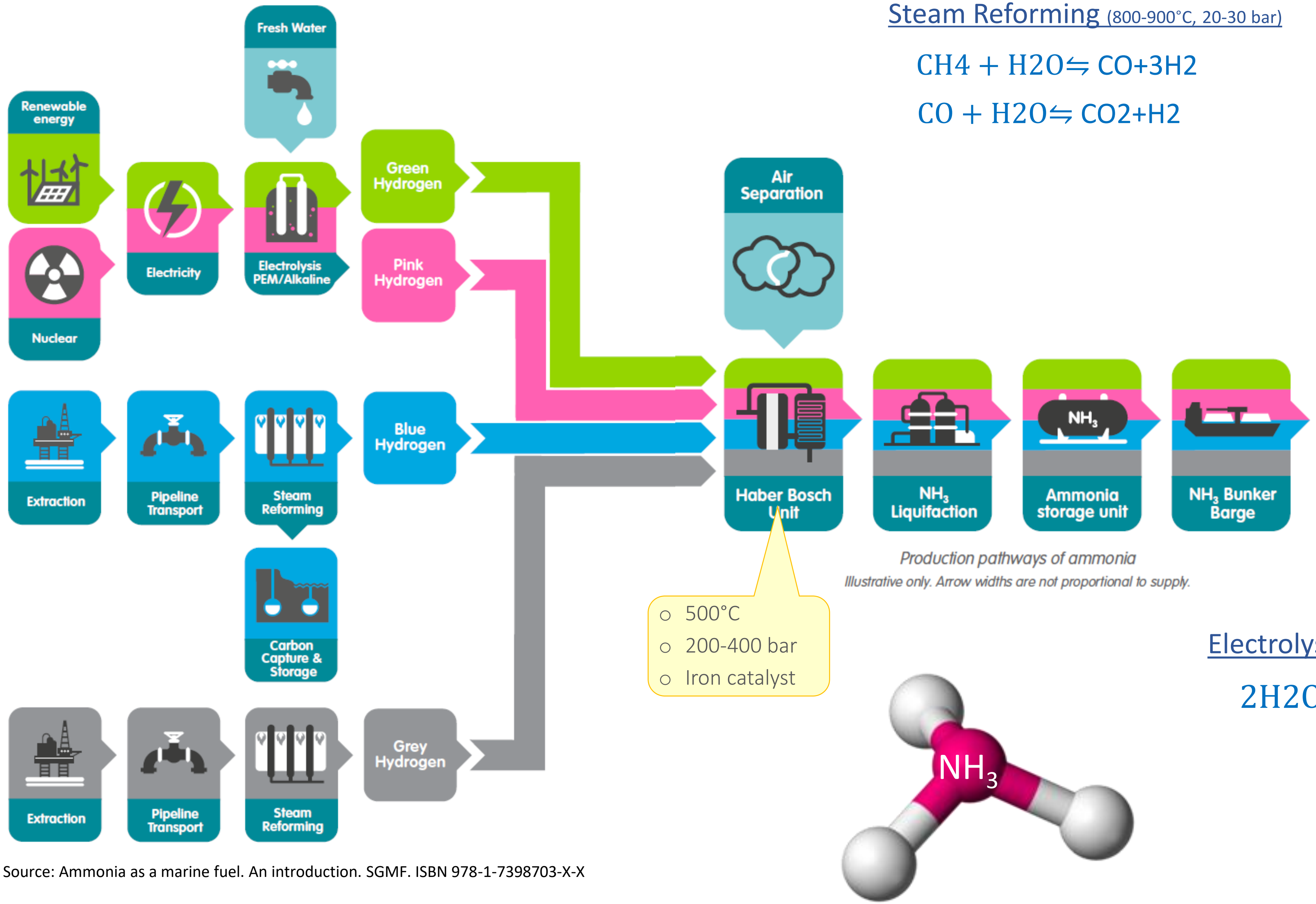
March 2023

Anhydrous Ammonia Production



Production pathways of ammonia

Illustrative only. Arrow widths are not proportional to supply.

- 500°C
- 200-400 bar
- Iron catalyst

Source: Ammonia as a marine fuel. An introduction. SGMF. ISBN 978-1-7398703-X-X

Steam Reforming (800-900°C, 20-30 bar)

$$CH4 + H2O \leftrightharpoons CO+3H2$$

$$CO + H2O \leftrightharpoons CO2+H2$$

Grey Ammonia

- Extracted from natural gas or coal by steam reforming
- Emits on average around 2.4 tonnes of carbon dioxide (CO2) for each ton of ammonia produced (*)

Blue Ammonia

- Equal to grey ammonia +CCUS

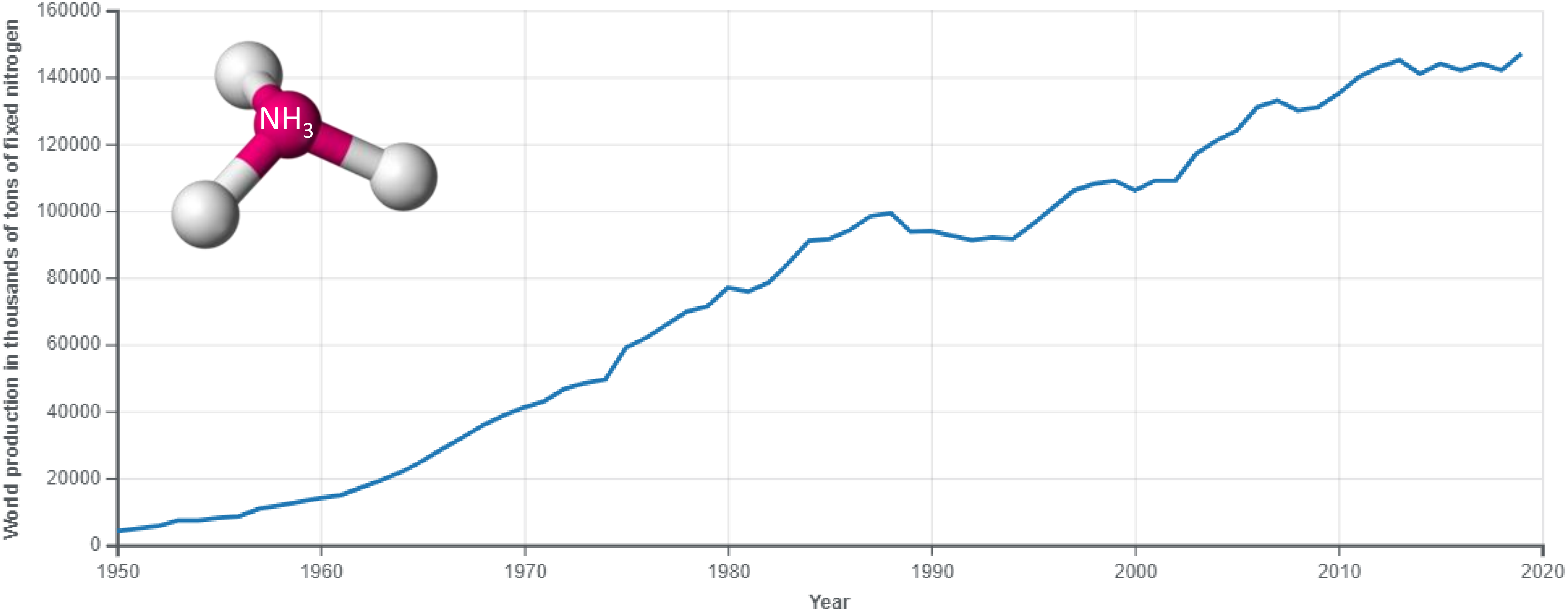
Green Ammonia

- Manufactured with chemical reactions involving water, air and sustainable electricity.
- 100 percent renewable and “carbon-free”

Electrolysis

$$2H2O + \text{electricity} \rightarrow 2H2+O2$$

Anhydrous Ammonia Production



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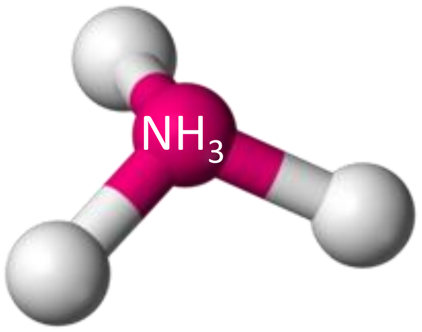
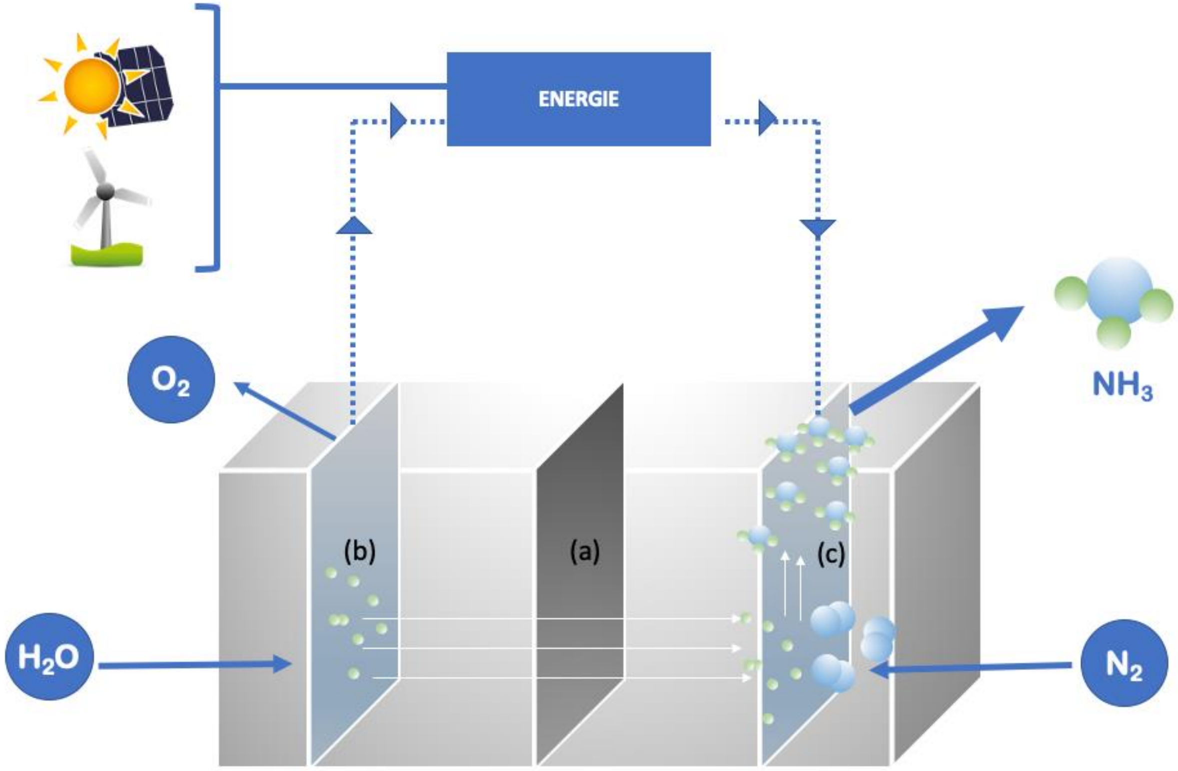
NH_3 Process by Electrolysis



- A carbon free method to produce NH_3
- Other disruptive pathways are also being explored, envisaging a low-pressure, low-temperature electrolysis and combination approach to the production of H2 and N2, powered by solar and wind energy.
- A pilot unit of this type is currently being evaluated by in Australia



Storage and Transport

- Ammonia is stored and transported in bulk on vessels that are designed to carry liquefied gases (atmospheric boiling point of ammonia = -33°C), either fully refrigerated or in pressurized storage conditions
- Most ammonia is shipped in the fully refrigerated state in mid-sized vessels (20.000 – 50.000 m^3) but larger vessels may also be used.
- Many vessels also trade ammonia at ambient temperature in pressurized tanks.
- Containerized pressure vessels may also be used for quantities limited by ISO tank containers, if they meet IMDG code criteria

Ammonia truck

Fully refrigerated LPG/ammonia carrier vessel

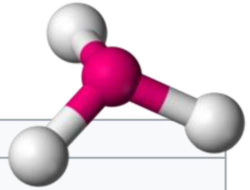
Refrigerated ammonia storage

Properties of Anhydrous Ammonia

PSR/HSE/RM/SPI©
March 2023

Properties

- Ammonia is a compound of nitrogen and hydrogen with the formula NH_3. A stable binary hydride, and the simplest pnictogen hydride, ammonia is a colorless gas with a distinct pungent smell. It is a common nitrogenous waste, particularly among aquatic organisms, and it contributes significantly to the nutritional needs of terrestrial organisms by serving as a precursor to 45 percent of the world's food and fertilizers.
- Although common in nature and in wide use, ammonia is both caustic and hazardous in its concentrated form.
- The global industrial production of ammonia in 2021 was 185 million tons (of which 44 MT being merchant capacity, i.e. NH_3 that can be exported as such from a production site instead of being consumed onsite).
- Industrial ammonia is sold either as ammonia liquor (usually 28% ammonia in water) or as pressurized or refrigerated anhydrous liquid ammonia transported in tank cars or cylinders.
- Ammonia is a chemical found in trace quantities in nature, being produced from nitrogenous animal and vegetable matter.
- Ammonia is a colorless gas with a characteristically pungent smell. It is lighter than air, its density being 0.589 times that of air. It is easily liquefied due to the strong hydrogen bonding between molecules. The liquid boils at −33.1 °C and freezes to white crystals at −77.7 °C.
- NH_3 boils at −33.34 °C at a pressure of one atmosphere, so the liquid must be stored under pressure or at low temperature.



Chemical formula	NH_3
Molar Mass	17.03 g/mol
Appearance	Colorless gas
Odor	strong pungent odor
Gas Density	0.86 kg/m^3 (1.013 bar at boiling point) 0.772 kg/m^3 (0° C, 1.013 bar) 0.610 kg/m^3 (20°C, 1.013 bar)
Melting Point	−77.73 °C
Boiling Point	−33.34 °C
Critical Point (T, P)	132.42 °C, 114.8 bar
Solubility in water	895 g/l (0 °C) 529 g/l (20 °C) 316 g/l (40 °C) 168 g/l (60 °C)
Solubility	soluble in chloroform, ether, ethanol, methanol
Acidity (pKa)	32.5 (−33 °C), 10.5 (DMSO)
Basicity (pKb)	4.75
Conjugated acid	Ammonium
Conjugated base	Amide
Magnetic susceptibility (χ)	$-18.0\cdot10^{-6}$ cm^3/mol
Refractive index	1.3327
Viscosity	10.225 mPa·s (−33.5 °C)
Melting Heat at 1.013 bar	332.3 kJ/kg
Vaporization Heat at -15 °C	1210 kJ/kg
Vaporization Heat at -33.4 °C	1370 kJ/kg
Standard molar entropy (S°_{298})	193 J/mol/K
Standard enthalpy of formation ($\Delta H^0_{f,298}$)	−46 kJ/mol

Sources: Air Liquide (1980), Ulmann (1985), SNIE (1991), WHO (1986)

Properties

Property	NH_3	Reference
Molar mass in g/mol	17.03	Air Liquide (1980), Ulmann (1985), SNIE (1991)
Liquid density (at boiling point) in kg/m^3	682	Air Liquide (1980), Ulmann (1985), SNIE (1991)
Melting temperature in °C	-77.73	Air Liquide (1980), Ulmann (1985), SNIE (1991)
Boiling temperature (at atm. pressure) in °C	-33.34	Air Liquide (1980), Ulmann (1985), SNIE (1991)
Auto-ignition temperature in °C	650	Chaineaux (1991)
LFL (Lower Flammable Limit) in vol%	16	INRS (1989), Sax (1996)
UFL (Upper Flammable Limit) in vol%	25	INRS (1989), Sax (1996).
Minimum ignition energy in air in mJ	680	Buckley and Husa (1962)
Vapor density (1 atm, 20 °C) in kg/m^3	0.708	Air Liquide (1980), Ulmann (1985), SNIE (1991)
Maximum Laminar Burning Velocity (m/s)	+/- 0.07	Li et al. (2021)

Ammonia is an effective hydrogen carrier: 10.7 kg of hydrogen are contained in 100 l of liquid NH3

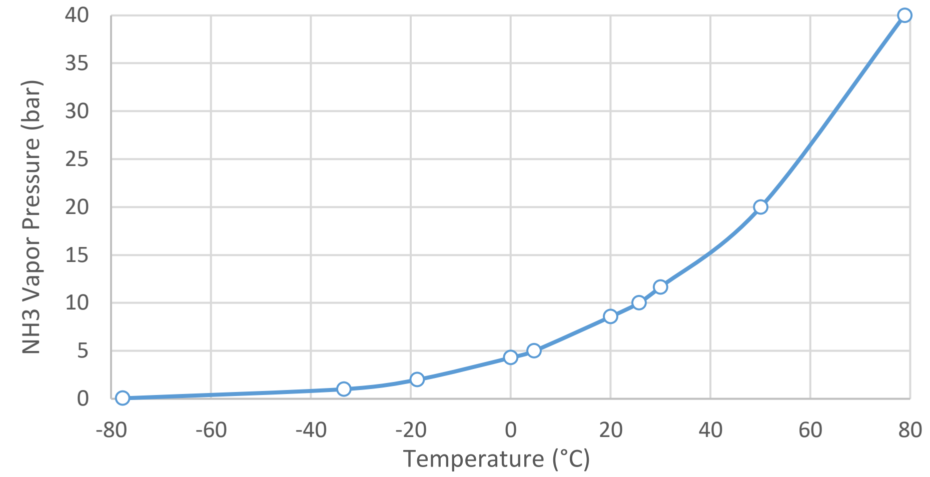
- The dissolution of ammonia in water is highly exothermic (2 MJ/kg NH_3 dissolved).
- The dissolution of one kilogram of ammonia releases enough energy to evaporate almost one and a half kilograms of water

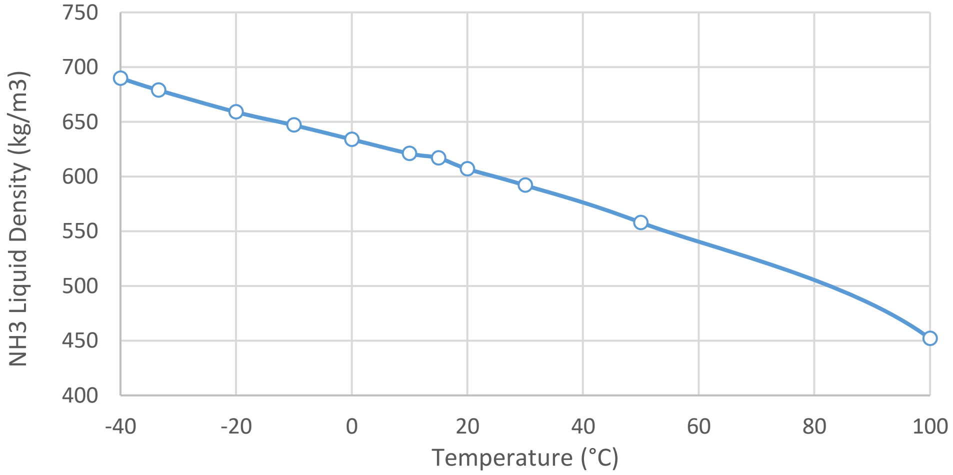
Temperature (°C)	-33,2	-18.7	0	20	25	30	50.1
Vapour Pressure (bar)	1.013	2	4.29	8.56	9.9	11.66	20

Propane : - 42,1°C

Propane : 9.4 bar

Its vapor pressure is similar to that of propane





Product	Density relative to air
Hydrogen	0.069
Methane	0.550
Ammonia	0.597
Propane	1.530
Butane	2.014

Properties

Property	Anhydrous Ammonia
Molar mass in g/mol	17.03
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Boiling temperature (at atm. pressure) in °C	-33.34
Auto-ignition temperature in °C	650
LFL (Lower Flammable Limit) in vol%	16
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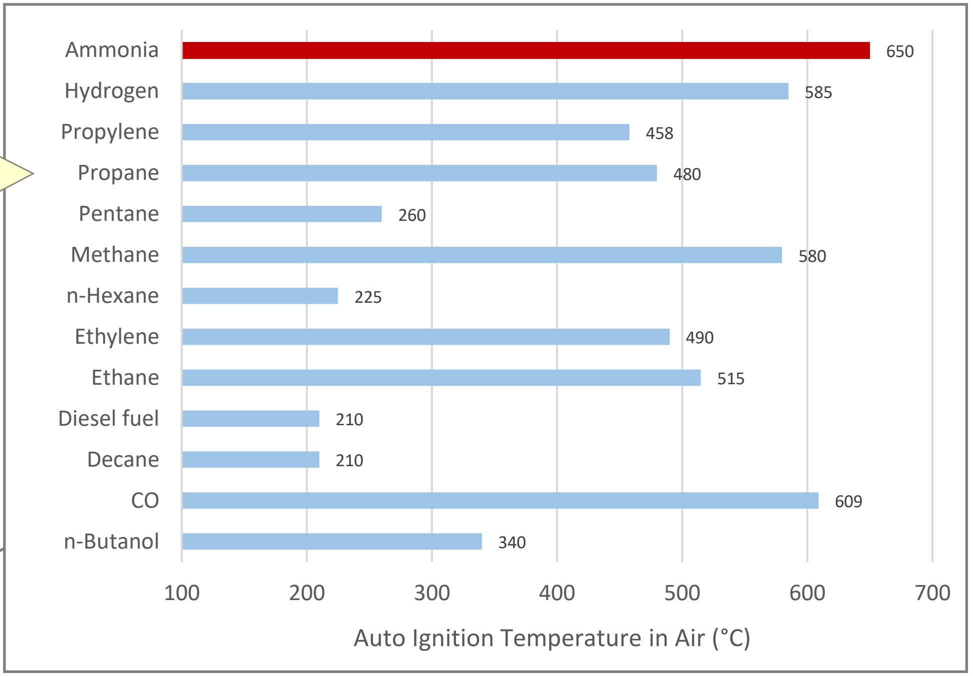
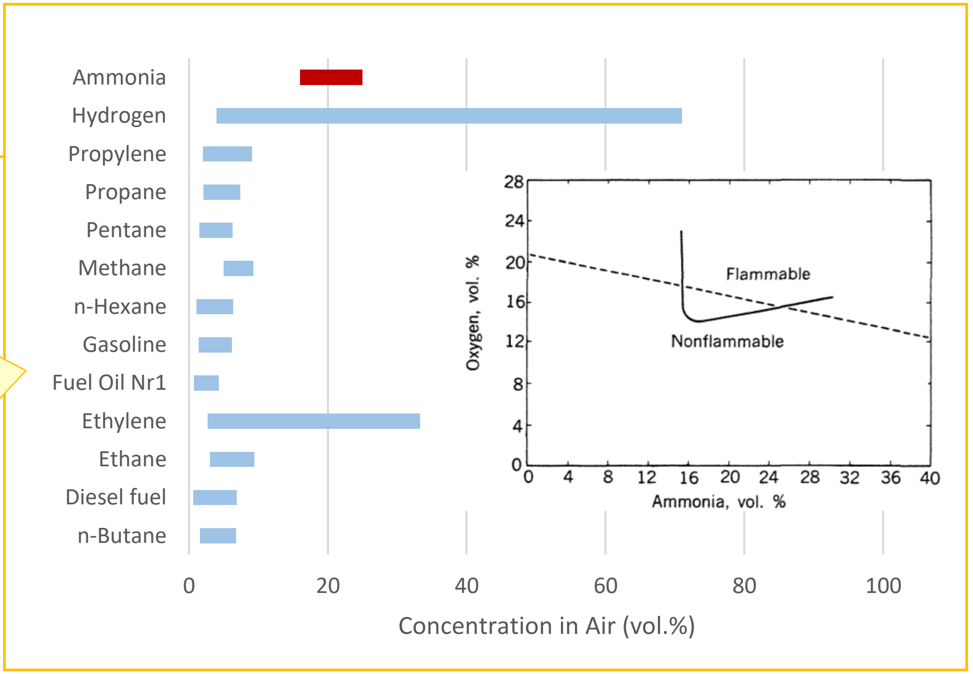
Minimum ignition energy in air in mJ	680
Vapor density (1 atm, 20 °C) in kg/m^3	0.708
Maximum Laminar Burning Velocity (m/s)	+/- 0.07

- The auto ignition temperature of ammonia is higher than most heavier hydrocarbons





- Most hydrocarbons have LFL/UFL ranges in the order of LFL = 1 to 4% and UFL = 6 to 10%
- The flammability range of ammonia is a bit wider with a higher LFL

Properties

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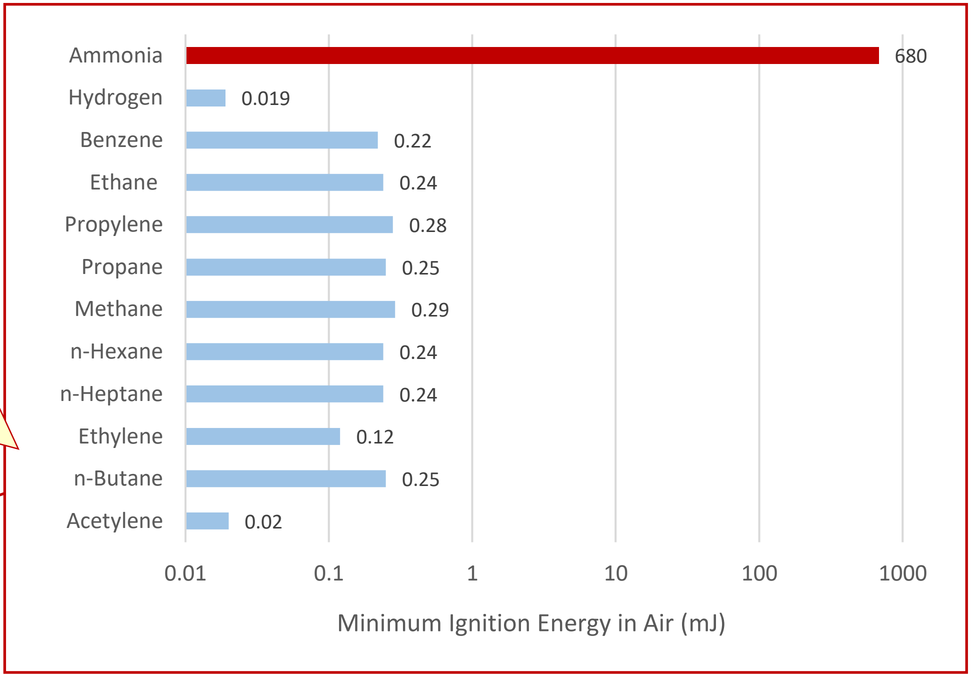
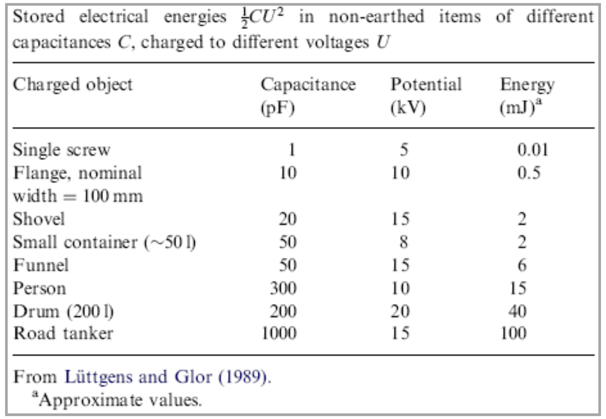
Minimum ignition energy in air in mJ	680
Vapor density (1 atm, 20 °C) in kg/m^3	0.708
Maximum Laminar Burning Velocity (m/s)	+/- 0.07

- The minimum ignition energy for ammonia/air mixtures is extremely high (680 mJ)
- Typical electrostatic spark discharge energies can vary from 0.01 to 100 mJ.
- Ammonia is difficult to ignite by common ignition sources





Stored electrical energies $\frac{1}{2}CU^2$ in non-earthed items of different capacitances C, charged to different voltages U

Charged object	Capacitance (pF)	Potential (kV)	Energy (mJ)[a]
Single screw	1	5	0.01
Flange, nominal width = 100 mm	10	10	0.5
Shovel	20	15	2
Small container (~50 l)	50	8	2
Funnel	50	15	6
Person	300	10	15
Drum (200 l)	200	20	40
Road tanker	1000	15	100

From Lüttgens and Glor (1989).
[a] Approximate values.


Ammonia : very difficult to ignite, flame is visible

Properties

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Minimum ignition energy in air in mJ	680
Vapor density (1 atm, 20 °C) in kg/m^3	0.708
Maximum Laminar Burning Velocity (m/s)	+/- 0.07

- In case of accidental releases of anhydrous ammonia, the vapor cloud may contain liquid ammonia and the cold temperatures of the release may condense water vapor in ambient air, in which case the density of the vapor cloud is heavier than air (see picture on right of an ammonia release).
- Because of the very high affinity of anhydrous ammonia for water (forming NH_4OH), it reacts immediately with the humidity in the air, forming a dense cloud and remaining remain close to the ground.

Dispersing ammonia cloud following a truck accident (Houston, 1976)

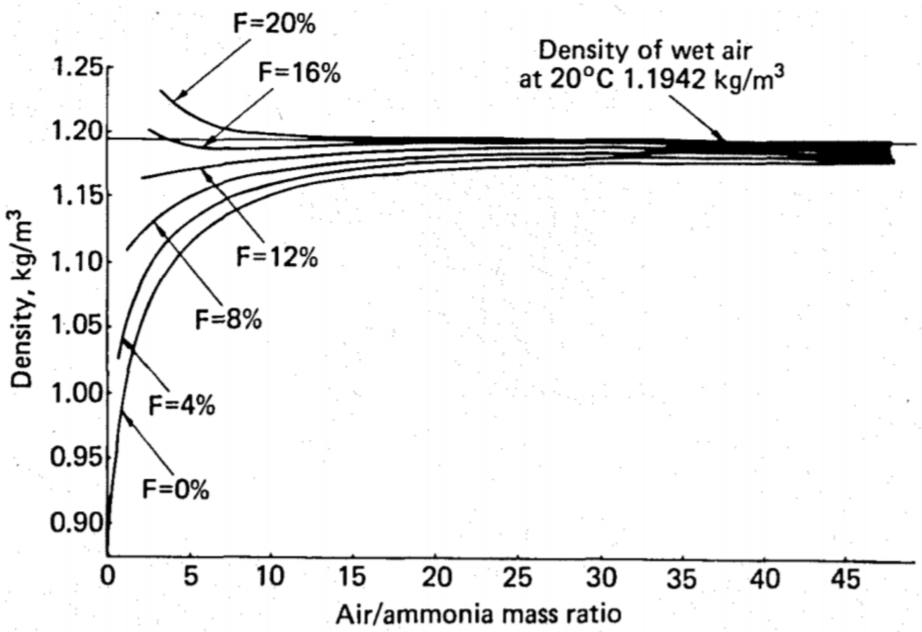


Figure 4. Density of an ammonia cloud initially containing some liquid ammonia as it is diluted with wet air. *F* = percentage of total mass of airborne ammonia initially in the liquid phase. Reproduced from Haddock and Williams.[5]

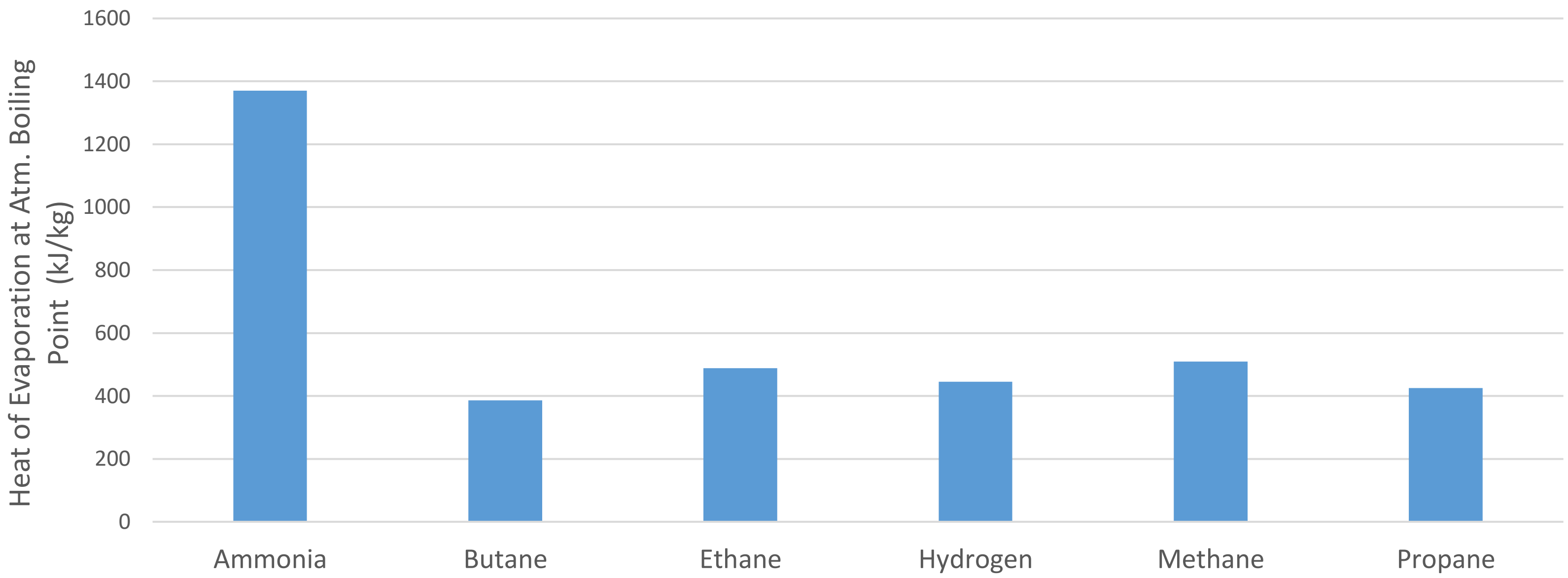
Liquid Pool Evaporation

○ Liquid ammonia has a very high standard enthalpy change of vaporization (23.35 kJ/mol, for comparison water 40.65 kJ/mol, methane 8.19 kJ/mol, phosphine 14.6 kJ/mol) and can therefore be used in laboratories in uninsulated vessels without additional refrigeration.

○ Tests by INERIS have shown that solid obstacles (wall or ground) placed in a two-phase ammonia jet at a distance of a few meters from the release point have a major influence on the concentration values measured after the obstacle. In the test campaign, approximately two times lower concentrations were measured after the obstacle with respect to an open-field release.

○ If the release is pointed towards the retention dike, the dike can retrieve a large quantity of ammonia in liquid form. For two tests, quantities greater than 50% of the total mass released were collected in liquid form at a temperature of approximately -60°C. The liquid ammonia sheet formed in this way is not evaporated rapidly.

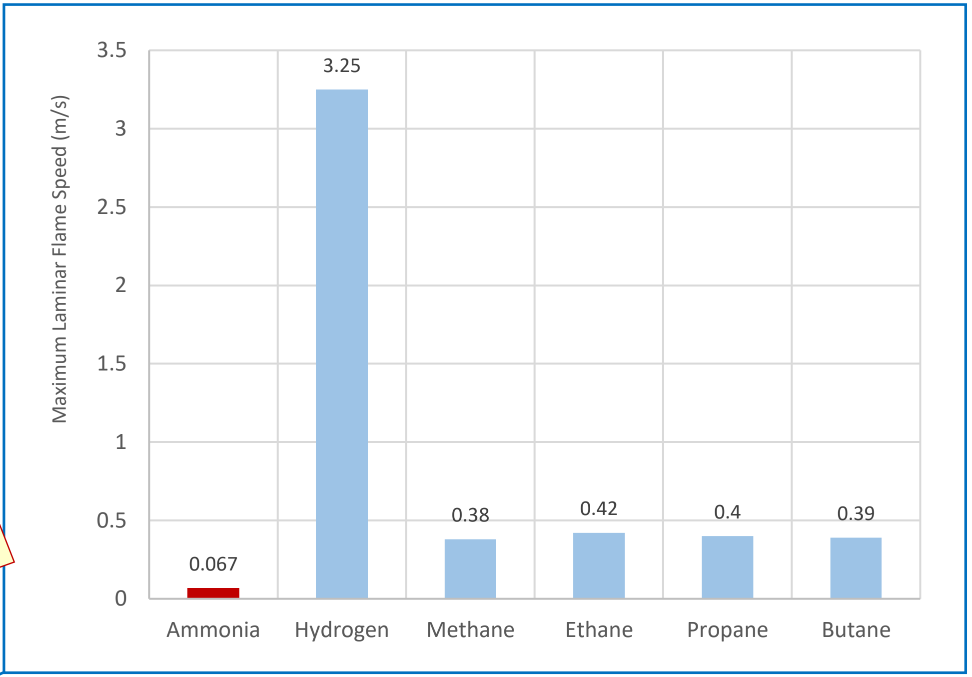
○ The graph below show the heat of evaporation of some liquefied gases at their boiling point. The heat of evaporation of ammonia is about 3 times higher than for flammable liquefied gases such as methane, ethane, propane, butane and hydrogen.

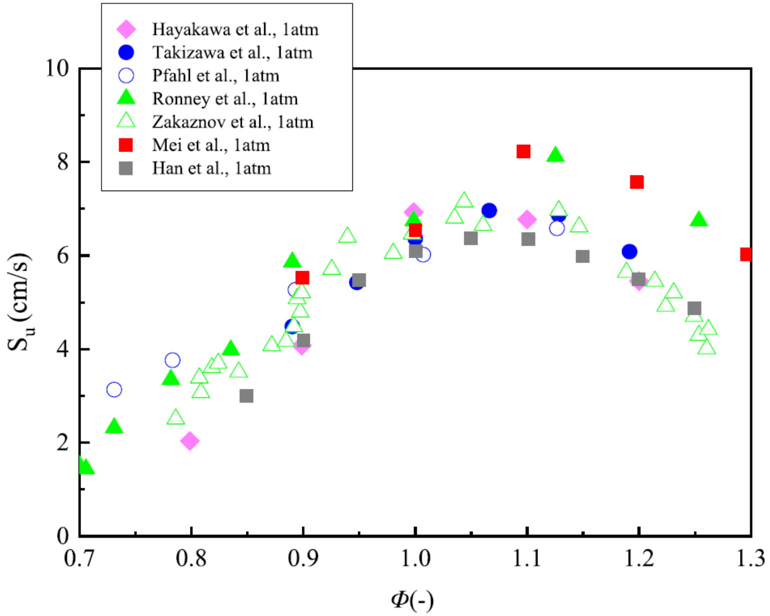


Flammability

Property	Anhydrous Ammonia
Molar mass in g/mol	17.03
Liquid density (at boiling point) in kg/m^3	682
Melting temperature in °C	-77.73
Boiling temperature (at atm. pressure) in °C	-33.34
Auto-ignition temperature in °C	650
LFL (Lower Flammable Limit) in vol%	16
UFL (Upper Flammable Limit) in vol%	25
Minimum ignition energy in air in mJ	680
Vapor density (1 atm, 20 °C) in kg/m^3	0.708
Maximum Laminar Burning Velocity (m/s)	+/- 0.07

- The maximum laminar burning velocity is a measure for the combustion reactivity of a substance
- Most hydrocarbons encountered in oil & gas industry have a burning velocity of about 40 to 80 cm/s
- Ammonia has the lowest maximum laminar burning velocity
- Hydrogen has the highest maximum laminar burning velocity





Laminar burning velocity of NH_3 flame as a function of equivalence ration at 298 K and 1 atm (Han et al., 2019; Kobayashi et al., 2019, Mei et al., 2019)

- The combustion of ammonia to form nitrogen and water is exothermic: $4\ NH_3 + 3\ O_2 \rightarrow 2\ N_2 + 6\ H_2O\ (g)$
  $\Delta H°r = -1267.20$ kJ (or -316.8 kJ/mol if expressed per mol of NH_3)
- The combustion of ammonia in air is very difficult in the absence of a catalyst due to the relatively low heat of combustion, a lower laminar burning velocity, high auto-ignition temperature, high heat of vaporization, and a narrow flammability range.

Fire & Explosion Risk

- Ammonia explosions have occurred, but only in confined spaces when high leak rates cause a minimum of 16% in air to be reached.
- In open air, the vapor phase of an atmospheric boiling liquid pool is very difficult to ignite. To reach ignition, heat must be provided to the boiling liquid in order to artificially increase the evaporation rate and reach the lower flammable limit.
- In addition to the narrow flammable window, both the ignition temperature and minimum ignition energy are high. The likelihood of an ammonia gas cloud ignition is low.
- Even if the gas cloud ignites, ammonia burns very slowly, leading to a flash fire rather than an explosion. The damage that can be expected to be causes by the generated pressure wave is therefore limited.
- Significant overpressures can be reached when a flash fire occurs in a confined space.

The only extinguishing agents that should be used are CO_2 or powders where ammonia in a liquid state may be present. This is because the contact of water with liquid ammonia imports heat to the ammonia and promotes its vaporization.

Density of NH_3/ Air Mixtures

- Accidental releases of ammonia from pressurized containers frequently flash into tiny droplets and form aerosol clouds with are heavier than air
- Several studies (Fthenakis, 1998) have shown that ammonia releases in moist air will form a denser-than-air cloud if the release contains more than 16% aerosol (because of aerosol density and cooling effects upon evaporation of the aerosol droplets)
- For releases in dry air, dense gas may be formed at lower aerosol fractions (reaction between water vapor and ammonia is exotherm and a mixture of ammonia and moist air is warmer and less dense than a mixture of ammonia and dry air)
- If the initial release contains less than 4-8% aerosol, is mixture with air produces a buoyant cloud, limiting the possibilities for mitigating action (such as water sprays)

Toxicity of Anhydrous Ammonia

Human Toxicity

How can people be exposed to ammonia?

- Most people are exposed to ammonia from inhalation of the gas or vapors. Since ammonia exists naturally and is also present in cleaning products, exposure may occur from these sources. Anhydrous ammonia gas is lighter than air and will rise, so that generally it dissipates and does not settle in low-lying areas. However, in the presence of moisture (such as high relative humidity), the liquefied anhydrous ammonia gas forms vapors that are heavier than air. These vapors may spread along the ground or into low-lying areas with poor airflow where people may become exposed.

What is ammonia's mechanism of action?

- Ammonia interacts immediately upon contact with available moisture in the skin, eyes, oral cavity, respiratory tract, and particularly mucous surfaces to form the very caustic ammonium hydroxide. Ammonium hydroxide causes the necrosis of tissues through disruption of cell membrane lipids (saponification) leading to cellular destruction. As cell proteins break down, water is extracted, resulting in an inflammatory response that causes further damage.

What are the immediate health effects of ammonia exposure?

- <u>Inhalation</u>:

  Ammonia is irritating and corrosive. Exposure to high concentrations of ammonia in air causes immediate burning of the nose, throat and respiratory tract. This can cause bronchiolar and alveolar edema, and airway destruction resulting in respiratory distress or failure. Inhalation of lower concentrations can cause coughing, and nose and throat irritation. Ammonia's odor provides adequate early warning of its presence, but ammonia also causes olfactory fatigue or adaptation, reducing awareness of one's prolonged exposure at low concentrations. Children exposed to the same concentrations of ammonia vapor as adults may receive a larger dose because they have greater lung surface area-to-body weight ratios and increased minute volumes-to-weight ratios. In addition, they may be exposed to higher concentrations than adults in the same location because of their shorter height and the higher concentrations of ammonia vapor initially found near the ground.
- <u>Skin or eye contact:</u>

  Exposure to low concentrations of ammonia in air or solution may produce rapid skin or eye irritation. Higher concentrations of ammonia may cause severe injury and burns. Contact with concentrated ammonia solutions such as industrial cleaners may cause corrosive injury including skin burns, permanent eye damage or blindness. The full extent of eye injury may not be apparent for up to a week after the exposure. Contact with liquefied ammonia can also cause frostbite injury.
- <u>Ingestion:</u>

  Exposure to high concentrations of ammonia from swallowing ammonia solution results in corrosive damage to the mouth, throat and stomach. Ingestion of ammonia does not normally result in systemic poisoning.

How is ammonia exposure treated?

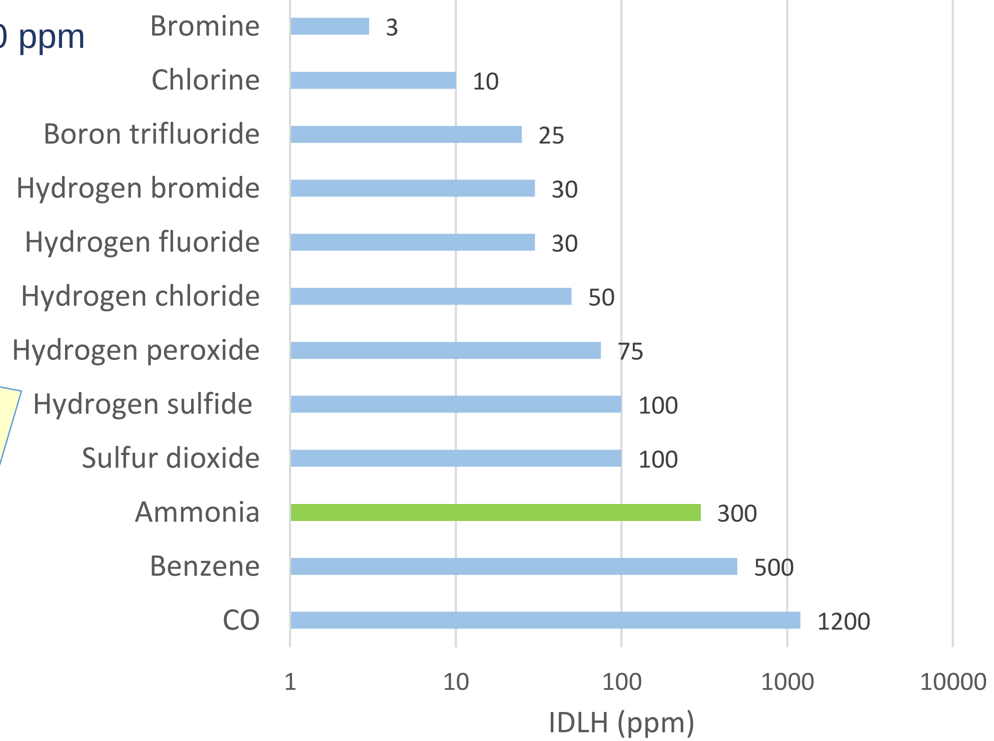
- There is no antidote for ammonia poisoning, but ammonia's effects can be treated, and most people recover. Immediate decontamination of skin and eyes with copious amounts of water is very important. Treatment consists of supportive measures and can include administration of humidified oxygen, bronchodilators and airway management. Ingested ammonia is diluted with milk or water.

Human Toxicity

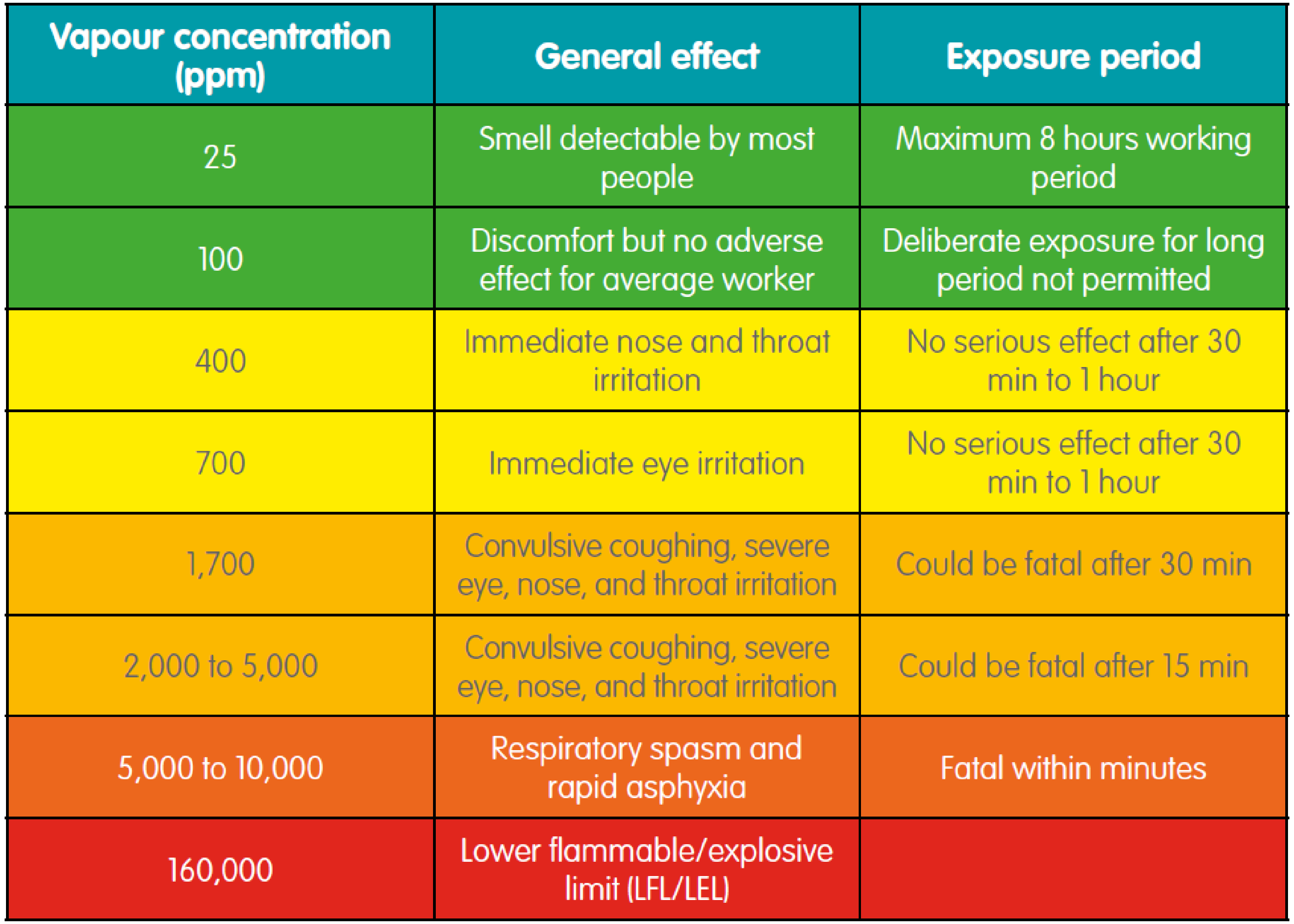
- ○ The EU regulates the Occupational Exposure Limits (OEL) to 20 ppm for 8 hours and 50 ppm for 15 minutes
- ○ Concentrations of 5000 to 10 000 ppm are reported to be fatal within minutes
- ○ Exposure for 30 minutes to concentrations between 2500 and 6000 ppm are assessed as seriously life-threatening

Detectable Odor	2-20 ppm
TWA PEL	25 ppm
STEL	35 ppm
General discomfort Runny eyes & nose No adverse effects	150 – 200 ppm
IDLH	300 ppm
Immediate nose/throat irritation	400 ppm
Immediate eye injury	700 ppm
May be fatal (30 minutes or less)	2500 ppm
Death in minutes	5000 ppm
Immediate Death	10.000 ppm
Skin Irritations Burns, blisters	30.000 ppm
Visible cloud	40.000 ppm
Lower Flammable Limit	150.000 ppm
Upper Flammable Limit	280.000 ppm

The IDLH concentration represents an estimate of the maximum concentration of a substance in air from which healthy workers can escape without loss of life or irreversible health effects under conditions of a maximum 30-minute exposure time.



Human Toxicity



Vapour concentration (ppm)	General effect	Exposure period
25	Smell detectable by most people	Maximum 8 hours working period
100	Discomfort but no adverse effect for average worker	Deliberate exposure for long period not permitted
400	Immediate nose and throat irritation	No serious effect after 30 min to 1 hour
700	Immediate eye irritation	No serious effect after 30 min to 1 hour
1,700	Convulsive coughing, severe eye, nose, and throat irritation	Could be fatal after 30 min
2,000 to 5,000	Convulsive coughing, severe eye, nose, and throat irritation	Could be fatal after 15 min
5,000 to 10,000	Respiratory spasm and rapid asphyxia	Fatal within minutes
160,000	Lower flammable/explosive limit (LFL/LEL)	

Source: Ammonia as a marine fuel. An introduction. SGMF. ISBN 978-1-7398703-X-X

Human Toxicity

Concentration	1 min	3 min	10 min	20 min	30 min	60 min
Significant lethal effects – mg/m3	19623		6183	4387	3593	2543
Significant lethal effects – ppm	28033		8833	6267	5133	3633
First lethal effects – mg/m3	17710	10290	5740	4083	3337	2380
First lethal effects – ppm	25300	14700	8200	5833	4767	3400
Irreversible effects – mg/m3	1050	700	606	428	350	248
Irreversible effects – ppm	1500	1000	866	612	500	354
Reversible effects – mg/m3	196	140	105	84	77	56
Reversible effects - ppm	280	200	150	120	110	80

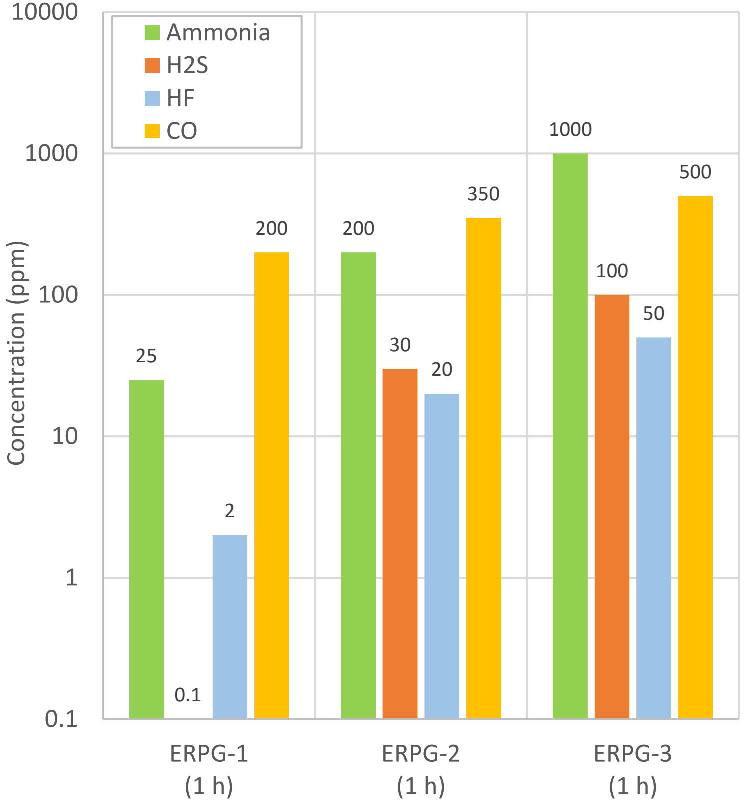
Source: INERIS-DRC-08-94398-11812A

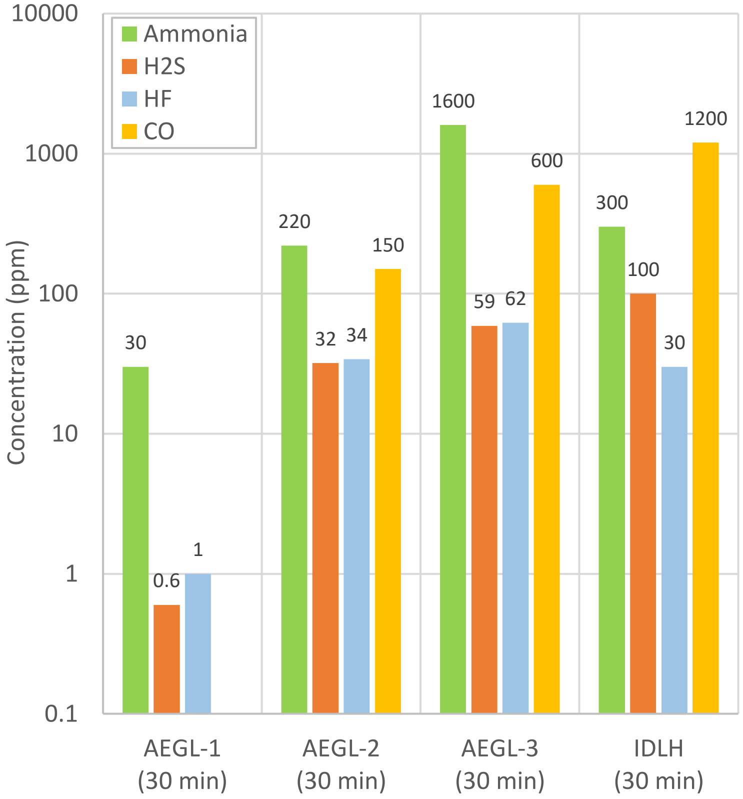
Concentration	1 min	3 min	10 min	20 min	30 min	60 min
LC1% - ppm	14700	8500	4600	3300	2700	1900

Source: TNO, Green Book (probit coëfficients (mg/m3): A=-15.8, b=1, n=2)

Concentration	Explanation	10 min	30 min	1 h	4 h	8 h
AEGL1 - ppm	Notable discomfort, irritation, or certain asymptomatic non-sensory effects. Effects are not disabling and are transient and reversible upon cessation of exposure	30	30	30	30	30
AEGL2 – ppm	Reversible or other serious, long-lasting adverse health effects of an impaired ability to escape	220	220	160	110	110
AEGL3 - ppm	Life-threatening health effects or death	2700	1600	1100	550	390

Human Toxicity (EPRG values and AEGL values).





- ERPG-1 = maximum airborne concentration below which it is believed nearly all individuals could be exposed for up to 1 hour without experiencing more than mild, transient adverse health effects or without perceiving a clearly defined objectionable odor.
- ERPG-2 = the maximum airborne concentration below which it is believed nearly all individuals could be exposed for up to 1 hour without experiencing or developing irreversible or other serious health effects or symptoms that could impair an individual's ability to take protective action.
- ERPG-3 = maximum airborne concentration below which it is believed nearly all individuals could be exposed for up to 1 hour without experiencing or developing life threatening health effects.
- The IDLH concentration represents an estimate of the maximum concentration of a substance in air from which healthy workers can escape without loss of life or irreversible health effects under conditions of a maximum 30-minute exposure time.

- AEGL-1 is the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience notable discomfort, irritation, or certain asymptomatic, non-sensory effects. However, the effects are not disabling and are transient and reversible upon cessation of exposure.
- AEGL-2 is the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience irreversible or other serious, long-lasting adverse health effects, or an impaired ability to escape.
- AEGL-3 is the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience life-threatening health effects or death.

* *ERPG values (Emergency Response Planning Guidelines) are proposed by the American Industrial Hygiene Association (AIHA).*

** *Acute Exposure Guideline Levels (AEGL) are proposed by a National Academy of Sciences committee*

Toxicity for Aquatic Life

- NH_3 is very soluble in water
- In water NH_3 undergoes an exothermic dissolution reaction
- NH_3 is a serious threat to marine life when released to sea
  - LC50 for fish is 0.75-3.4 mg/L after 96h
  - Consistent with the classification of NH_3 using the risk phrase "R50 Very toxic to aquatic organisms"

Gas Dispersion Testing

PSR/HSE/RM/SPI©
March 2023

Dispersing Cloud


Anhydrous liquid ammonia leak


Anhydrous liquid ammonia plume (from INERIS, 2005)

Dispersing Cloud

Dispersing Cloud

Dispersing Cloud

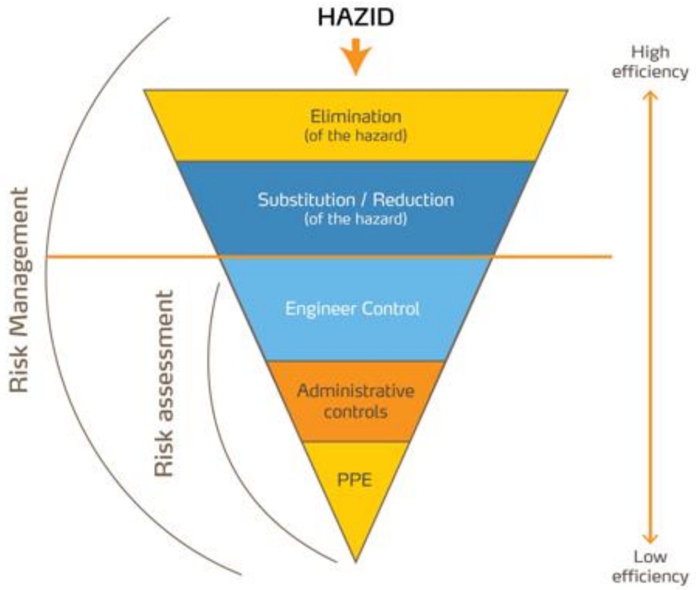
Management of NH_3 Risks

PSR/HSE/RM/SPI©
March 2023

Management of NH_3 Risks

The following principles apply for the management of NH_3 risks

- **Hazard isolation**
  Ammonia storage and associated equipment shall, as much as possible, be kept away from possible external impacts (for example tank location requirements in the IGF Code) to reduce the likelihood of a significant leak that affects individuals outside of the ship and/or the port. In addition, secondary confinement, for example a pipe in pipe system, associated with specific safety zones are very efficient in mitigating many possible leak consequences.
- **Hazard reduction**
  Liquid ammonia stored and handled in its cold and atmospheric form is inherently safer than warm and pressurized ammonia. The initial flash occurring on the liquid phase release being much reduced in its cold state, impacting significantly the initial size and dispersion of the toxic cloud.
- **Engineering controls**
  Integrating safety features as early as possible in the design stages is the most efficient approach for managing safety, where a good balance between cost and safety level can be achieved. The long experience available in ammonia handling onshore allows a wide variety of safety solutions to select from.



Management of NH_3 Risks

Examples of engineering controls:

- ○ Construction material selection to prevent well-known degradation mechanisms capable of initiating material failures
  - ✓ Stress corrosion cracking (SCC)
  - ✓ Corrosion under insulation (CUI)
  - ✓ Cold service
- ○ Auxiliary equipment/systems to handle expected process releases . Proper design should integrate these expected process releases so that no ammonia emission is expected during normal operations or maintenance.
  - ✓ Pressure and temperature relief valves (PSVs/PRVs, TRVs)
  - ✓ Inerting/purging associated with maintenance and start-up/shutdown operations.
- ○ Auxiliary equipment/systems to handle unexpected process loss of containment (leaks and spills).
  - ✓ A specific focus must be applied on early leak detection and automatic isolation to limit the released quantity.
  - ✓ Other features such as drip trays and water mist systems, etc. can efficiently impact the gas cloud size and dispersion, reducing significantly the area exposed to hazardous concentration levels.
  - ✓ The ultimate disposal of the spilt ammonia (for example in a drip tray) needs additional consideration as traditional disposal methods (for example, over the side) are unlikely to be possible.
- ○ Measurement and control of ammonia emissions should rely on detectors and not the human nose which may desensitize over time.

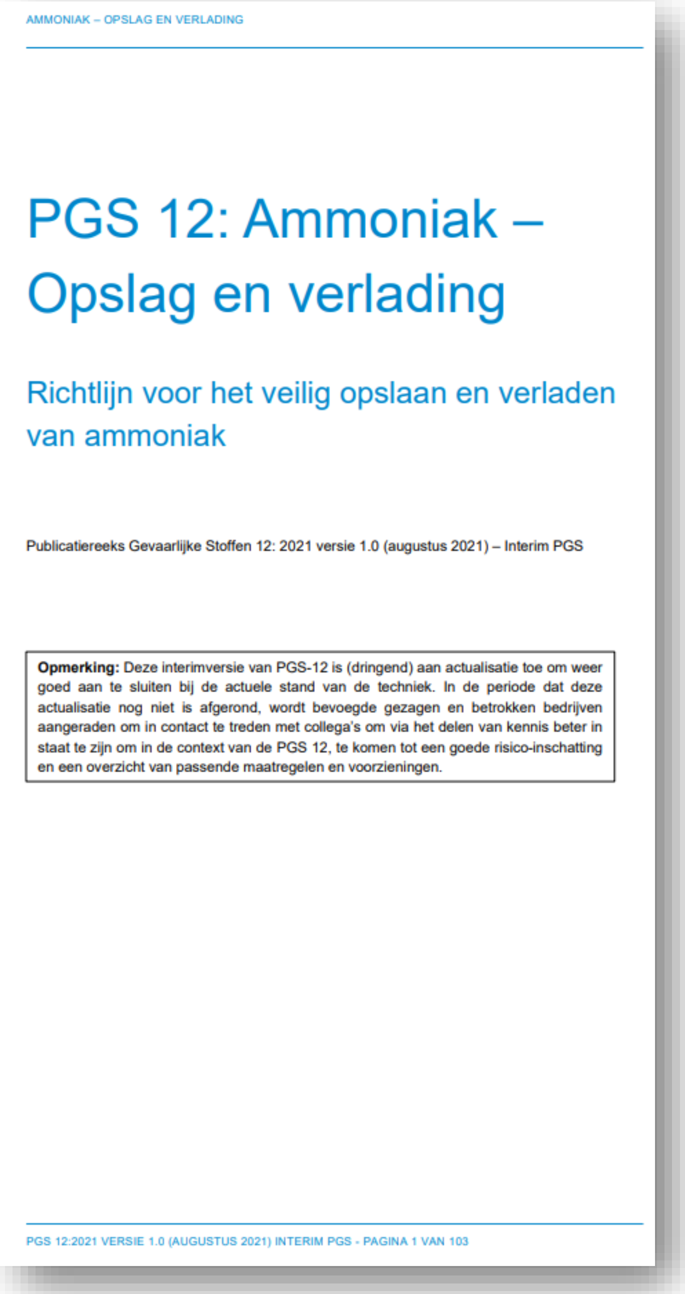
Management of NH_3 Risks

Examples of engineering controls:

- As the vast majority of accidents are caused by a human error, human factors must be taken into account in the design phases, and barriers such as automated sequences and interlocks or permissives must be considered.
- Organizational measures such as a comprehensive set of Standard Operating Procedures must be co-developed with end users. In this approach, proper Personal Protective Equipment (PPE) selection according to potential exposure type is key to ensure immediate users/responders' safety.
  - ✓ Normal Operating Conditions
  - ✓ Deviated/Non-standard Operating Conditions
  - ✓ Emergency response plans

Management of NH_3 Risks

- A document with detailed requirements related to the storage and loading/unloading of anhydrous ammonia (rail, road & maritime) can be found in PGS 12



AMMONIAK – OPSLAG EN VERLADING

PGS 12: Ammoniak – Opslag en verlading

Richtlijn voor het veilig opslaan en verladen van ammoniak

Publicatiereeks Gevaarlijke Stoffen 12: 2021 versie 1.0 (augustus 2021) – Interim PGS

Opmerking: Deze interimversie van PGS-12 is (dringend) aan actualisatie toe om weer goed aan te sluiten bij de actuele stand van de techniek. In de periode dat deze actualisatie nog niet is afgerond, wordt bevoegde gezagen en betrokken bedrijven aangeraden om in contact te treden met collega's om via het delen van kennis beter in staat te zijn om in de context van de PGS 12, te komen tot een goede risico-inschatting en een overzicht van passende maatregelen en voorzieningen.

PGS 12:2021 VERSIE 1.0 (AUGUSTUS 2021) INTERIM PGS - PAGINA 1 VAN 103

Gas Detection

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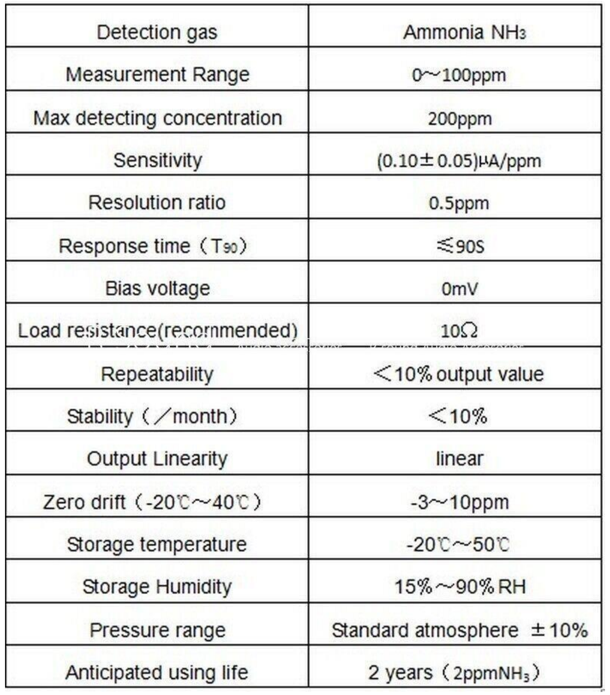
March 2023

Gas Detection

- Different technologies exist for detection of ammonia vapors:
  - ✓ Electrochemical cell (in different ranges, usually 0-100 ppm and 0-5000 ppm) with continuous measurement
  - ✓ Open path (based on UV)
  - ✓ Laser beam detection
  - ✓ Acoustic detection
  - ✓ FLIR (optical detection of ammonia cloud)

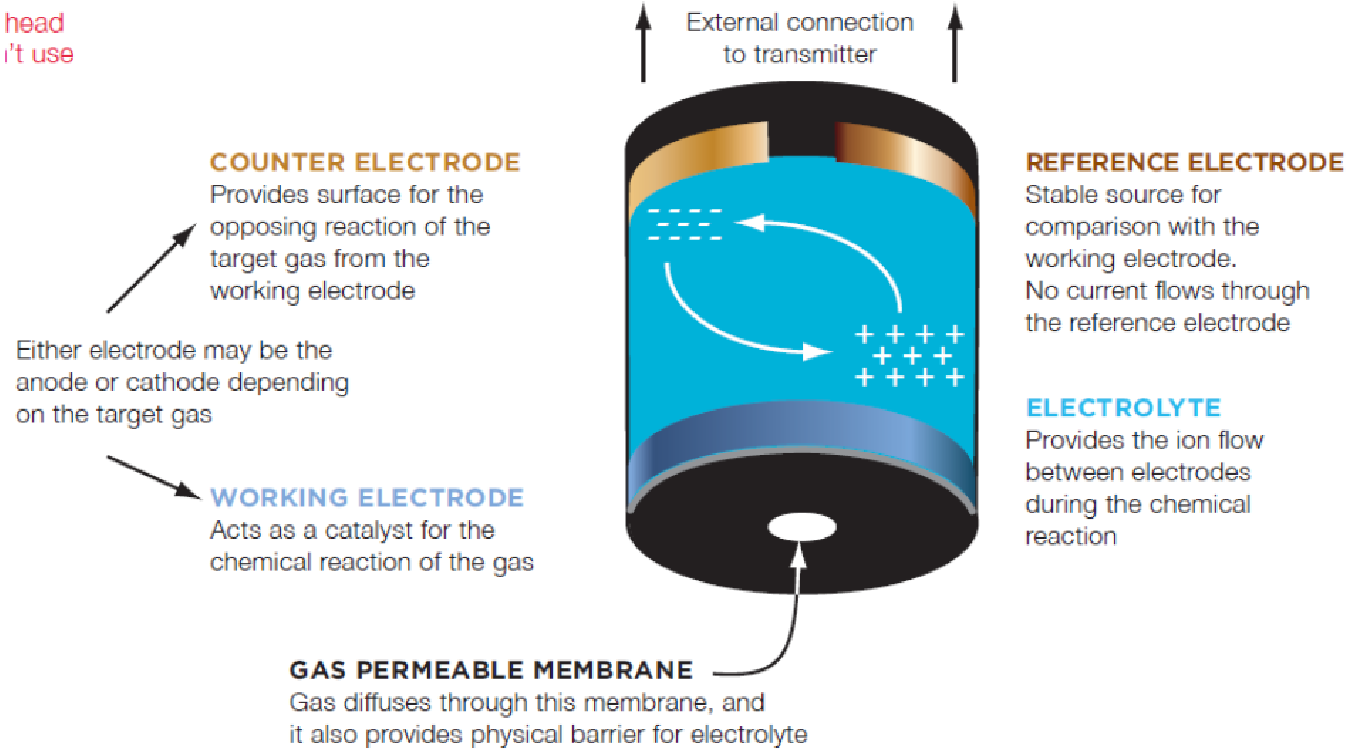

Electrochemical Cell



Detection gas	Ammonia NH_3
Measurement Range	0～100ppm
Max detecting concentration	200ppm
Sensitivity	(0.10±0.05)μA/ppm
Resolution ratio	0.5ppm
Response time（T_{90}）	≤90S
Bias voltage	0mV
Load resistance(recommended)	10Ω
Repeatability	＜10% output value
Stability（／month）	＜10%
Output Linearity	linear
Zero drift（-20℃～40℃）	-3～10ppm
Storage temperature	-20℃～50℃
Storage Humidity	15%～90% RH
Pressure range	Standard atmosphere ±10%
Anticipated using life	2 years（2ppmNH_3）

Electrochemical Cell

- In an electrochemical sensor an aqueous electrolyte solution provides a conductive path for ions to travel between electrodes.
- Target gases are either reduced or oxidized at the working electrode resulting in a current flow between the working and counter electrode.
- The reference electrode provides a zero-reference point from which the resulting difference in potential between the counter and working electrodes can be compared.



External connection to transmitter

COUNTER ELECTRODE
Provides surface for the opposing reaction of the target gas from the working electrode

Either electrode may be the anode or cathode depending on the target gas

WORKING ELECTRODE
Acts as a catalyst for the chemical reaction of the gas

REFERENCE ELECTRODE
Stable source for comparison with the working electrode.
No current flows through the reference electrode

ELECTROLYTE
Provides the ion flow between electrodes during the chemical reaction

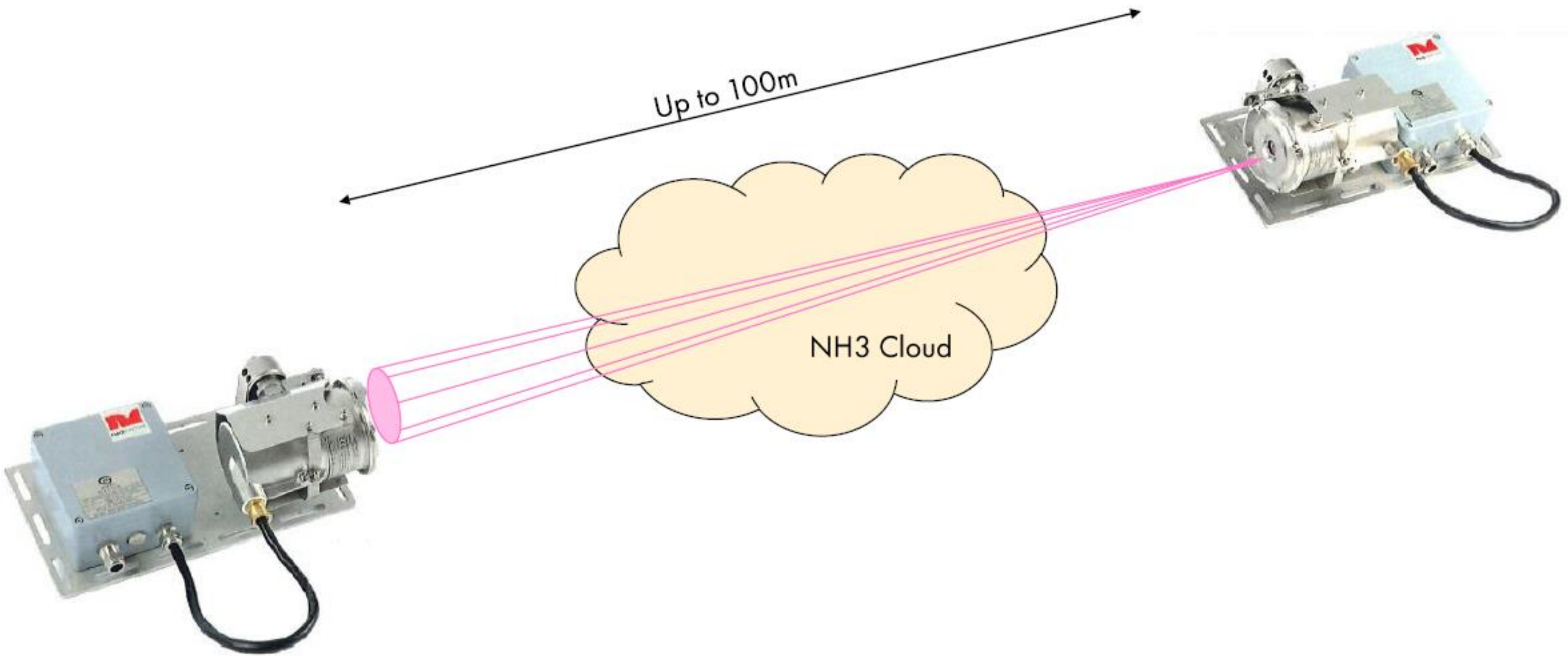
GAS PERMEABLE MEMBRANE
Gas diffuses through this membrane, and it also provides physical barrier for electrolyte

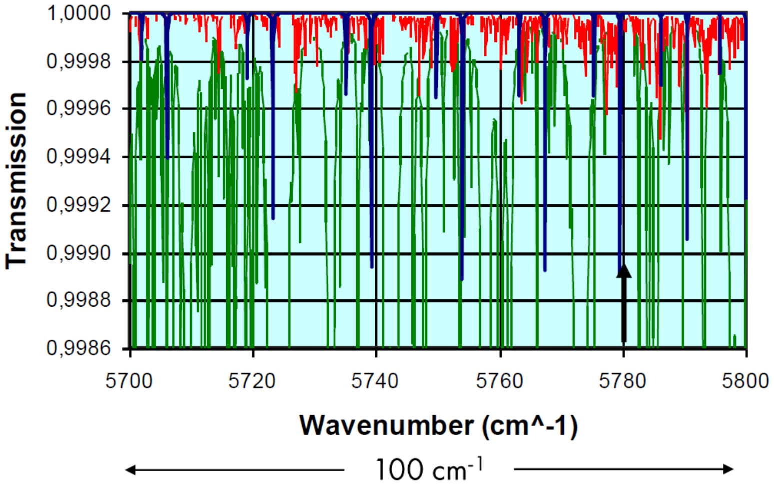
Electrochemical Cell

- Benefits
  - ✓ Cheap
  - ✓ Low power requirements
  - ✓ Easy to install
  - ✓ Specific to ammonia (no interference issues with other gases)
  - ✓ Maximum response time of about 30 seconds
  - ✓ Periodicity of calibration depend on external factors (max. once per month)
  - ✓ Wireless solutions exist (but batteries needed)
  - ✓ Experience (from Teledyne) do not indicate rapid degradation of the cell in a saline environment (offshore conditions)
- Drawbacks
  - ✓ Possibility of saturation (and destruction of cell) in case of exposure to very high concentrations
  - ✓ In case of high humidity, the NH3 vapors will react with ambient humidity to form an ammonia solution
  - ✓ Typically requires oxygen to work
    - Electrochemical reaction = reaction of electrolyte (redox)
    - Minimum O_2 concentration is needed (about 1 vol%) for NH_3 detection (0 – 100 ppm range)
    - 100 ppm NH_3 detection needs min 150 ppm O_2 in the environment
  - ✓ Does not work in liquid environments, at extreme temperatures or pressures, in high velocity duct mounts

Open Path. Laser Spectroscopy.

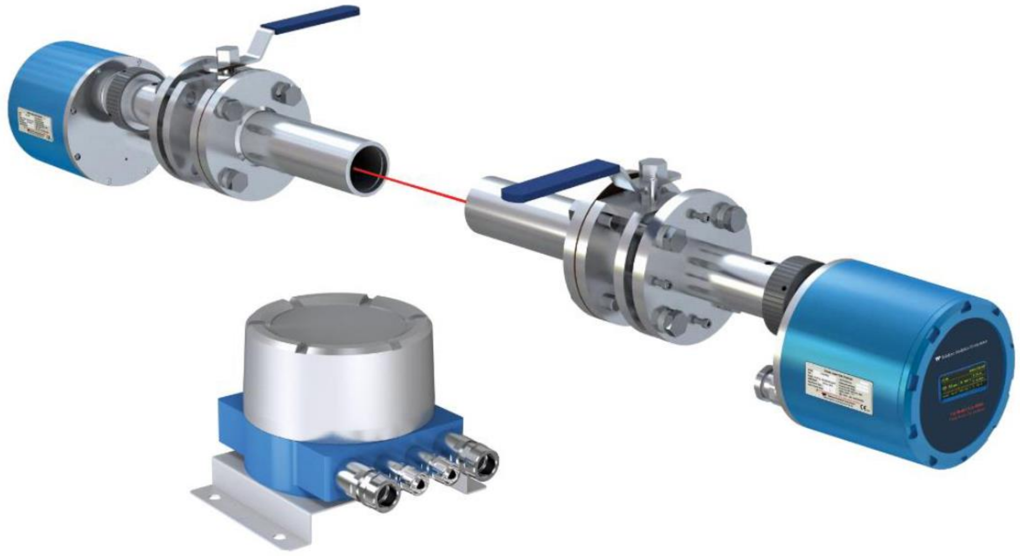
- Photonics-based technologies for gas concentration measurements exploit the fact that every gas has a characteristic absorption spectrum or “fingerprint”. In many cases, this allows a distinct identification of gaseous components including a quantification of the respective concentration levels.
- Many gases have single absorption lines in the NIR (1300 to 2000 nm). At high resolution, the absorption bands are made up of many individual absorption lines, many of which have interfering or overlapping lines from other substances.
- Tuneable Diode Lasers minimize cross interference by locking on a single line where there is practically no cross-sensitivity (e.g., from water) due to the sharpness of the absorption lines
- The transmitter and receiver units can be mounted up to 100 meters apart (application dependent)

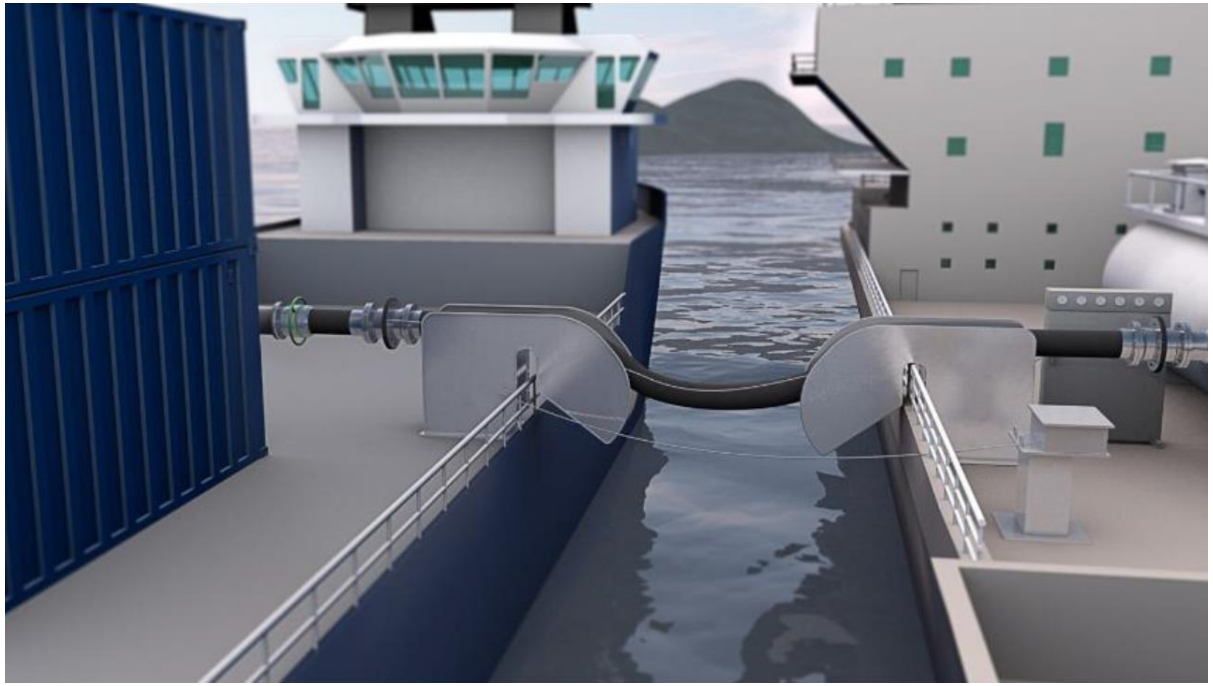




Open Path. Laser Spectroscopy.

- Benefits
  - ✓ Suitable for use in SIL2 rated systems
  - ✓ Compact footprint
  - ✓ Automatic continuous system health check
  - ✓ Low power requirements (< 15 W)
  - ✓ Factory calibrated with no zero drift
  - ✓ No interference from other background gases
  - ✓ Low maintenance
  - ✓ Detection limit: 2 ppm·m
  - ✓ Range: 5 – 100 m
  - ✓ Minimum range: 0 – 40 ppm·m

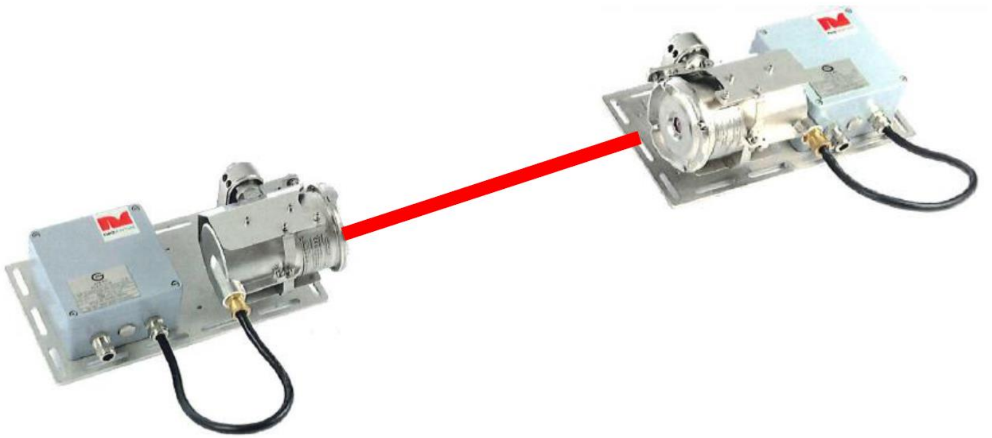




Electrochemical Cell vs Open Path

- Electrochemical Cell
  - Point gas detection technology
  - On site calibration needed
  - No interference from other background gases
  - Cells replacement needed
  - Cells average life expectancy: 24 months
  - No alarm level possible < 10% of the full range (10 ppm for a 100 ppm range)
  - Accuracy: ± 5 ppm (100 ppm range model)

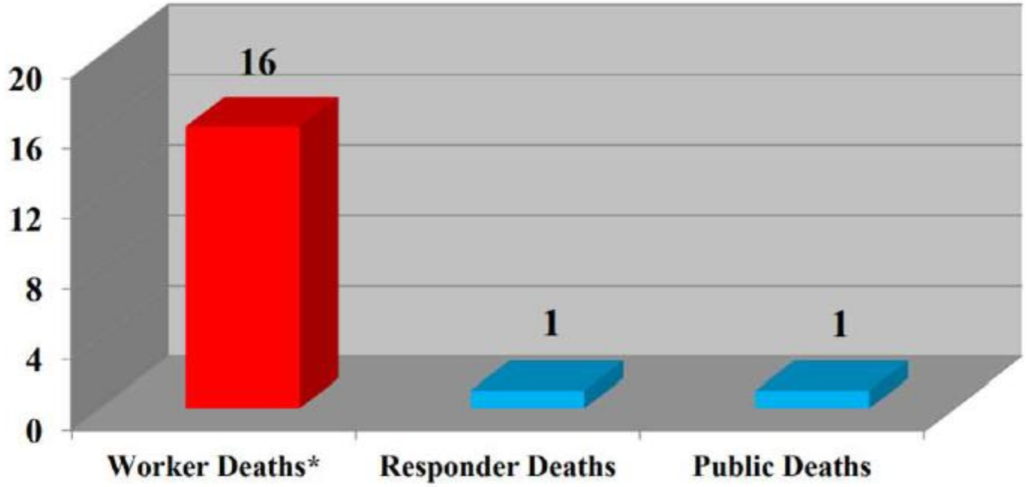
- Open Path
  - Not a point gas detection technology (measurement in ppm·m)
  - Cannot determine the size of the NH_3 leak
  - Factory calibrated with no-zero drift
  - No interference from other background gases
  - Low maintenance
  - Detection limit: 2 ppm·m

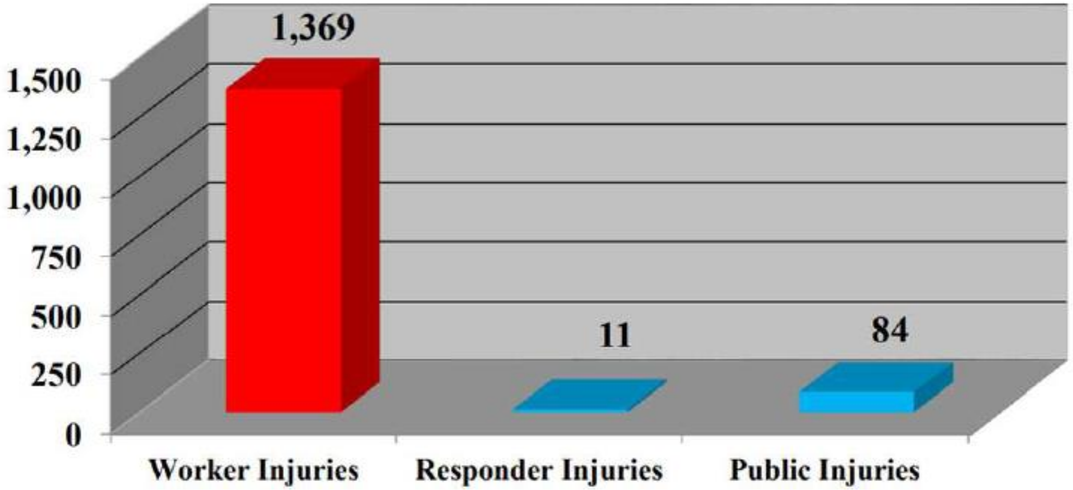


Return On Experience

Return of Experience Anhydrous Ammonia

- ○ According to the RMP database (1994 – 2013) victims of NH_3 releases are those closest to a release, exposed to very high concentrations, and unable to escape or shelter-in-place.
- ○ Most fatalities are to workers, not responders or the public.



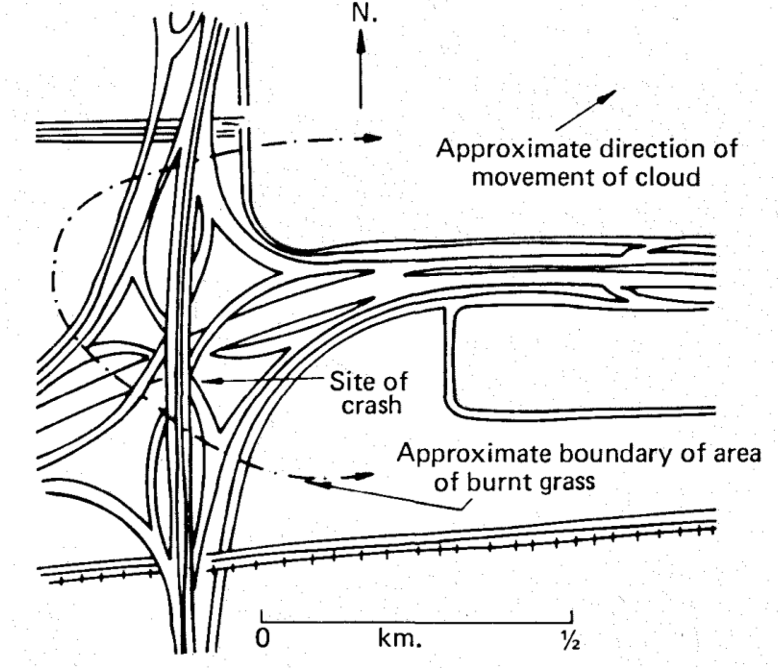


Return of Experience Anhydrous Ammonia Transport Accidents

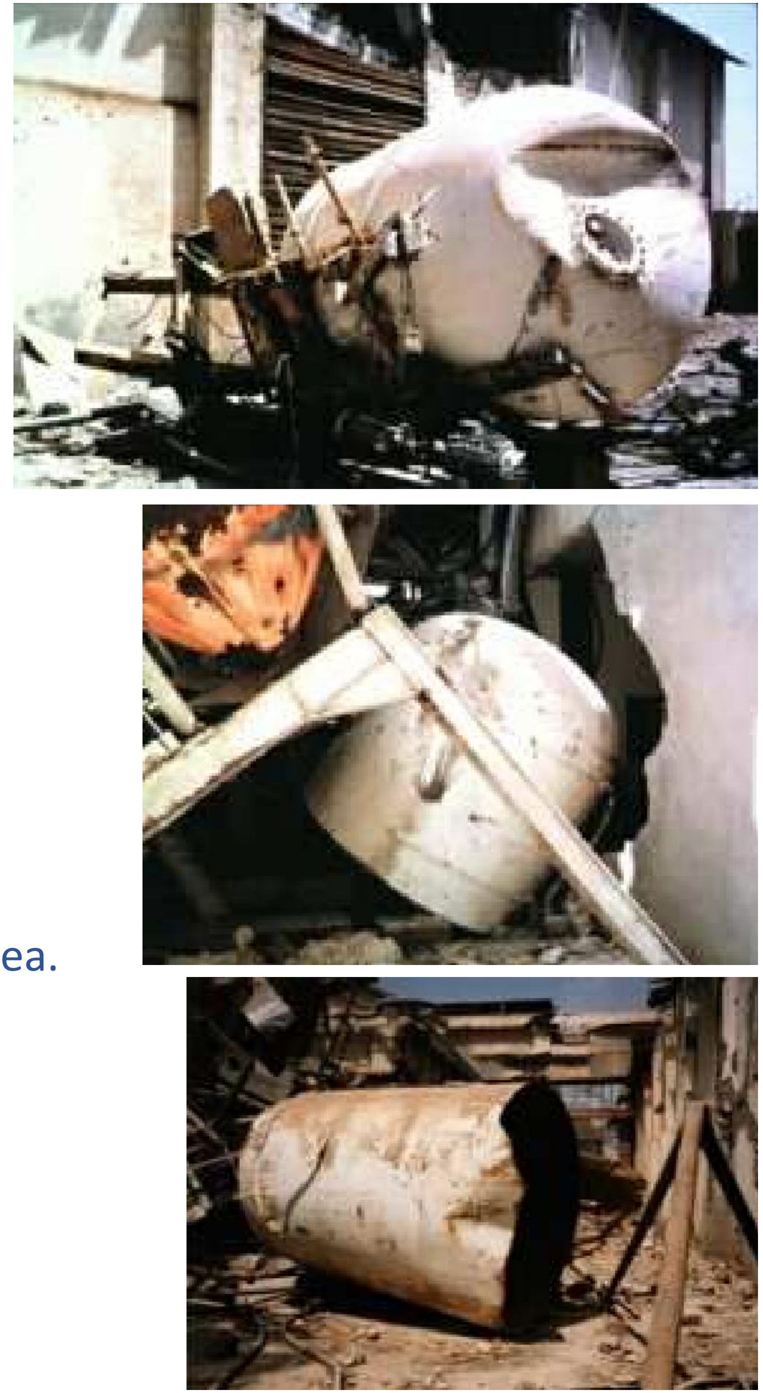
- ○ A review was conducted of the ARIA database (Analysis, Research and Information on Accidents) of BARPI (Bureau for Analysis of Industrial Risks and Pollutions) – details in backup slides
  - ✓ Related to anhydrous liquid ammonia releases
  - ✓ Involving pipelines, marine transport and road transport
- ○ In total 69 events were reported in the ARIA database (13 about pipelines, 13 about marine transport and 43 about road transport)
- ○ An analysis of the 69 cases reported in the ARIA database is given in the graphs below:
  - ✓ The percentage of accidents with of fatalities (15 – 30%) and injuries (50 – 70%) is significant in case of anhydrous ammonia releases (see next slide)
  - ✓ Pipeline accidents are mainly related to external impact during e.g., excavation works
  - ✓ Marine transport accidents are mainly related to failure of flexible discharge hoses/loading arms and failure of flanges and gaskets
  - ✓ Road transport accidents are mainly related to traffic accidents and failure of valves, joints, vessels
  - ✓ The number of accidents over the years remains constant (about 2 per year on average)

Houston, 1976

- On May 11th in 1976 in Houston, TX, a road tanker with 20 tons of ammonia drove off an elevated highway ramp and burst on falling to the ground.
- 7 fatalities, 200 people injured
- Photographs which show the scene from the air some four days later and illustrate that the grass was burnt in all directions around the site of the crash, as is shown in the figure below.
- This is to be expected of a denser than air vapor.



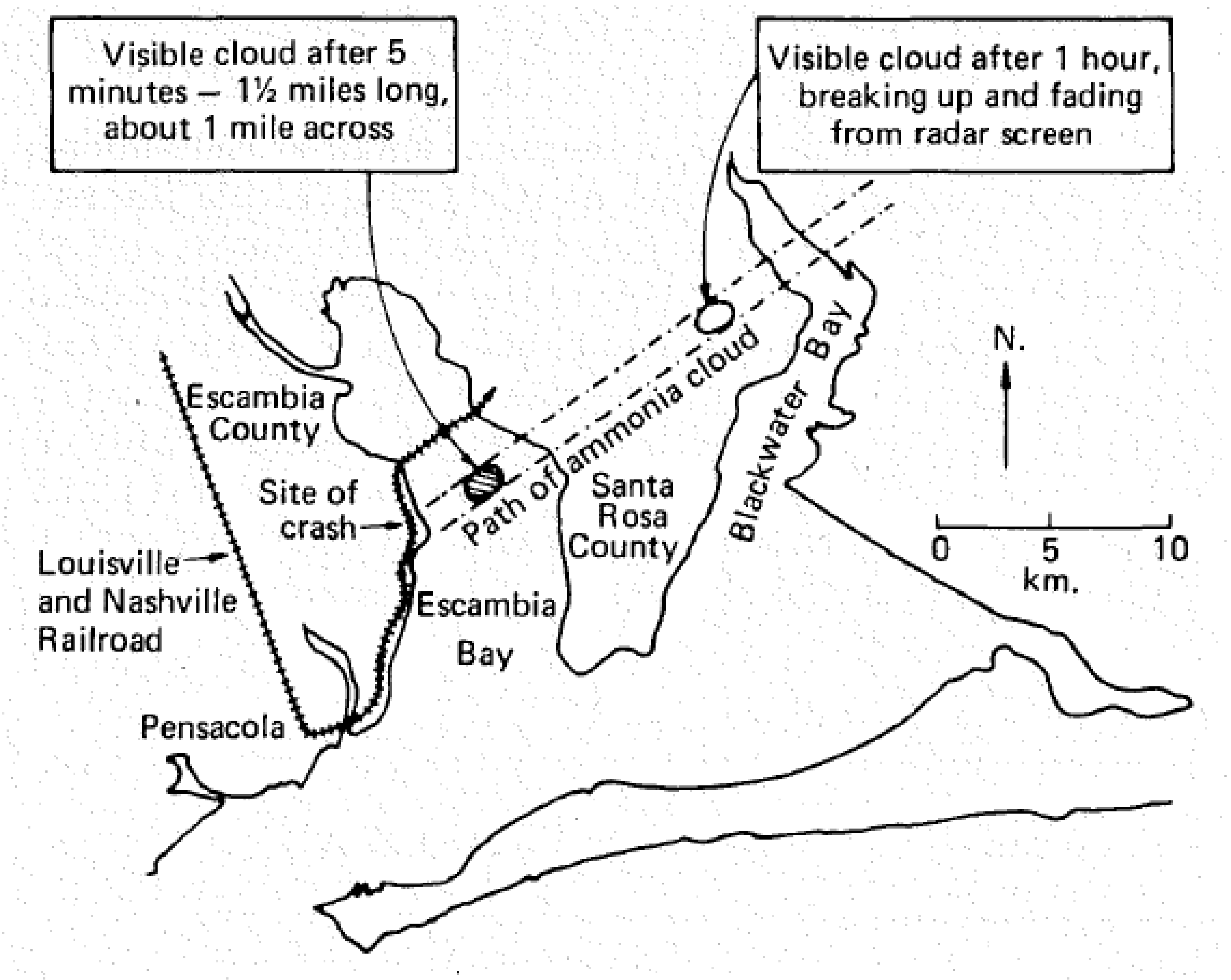
Dakar, 1992



- ○ Dakar (Senegal), 24 March 1992
- ○ Catastrophic rupture of 22 ton ammonia truck due to overfilling
- ○ 129 fatalities and more than 1100 people injured.
- ○ Causes
  - ✓ Tank repaired in 1991 following a leak noted during a hydraulic test. The rupture of the tank started at the level of this repair.
  - ✓ The tank that ruptured had been overfilled on several occasions.
- ○ Aggravating Factors
  - ✓ The time of day (1:30 pm - shift change)
  - ✓ The location of the accident (near the industrial port's catering area).
  - ✓ The victims / onlookers (alerted by the explosion), rushed to the accident area.

Pensacola, 1977

- A train was derailed and an ammonia tank car punctured so that about 40 Te 'quickly vaporized.
- About four minutes after the crash the air traffic controller at the nearby Pensacola airport, which was directly upwind, observed the ammonia cloud on radar.
- It appeared to be roughly a mile in diameter and 125 feet high.
- The cloud remained visible on the radar for an hour, during which time it travelled some nine miles and did not lift off the ground.



Chittagong, 2016

- On 22 August 2016, an enormous quantity of toxic ammonia gas was released because of overpressure explosion of an ammonia tank in the Di-ammonium Phosphate Factory Limited in Bangladesh.
- The Di-ammonium phosphate factory has a production capacity of 1600 ton di-ammonium phosphate per day. It has two 500 ton ammonia tanks which supply ammonia to the process through pipeline during the operation.
- One of the tanks which exploded was partially full containing 325 ton of anhydrous ammonia at the time of the incident, completely rift from its base and landed about 10 meters feet away from its base. Hence, a huge gas cloud was formed and dispersed into air.
- The toxic ammonia gas spread over several kilometres and wind carried away the gas to the corresponding side of the Karnaphuli River leaving nearly 250 people falling sick due to inhaling the toxic ammonia gas.

Firouzabad, 2020

- Fires of ammonia are rare but not impossible
- Ammonia does not burn easily in open space, requiring a supporting flame to sustain combustion.
- An explosion at a chemical plant in southern Iran injured 133 people on June 13 after a leak from an ammonium tank ignited. The incident happened in the city of Firouzabad, around 480 miles (770km) south of Tehran near Iran's Persian Gulf coast.
- The majority of the injured were workers at the chemical facility which opened in 2020. By June 14, 114 of the injured had been released from hospital. A health official said that the majority of the injures were respiratory. Several surrounding roads were closed in the hours after the incident after a toxic gas clous developed.

Summary Hazards and Risks of Anhydrous Ammonia

- The safety aspect of anhydrous ammonia are dominated by its toxic and corrosive properties:
  - ✓ Very high minimum ignition energy (difficult to ignite)
  - ✓ Very low maximum burning velocity
  - ✓ IDLH of 300 ppm
  - ✓ Toxic to environment
  - ✓ Corrosive in contact with water for some construction materials
- Anhydrous ammonia releases are very difficult to ignite: no ignition is observed in accidental ammonia releases (see review of REX).
- In case of anhydrous ammonia releases, the human consequences may involve rescue workers and the general public. Risk management related to anhydrous ammonia transport needs to include its wider external environment, also because of the impact of ammonia on the fauna and flora may be significant.
- The percentage of anhydrous ammonia transport accidents involving fatalities (15 – 30 %, depending on transport mode) and injuries (50 – 70 %, depending on transport mode) is significant*
- Since ammonia dissolves rapidly in water and since the latent vaporization heat of ammonia is high, possible effect mitigation measures include the installation if water curtains, and the orientation of possible leaks towards obstacles (impacting releases).
- Other effects mitigating measures include a robust gas detection system coupled with the automatic closing of remote isolation valves.
- Simulation results indicate that for realistic releases (≈ 1 inch), lethal concentrations can be reached at a distance of hundreds of meters relative to the release source. The simulation results are in line with the results obtained in large scale testing (INERIS, 2005).
- In case of using large quantities of anhydrous ammonia, robust effect mitigating measures (well design water curtains, gas detection with fast reaction time, emergency isolation valves,….) are necessary.

* Based on review of accidents reported in the ARIA database

Thanks for your attention