AMMONIA AS A MARINE FUEL
SAFETY HANDBOOK

DNV·GL

Green Shipping Programme

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Executive Summary

The technology required to propel and power ships with ammonia as fuel is still immature, and extensive development and policy measures are needed for its use on a larger scale over the next decade.

Effective safety regulations for the use of ammonia as fuel on board ships are currently not in place and must be established. Ammonia is a toxic chemical and it is important that the additional safety challenges are thoroughly addressed before considering ammonia as a marine fuel.

The maritime industry has experience with transport of ammonia cargo in gas carriers and the use of ammonia as refrigerant. However, the introduction of ammonia as fuel creates new challenges related to safe ammonia fuel bunkering, storage, supply and consumption for different ship types.

Current international regulatory framework and maritime industry experience with alternative fuels is mainly related to methane (LNG). A comparison of the properties of ammonia and methane is made to evaluate whether the safety barriers developed for methane are relevant for ammonia.

Ammonia is less flammable than methane and constitutes a lower, but not ignorable, explosion risk. Due to the toxicity it is still considered essential to be able to control all leakage scenarios in order to design and operate a safe ship. In our view, the safety principles developed for LNG fuel related to segregation, double barriers, leakage detection and automatic isolation of leakages will also be suitable guidance when establishing safety requirements for ammonia fuelled ships.

On this background, we discuss how the ship arrangement is affected by the ammonia fuel installation and in general terms how to accommodate for ammonia fuel in the different parts of the system. The additional safety barriers and arrangements affects the ship arrangement.

This handbook is developed in the Green Shipping Programme (GSP) as a work package on “safety standardization” in the Colorline Pilot on Ammonia as Fuel.

Foreword

Shipping faces major challenges adjusting to zero emissions over the next decades.

Among the solutions pointed out - both for existing tonnage and newbuilds - we often find ammonia.

This handbook is an important contribution on the path to the safe and efficient use of ammonia as a marine fuel and assists the industry with practical guidance on how the most important safety barriers associated with ammonia can be solved.

The handbook is developed by DNV GL on behalf of the Green Shipping Programme, with input from the Norwegian Maritime Authority and other partners in the Ammonia Pilot.

The Green Shipping Programme is a collaborative project between the authorities and the private business community and aims to support increased uptake of environmentally friendly solutions for ships. The goal of the programme is for Norway to become a world leader in environmentally friendly and efficient shipping.

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1 Introduction

Many studies have pointed to ammonia (NH3) as a potential fuel for shipping (e.g. Maritime Knowledge Centre, TNO & TU delft, 2017; OECD, 2018; DNV GL, 2020a).

The technology required to propel and power ships with ammonia as fuel is still immature, and extensive development and policy measures are needed for its use on a larger scale over the next decade.

Several engine manufacturers are currently looking into the challenges of burning ammonia in their engines, with the aim of having engines available 3 to 4 years from now. Fuel cell technology using ammonia as a fuel is also under development.[1,2,3]

Effective safety regulations for the use of ammonia as fuel on board ships are currently not in place and must be established. Ammonia is a toxic chemical and it is important that the additional safety challenges are thoroughly addressed before considering ammonia as a marine fuel.

The maritime industry has experience with carriage of ammonia in gas carriers and the use of ammonia as refrigerant. However, the introduction of ammonia as fuel creates new challenges related to safe ammonia fuel bunkering, storage, supply and consumption for different ship types.

DNV GL has issued a white paper on ammonia as a marine fuel examining the current use of ammonia in shipping and other industries and considering what it would take for ammonia to be adopted at scale as a maritime fuel (DNV GL, 2020b).

This handbook is developed in the Green Shipping Programme (GSP) as a work package on "safety standardization" in the Colorline Pilot on Ammonia as Fuel with the intention to provide practical guidance on safety aspects of ship design in the development of ammonia fuelled ships for ship owners, yards and designers.

This handbook has the following structure:

- Chapter 2 – Ammonia as fuel
- Chapter 3 – Toxicity
- Chapter 4 – Regulatory framework
- Chapter 5 – Design implications of differences between ammonia and methane (LNG)
- Chapter 6 – General design of ammonia fuelled ships

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[1] https://www.wartsila.com/media/news/30-06-2020-world-s-first-full-scale-ammonia-engine-test---an-important-step-towards-carbon-free-shipping-2737809

[2] https://man-es.com/discover/two-stroke-ammonia-engine

[3] https://www.prototech.no/news/2020/01/23/prototech-awarded-contract-to-supply-2mw-zero-emission-ammonia-fuel-cell-module/

2 Ammonia as a fuel

2.1 Properties of ammonia

The basic properties of ammonia are summarized and compared with methane in Table 2-1. Under atmospheric temperature and pressure, ammonia is a colourless, toxic gas with a sharp and penetrating odour.

Ammonia in its pure form is referred to as anhydrous ("without water") ammonia. Ammonia is hygroscopic, which means it has a high affinity for water.

In gaseous form it is lighter than air. However, due to its hygroscopic properties, released anhydrous ammonia will rapidly absorb moisture from air and form a dense and visible white cloud that may have a higher density than air.

Ammonia also dissolves easily in water to form ammonium hydroxide (NH_4OH), a caustic solution and weak base.

Ammonia has alkaline properties and is corrosive. Ammonia will corrode galvanized metals, cast iron, copper, brass or copper alloys. Hence, careful material selection is required.

Ammonia is flammable, but hard to ignite. Outdoors, ammonia vapours will generally not constitute a fire hazard. Indoors, in confined areas, the risk of ignition will be higher, especially if oil and other combustible materials are present. Pressure vessels used for storage of ammonia may explode when exposed to high heat input.

Ammonia is transported in the liquid state; therefore, it must either be compressed or refrigerated or some combination of the two. Fully refrigerated ammonia storage tanks contain liquid at -33°C at atmospheric pressure, while fully pressurised tanks are designed for 18 bar which corresponds to the ammonia vapour pressure at 45°C.

2.2 Comparison with methane (LNG)

Current international regulatory framework and maritime industry experience with alternative fuels is mainly related to methane (LNG). A comparison of the properties of ammonia and methane is made in Table 2-1. This comparison may be useful when evaluating whether the safety barriers developed for methane are also relevant for ammonia.

Table 2-1 Properties of ammonia compared with methane

Property	Ammonia (NH_3)	Methane (CH_4)
Boiling temperature (1 bar)	-33 °C	-162 °C
Vapour pressure (45 °C)	18 bar	–
Density (at boiling temp.)	0.68 t/m^3	0.43 t/m^3
Flammability range[4]	15-28%	5.3-17%
Auto ignition temperature	651°C	537°C
Minimum ignition energy	8 mJ	0.27 mJ
Solubility in water (at 20 °C)	531 g/l	No
Main hazards	Toxic Explosive Corrosive Flammable	Explosive Cryogenic Flammable Asphyxiating

Compared with methane, ammonia has a lower, but not ignorable, explosion risk. However, it is a lethal toxin at much smaller concentrations than the flammability range of either methane or ammonia vapours becomes flammable. As opposed to LNG, ammonia is not stored at cryogenic temperatures.

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[4] The minimum concentration of a particular combustible gas or vapour necessary to support its combustion in air is defined as the Lower Explosive Limit (LEL). The maximum concentration of a gas or vapor that will burn in air is defined as the Upper Explosive Limit (UEL). Above this level, the mixture is too "rich" to burn. The range between the LEL and UEL is known as the flammable range for that gas or vapour.

3 Toxicity

3.1 Health effects

Ammonia is a toxic substance. Acceptable human exposure limits to ammonia are defined by legislation and is typically a function of concentrations and exposure time. The limit is set between 25-50 ppm with dangerous consequences for exposure to concentrations above 300 ppm (Valera-Medina et al., 2018). Examples of exposure guidance are shown in in Table 3-1 and Table 3-2.

Table 3-1 Exposure guidance (Karabeyoglu A, Brian E., 2012)

Effect	**Ammonia concentration in air (by volume)**
Readily detectable odour	20 – 50 ppm
No impairment of health for prolonged exposure	50 – 100 ppm
Severe irritation of eyes, ears, nose and throat. No lasting effect on short exposure	400 – 700 ppm
Dangerous, less than ½ hours exposure may be fatal	2000 – 3000 ppm
Serious edema, strangulation, asphyxia, rapidly fatal	5000-10000 ppm

Based on Acute Exposure Guideline Levels (AEGL) for airborne chemicals defined by the Environmental Protection Agency (EPA) US, the limits to ammonia exposure can be identified as shown in Table 3-2.

Table 3-2 EPA Acute Exposure Guideline Levels (EPA, 2016)

Ammonia 7664-41-7 Expressed in ppm					
	10 min	30 min	60 min	4 h	8 h
AEGL 1	30	30	30	30	30
AEGL 2	220	220	160	110	110
AEGL 3	2700	1600	1100	550	390

AEGL 1: 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: Irreversible or other serious, long-lasting adverse health effects or an impaired ability to escape.

AEGL 3: Life-threatening health effects or death.

Anhydrous ammonia is a hydroscopic compound, which means that it seeks water from the nearest source, including the human body. This places the eyes, lungs, and skin at greatest risk because of their high moisture content. Caustic burns result when the anhydrous ammonia dissolves into body tissue.

An additional concern is the low boiling point of anhydrous ammonia. The chemical freezes on skin contact at room temperature. It will cause burns similar to, but more severe than, those caused by dry ice (Schwab, Charles V. et al., 1993).

Most deaths from anhydrous ammonia are caused by severe damage to the throat and lungs from a direct blast to the face. When large amounts are inhaled, the throat swells shut, and victims suffocate. Exposure to vapours or liquid also can cause blindness.

Combustion of ammonia may form toxic nitrogen oxides. It is recognised that NO_2 from other sources can aggravate cardiovascular and respiratory diseases, with an estimate of 23,500 premature deaths per year only in the UK alone. Although considerable research has been conducted understanding the formation process of this pollutant, its formation and consumption during combustion and post-combustion processes using ammonia are still at the core of the research agendas of various research groups (Valera-Medina et al., 2018).

3.2 Environmental effects

From a safety point of view, drainage of ammonia spills overboard and discharge of ammonia vapour underwater is preferable to keeping ammonia onboard. However, release of ammonia to the sea has impact on the environment. Ammonia is classified as toxic to aquatic life with long lasting effects according to GHS[5].

Combustion of ammonia in internal combustion engines may generate NOx and also N_2O which is a powerful greenhouse gas. It is assumed that existing SCR technology is capable of handling the NOx problem, and that engine manufacturers will need to find solutions to handle N_2O if ammonia is going to be a viable zero emission fuel.

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[5] Globally Harmonized System of Classification and Labelling of Chemicals (GHS). United Nations, New York and Geneva, 2011. https://www.unece.org/fileadmin/DAM/trans/danger/publi/ghs/ghs_rev04/English/ST-SG-AC10-30-Rev4e.pdf

4 Regulatory framework

4.1 SOLAS

The use of fuels is regulated by the International Maritime Organization (IMO) through the International Convention for the Safety of Life at Sea (SOLAS). The regulations for conventional fuel oils are prescriptive and based on decades of experience. Utilizing fuels with a flashpoint below 60°C (defined as Low Flashpoint Fuels) has generally been prohibited to prevent tank explosions and fires.

In 2015, the SOLAS Convention was amended to allow the use of low flashpoint fuels for ships complying with the International Code of Safety for Ships Using Gases or Other Low-Flashpoint Fuels (IGF Code).

4.2 The IGF Code

The IGF Code provides an international standard for the safety of ships using low-flashpoint fuel, other than gas carriers which have to comply with separate requirements in the IGC Code (see 4.3).

The IGF Code requires that the safety, reliability and dependability of the systems shall be equivalent to that achieved by new and comparable conventional oil-fuelled main and auxiliary machinery.

The IGF Code specifies a set of functional requirements applicable for all fuel types covered by the Code, but only contains specific design requirements to LNG. Specific design requirements for other low-flashpoint fuels (like e.g. ammonia) will be added as, and when, they are developed by the Organization.

Until such regulations are in place, approval of ships using other fuels than LNG will be based on first-principle analysis demonstrating that the design complies with the basic functional requirements of the IGF Code. This risk-based approval process is referred to as the 'alternative design' approach, where an equivalent level of safety needs to be demonstrated.

The alternative design approach can be a time-consuming process with a high degree of uncertainty and therefore potentially higher business risk than the prescriptive experience-based rules that the maritime industry is used to working with. This must be considered as a barrier against uptake of alternative fuels in the industry.

4.3 The IGC Code

The IGC Code provides an international standard for the safe carriage by sea in bulk of liquefied gases.

The IGC Code includes a separate chapter on the use of cargo as fuel but does not permit the use of cargoes identified as toxic products like ammonia for this purpose. This means that the Code, in its current form, does not permit gas tankers to use ammonia as a fuel.

Ammonia is transported as cargo in large quantities in gas carriers. The requirements in the IGC Code can therefore provide useful guidance in how to design fuel storage systems for ammonia.

4.4 How to advance regulatory framework

Classification Societies tend to have a faster rule development cycle than IMO. When a Classification Society has developed a set of rules covering the use of a fuel where specific design requirements are not included in the IGF Code, a Flag Administration may accept the application of this rule set to ease the alternative design approach. A set of class rules may also form basis for development of international regulations in IMO.

5 Design implications of differences between ammonia and methane (LNG)

Most alternative fuels have chemical and physical properties which generate more severe safety challenges and requires a more complex fuel containment system than conventional fuel oils. Additional safety barriers are required to maintain the safety level. Each alternative fuel has its unique properties and associated hazards requiring special consideration.

Both anhydrous ammonia and methane are gases with a boiling temperature which is not compatible with conventional storage tanks onboard ships. Consequently, both gases need a storage and supply system that can manage the pressure increase and boil-off gas that is generated by heat input to the system.

The low boiling temperature of methane (-163°C at atmospheric conditions) introduces a design challenge with respect to selection of materials to ensure ductility at low temperatures. This can also be an issue for ammonia (-33°C at atmospheric conditions) but can be overcome with less sophisticated material selections. On the other hand, for ammonia the corrosive properties require special consideration in the choice of materials.

Due to the high flammability and low minimum ignition energy of methane, it is essential to prevent leakages from the fuel storage and supply system. Ignition of leaking methane in enclosed spaces may result in explosions with severe consequences for the ship and persons onboard. Ammonia is less flammable than methane and constitutes a lower explosion risk.

5.1 Safety concept of current regulations in the IGF Code and DNV GL rules for LNG fuel

The existing DNV GL rules for LNG fuel cover the specific design requirements in the IGF Code. Both the IGF Code and the class rules mainly focus on managing different leakage scenarios and as indicated in Figure 5-1, the essential safety barriers are related to:

- **Segregation;** keeping the installation away from areas where it may be damaged by collision or grounding, external fires, cargo handling or other ship operations.
- **Double barriers;** arrangements that allows leakages from the fuel system to be managed safely. This will typically be to provide a secondary barrier around any leakage point. In practice, such barriers consist of specially designed spaces (e.g. tank connection spaces, fuel preparation rooms) and double piping arrangements.
- **Leakage detection;** systems that can detect leakages of gases and liquids from the fuel system. The detection methods are dependent on arrangements, but normally includes gas detection systems, low temperature measurements, changes in pressure and temperature.
- **Automatic isolation of leakages;** systems and arrangements that can isolate the leakage from the leakage source when the detection systems above find something wrong with the fuel system. In order to achieve this, a number of isolation devices are required in the system enabling automatic shut-down of the fuel supply to the damaged system.

Segregation Protect fuel installation from external events	**Double barriers** Protect ship against leakages
Leakage detection Give warning and enable automatic safety actions	**Automatic isolation of leakages** Reduce consequence of a leakage

Figure 5-1 Safety concept of the current regulations in the IGF Code and DNV GL rules for LNG fuel.

In our view, the safety principles described above will also be suitable guidance when establishing safety requirements for ammonia fuelled ships:

- **Segregation;** keeping the installation away from areas where it may be mechanically damaged is equally important for ammonia.
- **Double barriers;** arrangements that allows leakages from the fuel system to be managed safely is also essential for ammonia due to toxicity and explosion risk.
- **Leakage detection;** systems that can detect leakages of gases and liquids from the fuel system is even more important when ammonia is used as a fuel since it is a lethal toxin at low concentrations.
- **Automatic isolation of leakages;** as for the leakage detection above it will be important to limit the amount of ammonia in a leakage scenario.

6 General design of ammonia fuelled ships

In this chapter we discuss how the ship arrangement is affected by the ammonia fuel installation and in general terms how to accommodate for ammonia fuel in the different parts of the system.

The different parts of an ammonia fuel installation are illustrated in Figure 6-1. The additional safety barriers and arrangements affects the ship arrangement.

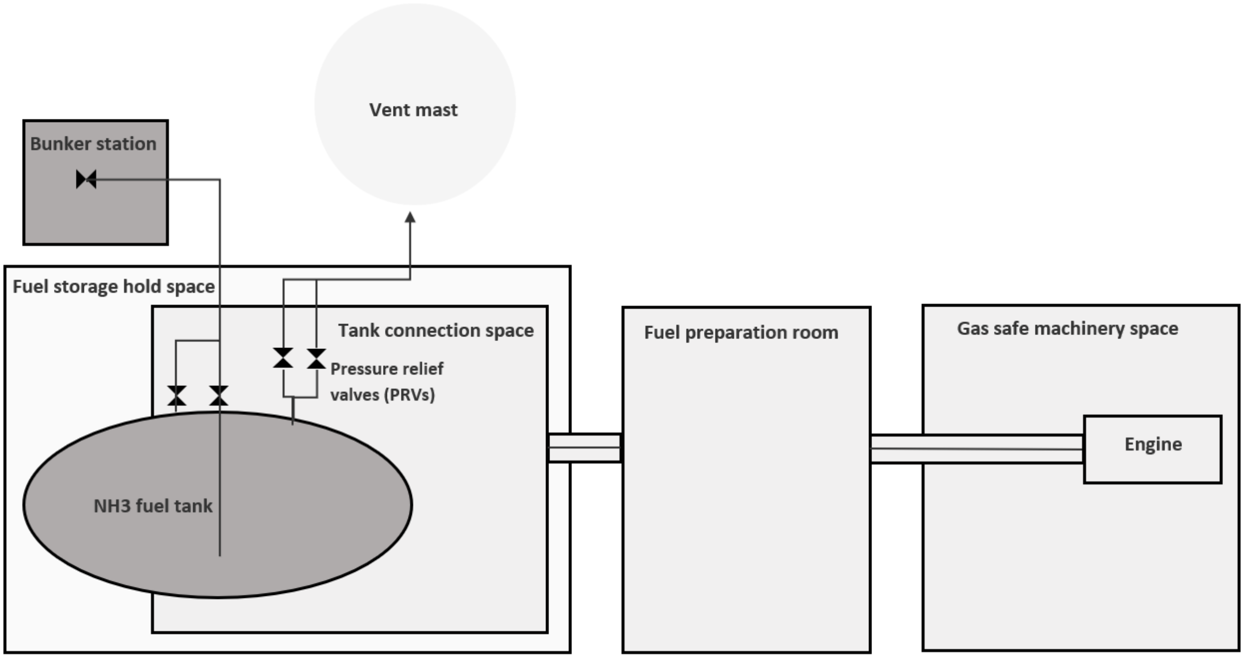

Figure 6-1 Principle diagram ammonia fuelled installation (DNV GL).

6.1 Bunkering

Focus area: Reduce the risk of ammonia leakages during bunkering and limit risk and consequences of exposure to ammonia for personnel involved in the bunkering operations.

The bunkering operation with its handling, connection and disconnection of heavy bunkering hoses is subjecting the personnel involved to the risk of being directly exposed to ammonia.

In order to reduce the risk of leakages, the lay-out of the bunkering station should enable a smooth bunkering procedure by providing ample space for the necessary operational steps with lifting equipment supporting the mounting of heavy bunkering hoses. Bunkering hoses should be equipped with dry-disconnect couplings and break-away devices that will prevent overstressing hoses and manifold in case of a drift-off scenario.

To limit the exposure time, the bunkering control station should preferably be in a safe location enabling the crew to remotely oversee the bunkering operation.

The bunkering lines onboard should be arranged in such a way that it is possible to drain the ammonia to the storage tank and the bunkering hose back to the bunkering facility. The ship bunkering line should be purged with inert gas after fuelling operations to eliminate the risk of ammonia leakages when it is not in use.

Development of proper bunkering procedures including communication with the bunker supplier and training of crew is also considered essential to refuel safely.

It is recognized that the risk of ammonia exposure cannot be eliminated by good design and proper operating procedures.

Therefore, people involved in the bunkering operations should be equipped with Personal Protective Equipment (PPE) to protect them from exposure to anhydrous ammonia. The PPE should consist of large aprons, special gloves with long sleeves, suitable footwear, coveralls of chemical-resistant material, and tight-fitting goggles or face shields or both. The protective clothing and equipment should cover all skin so that no part of the body is unprotected.

If a person is exposed to anhydrous ammonia, showering the contaminated areas with ample amounts of water is the best first aid treatment. For this purpose, emergency showers and eyewashes should be provided in convenient locations outside the bunkering station.

There are several other design features which may reduce the consequence of a leakage during bunkering:

- proper mechanical shielding of all leakage points on the bunkering manifold including temporary mechanical shielding of the bunkering connection
- leakage detection with automatic closing of bunker valve
- water spray system above the bunkering manifold to reduce toxic vapours in the bunkering station
- spill tray below the bunkering manifold to collect any leakage and to drain the water/ammonia overboard
- manual emergency stop
- a ship-shore link (SSL) or an equivalent means for automatic and manual ESD communication to the bunkering source.

6.2 Fuel storage

Focus area: Storage of ammonia without vapour release to the atmosphere.

Ammonia is transported in the liquid state; therefore, it must either be compressed or refrigerated or some combination of the two. Fully refrigerated ammonia storage tanks contain liquid at -33°C at atmospheric pressure, while fully pressurised tanks are designed for 18 bar which corresponds to the ammonia vapour pressure at 45°C.

In principle, tank types accepted for cargo carriage in the IGC Code will also be accepted as fuel tanks. In practice type A (fully refrigerated) and C (semi- or fully pressurized) tanks as defined in the IGC code are used for transport of ammonia cargo in gas carriers.

There are several safety related factors to consider when choosing type of fuel tank:

- Venting of tank vapours should be prevented at all times. This implies that tanks for ammonia will need a boil-off gas (BOG) management system unless they are designed for the full vapour pressure of ammonia at ambient temperatures (18 bar).
- For tanks requiring secondary barriers, management of leakage scenarios and the subsequent emergency venting of fuel gases must be specially considered.
- The choice of fuel tank may also impact flexibility with regard to compatibility with bunkering facilities with respect to pressure and temperature.

Due to the corrosivity of ammonia, special requirements in the IGC Code for materials used in ammonia storage tanks and associated systems should be observed.

Focus area: Protect the ammonia fuel installation from external events that could damage the tank causing accidental release of ammonia.

To reduce the risk of accidental release of ammonia, the tank location should be carefully considered with respect to any external events that could potentially damage the tank.

For collision and grounding protection, the requirements defined in the IGF Code for LNG tanks and piping are considered relevant.

Ammonia tanks should preferably be located away from exposure to ship and cargo operations. Alternatively, appropriate mechanical protection should be considered.

6.3 Tank connection spaces and fuel preparation rooms

Focus area: Safely contain leakages to prevent leaking ammonia from spreading to other areas onboard.

Tank connection spaces (TCS) and fuel preparation rooms (FPR) should be arranged to provide a secondary barrier against ammonia leakages in areas where a double pipe protection is not practical to arrange. All tank connections should be located in a TCS mounted on the tank and all equipment necessary to process the fuel should be arranged in a dedicated FPR.

In order to be effective, the boundaries towards other spaces in the ship need to be gas tight. Ammonia has a boiling point of -33°C and will have a cooling effect on the surroundings if released into TCS or FPR. Consequently, the bulkheads should be designed to avoid embrittlement from low temperatures and potential cracking that will compromise the gas tightness.

Access points and bulkhead penetrations also need consideration if the gas tightness of the boundaries shall be maintained. The IGF Code requirements for methane (LNG) fuelled ships specify that access to the TCS shall be through a bolted hatch. Experience from operation indicates that access to TCS is more regular than initially assumed when the first rules were made. Considering the toxicity of ammonia at low concentrations it will likely be problematic to restore the gas tightness of the TCS if a leakage develops when the bolted hatch is open.

It is therefore considered that an air lock access will in sum provide a better access solution to TCS on ammonia tanks. It will be easier to escape if a situation develops, easier to retrieve injured persons and easier to close off the TCS after it is evacuated.

In refrigeration machinery spaces using ammonia as a refrigerant, a water-curtain is arranged on the outside of the entrance. The water-curtain is intended to catch escaping ammonia vapours by utilising the hygroscopic nature of ammonia and reduce the concentration of toxic gases on the outside. Water curtains should be arranged outside entrances to TCS and FPR for the same purpose.

The ventilation arrangement in TCS and FPR should dilute potential leakages, prevent leaked gas from spreading to other spaces and generate an under-pressure in the space compared to surrounding areas. The ventilation outlets could be a source of substantial ammonia discharge and should be located in areas where the risk of subjecting personnel to toxic vapours is as low as possible, and in areas where the gas will not spread to other spaces in the ship through ventilation inlets and outlets, doors or other openings.

In order to achieve the above, the ventilation fans need to be running continuously. This implies that the ventilation inlets and outlets must be located at height above deck where the Load Line Convention does not require weathertight closing devices.

To prevent toxic vapours from spreading, each space containing ammonia leakage sources should be fitted with mechanical extraction ventilation and dedicated inlet and outlet ducts not serving other spaces. In addition, catastrophe ventilation which will start automatically upon gas detection should be arranged.

Other design features which may reduce the consequence of a leakage in TCS or FPR:

- Leakage detection with automatic closing of isolation valves able to cut off the supply of ammonia to the leakage source.
- Proper mechanical shielding of all leakage points on in the space to reduce the risk of direct exposure of ammonia.

It is assumed that personnel will be equipped with proper PPE when working in such spaces, and that procedures for safe entrance and maintenance work is developed.

6.4 Fuel supply

Focus area: Safely contain leakages and prevent operational discharges of ammonia.

In order to prevent toxic vapours to reach areas where personnel can be exposed, the primary ammonia fuel piping system should be surrounded by a secondary enclosure which should be able to contain any leakages from the primary system. If the piping system is located in a tank connection space or a fuel preparation room, these spaces will function as a barrier against gas leakages so double walled piping would not be necessary.

In the IGF Code the same is required for methane pipes. The Code additionally requires that the secondary enclosure of methane pipes shall be mechanically ventilated. This necessitates inlet and outlet ducts plus a redundant fan arrangement for segregated pipe segments.

For ammonia we foresee that a single vent pipe led to safe area in open air will suffice. The purpose of this pipe is to lead the leaking ammonia to a relatively safe place, and to prevent excessive pressure build-up in the secondary enclosure. Using an arrangement as required for methane will increase the number of possible leakage points in the secondary barrier inside the vessel without any obvious advantage to the safety of the ship.

The material of ammonia pipes and their secondary enclosures must be chosen to ensure resistance to corrosion and low temperatures.

Fuel supply systems for methane are equipped with vent pipes and double-block-and-bleed valve arrangements to de-pressurise the piping system and to provide segregation by venting the pipe contents to atmosphere. Considering the toxicity of ammonia, and to a certain degree the issue of smell, a similar arrangement should be avoided for ammonia fuel systems.

Ammonia expands 850 times when going from liquid to gaseous state and can be lethal with short exposure times at 5000 ppm. This implies that 1 litre of liquid ammonia can expand into 170 000 litres of ammonia gas of lethal concentration and 170 000 m3 of gas with a detectable smell.

In order to avoid unnecessary operational discharges from the fuel system, it should be designed with a minimum design pressure of 18 bar. This corresponds to the vapour pressure of ammonia at 45°C which is what IACS specify as the highest temperature in the temperature range that all machinery shall be designed to operate.

Operational restrictions and safety considerations may require that the fuel system must be drained of ammonia. The de-pressurising and purging process should be possible without discharging the ammonia in the fuel system to open air.

6.5 Machinery space

Focus area: Reduce the risk of leakages in machinery spaces which would expose personnel to toxic vapours and make machinery spaces inaccessible.

As for other spaces in the ship, ammonia fuel systems (including systems pertaining to engines and other ammonia consumers) should be arranged with secondary barriers to prevent gas leaks from spreading to the engine room. For the same reason there should be no access between the engine room and spaces arranged to contain ammonia leakages.

Special care should be taken to ensure that it is possible to safely isolate equipment in machinery spaces from the fuel system for maintenance purposes. Manual valves and fuel line purging arrangements should be fitted to this effect.

6.6 Hazardous area - flammability and toxicity

As can be deduced from the comparison in Table 2-1, ammonia has a lower, but not ignorable, explosion risk compared to methane. However, it is a lethal toxin at much smaller concentrations than the level where it becomes flammable (0.5% vs 15% mixture in air).

6.6.1 Flammability

Focus area: Limit explosion risk by elimination of ignition sources in areas where it is likely that a release may result in flammable vapour concentrations.

Ammonia's flammability range is from 15 to 28 per cent mixture in air. Ammonia requires minimum ignition energy of 8 mJ, which is 30 times more energy than methane needs to ignite and 470 times more energy than for hydrogen. Ammonia can self-ignite if the temperature is above 651°C.

Ammonia burns with difficulty in open air and will generally need a supporting flame to keep burning. In confined spaces ammonia constitute an explosion risk, and it should be noted that oil contamination can increase the flammable properties of ammonia vapours.

Considering the above, we do not see a need for hazardous zone definitions on open deck. In enclosed spaces, electrical equipment should be certified for use in zone 1.

6.6.2 Toxicity

Focus area: Limit risk of exposure to toxic vapours from ammonia by reducing the risk of having toxic fuel vapours in areas where people can be exposed.

In order to protect people onboard from exposure to ammonia vapours, the primary focus should be to avoid venting of ammonia vapours during normal operation. It should be considered if vent systems can be provided with arrangements to reduce the amount of ammonia being discharged to open air.

However, it will not be possible to eliminate all discharge of ammonia vapours from vents and ventilation systems to open air. It will therefore be necessary to define toxic zones around sources of ammonia vapour on open deck to avoid that ammonia vapours are spreading to enclosed spaces through air intakes, air outlets or other openings to enclosed spaces on the vessel.

In managing the risk of handling toxic fuels in shipping we cannot draw on previous experience collected in rules or regulations. However, toxic cargoes are carried on gas tankers and chemical tankers. Requirements for venting of cargo tanks and ventilation of cargo handling spaces are described in the IGC Code and the IBC Code[6] for such vessels.

The design features described in this safety handbook for ship arrangements and piping design is mainly aimed at preventing exposure to any leaking fuel vapours internally in the ship. There is also a need to ensure that venting from fuel tanks and piping systems can be done with as low risk as possible, and also to consider the possibility of significant amounts of vapours being discharged to open air through the ventilation system of tank connection spaces and fuel preparation rooms after a leakage.

When looking for guidance in the statutory codes for gas and chemical tankers transporting toxic cargoes, the following requirements are found:

The IGC Code is generally requiring the following safety distance from vent mast outlets:

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[6] IBC Code: International Code for the construction and equipment of ships carrying dangerous chemicals in bulk.

Cargo PRV vent exits shall be arranged at a distance at least equal to B[7] *or 25 m, whichever is less, from the nearest air intake, outlet or opening to accommodation spaces, service spaces and control stations, other non-hazardous areas, exhaust outlet from machinery or from furnace installations onboard.*

For ventilation outlets, the IBC Code is requiring that ventilation openings from pump rooms for toxic cargoes comply with the following:

For products which in the IBC code ch.17 column o has a reference to 15.17 (toxic cargoes), the ventilation system as described in Sec.10 [2.3.1], shall have a capacity of at least 45 air changes per hour. The ventilation exhaust outlets shall be situated at least 10 m from ventilation inlets to the accommodation and other non-hazardous spaces and at least 4 m above the tank deck.

The above should also be applied to ammonia fuelled ships as minimum distances. Considering the differences in ship arrangement between tankers and other cargo ships it may be prudent to perform dispersion analyses of the worst-case scenarios like full venting from tank safety valves and ventilation of large amounts of gas following a maximum probable leakage through the ventilation system openings to ensure that the minimum distances are safe to apply.

For passenger ships, we foresee that special analyses on location of life saving equipment and mustering stations would need to be performed, and that evacuation scenarios with ammonia leakages are properly evaluated. In view of the sharp and penetrating odour of ammonia at very low concentrations, even small leakages may cause alarm with passengers which should also be considered in the design phase.

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[7] *Breadth (B)* means the maximum breadth of the ship, measured amidships to the moulded line of the frame in a ship with a metal shell, and to the outer surface of the hull in a ship with a shell of any other material. The breadth *(B)* shall be measured in metres.

6.7 Personnel protection

Focus area: Reduce consequences of ammonia exposure.

Time is critical when a person is sprayed with liquid ammonia or exposed to concentrated vapours. When ammonia contacts the skin or eyes, tissue damage occurs rapidly. Immediately flushing the exposed body area(s) with water is crucial. When someone has been exposed to anhydrous ammonia, the best course of action is to move him or her to a safe place and flush the exposed area immediately with water for a minimum of 15 minutes. Contaminated clothing should be removed. Note that anhydrous ammonia can freeze exposed clothing to skin below it. If you remove clothing before you thaw it with rinse water, extensive skin damage can result.

To facilitate essential first-aid procedures decontamination showers and eyewashes should be available near the exits from spaces containing ammonia piping systems. At least the following locations should be included:

- bunkering stations
- exit from tank connection spaces
- exit from fuel preparation rooms
- in engine rooms.

Suitable protective equipment should be available for people involved in bunkering operations and for working in areas where ammonia exposure is a risk. PPE consisting of large aprons, special gloves with long sleeves, suitable footwear, coveralls of chemical-resistant material, and tight-fitting goggles or face shields or both are providing suitable protection. The protective clothing and equipment should cover all skin so that no part of the body is unprotected.

Respiratory and eye protection for evacuation purposes should be available for everyone onboard.

Gas detection alarms should be arranged in such a way that personnel are warned against entering contaminated spaces. An alarm on open deck to warn personnel about discharges from ventilation and vent mast should be considered.

To permit entry and work in a gas-filled space, safety equipment providing adequate personal protection, including self-contained positive pressure air-breathing apparatus incorporating full face mask, should be available.

6.8 Fire safety

Focus area: Protect ammonia storage tanks from excessive heat input.

The flammability of ammonia in open air is significantly lower than for methane. Therefore, the relevance of adopting the IGF Code requirement for A60-shielding boundaries of superstructures facing fuel tanks on open deck, which is required for methane fuel tanks, should be considered.

On the other hand, we consider all IGF Code requirements aiming to protect storage tanks from heat input as relevant also for ammonia tanks. In order to protect ammonia tanks from excessive heat input in case of fire, they should be segregated from spaces with a high fire risk like e.g. machinery spaces of category A and be protected by a water spray system for cooling if located on open deck.

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8 The development of the Safety Handbook

The Ammonia as a Marine Fuel Safety Handbook was developed by a project team in DNV GL on behalf of the Green Shipping Programme during the autumn 2020, with input from the Norwegian Maritime Authority and other partners in the Ammonia pilot.

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Revision 01	2021-03-18	Correction in table 2-1