European Maritime Safety Agency

SAFETY OF AMMONIA FOR USE IN SHIPS

PART 1 – AMMONIA: PROPERTIES, REGULATIONS AND ACCIDENTS REVIEW

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EMSA

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Executive Summary

Among the alternative fuel options, anhydrous ammonia has drawn a lot of interest from the marine industry for its potential to become a long-term solution for decarbonisation. As a carbon-free substance, ammonia is being investigated as a promising future marine fuel that could contribute meeting the objectives of 2023 IMO GHG Reduction Strategy by offering a zero, or a near-zero, carbon solution on a tank-to-wake basis and for green ammonia near-zero can be met on a well-to-wake basis. Notwithstanding the many benefits, there are also significant risks associated with using ammonia that need to be properly considered to support legislation and safeguards for both the ship and health of persons onboard. The introduction of ammonia in fuel systems, the engine room and the engine itself creates potential risks that need to be properly addressed.

There is extensive land-based experience with the production and use of ammonia as a fertiliser, refrigerant and chemical. With a production of about 200 Mt in 2022, it is the second-largest chemical product manufactured globally.

On the other hand, there is no practical experience in using ammonia as a fuel in shipping and ammonia-based concepts for propulsion, such as ammonia internal combustion engines, are still at development stages. Despite that, a relatively large number of ammonia fuelled ships have been ordered already. Because of its use in other industries, neither handling nor transportation of ammonia as cargo in shipping is a novel concept and there is solid experience with its carriage in liquefied gas carriers that can provide guidance to the development of statutory requirements for its application as marine fuel.

Feedback and lessons learned from land-based industry can be useful. The comprehensive review of accidents, as outlined in section 2.4, underscored critical causes of these incidents that allow identifying recurring patterns and highlighting critical areas for preventive or corrective measures for application in the maritime sector. Valve failures are the most common, leading to ammonia dispersion, severe injuries, and environmental damage. Other root causes are electrical problems and power failures triggering critical events like explosions or safety system failures. Corrosion in pipes and equipment due to chemical exposure and lack of maintenance is also identified. Additionally, design errors, technical specification mistakes, and human errors such as misuse of alarms, incorrect operating procedures, and training deficiencies contribute to incidents, sometimes by delayed or inefficient emergency response exacerbating consequences. These assessments help pinpointing vulnerable equipment and systems prone to failure, enabling the implementation of robust mitigation measures to avert ammonia-related accidents and their adverse impacts on human safety and the ship.

Task 1 of this study presents an extensive analysis of ammonia properties and characteristics and how these are applicable as marine fuel. The main hazard of ammonia in comparison to other conventional and alternatives fuels is toxicity, which can start being dangerous to health from low concentrations (25-50 ppm) and can be fatal when in higher concentrations (300 ppm), and corrosivity. This study provides an analysis of the toxicity and exposure limits of ammonia comparing several regulatory frameworks. Aside from toxicity, the general behaviour of ammonia was investigated, how this reacts with air and water and how that affects other materials with its corrosive nature and through the stress corrosion cracking.

This report includes a review of the current onshore and offshore regulatory framework related to the use and transport of ammonia and acknowledges that there is still work to do to address properly the safety hazards of ammonia as fuel. Nevertheless, the IMO has significantly progressed in the development of interim guidelines for ships using ammonia as fuel to supplement IGF Code and has included in the work plan the approval of those guidelines for December 2024. This timeframe would match the delivery plan of the first ammonia engines announced for the end of 2024 or beginning 2025. Design work on the first ammonia internal combustion engine is already under advanced development from major engine manufacturers such as MAN ES, Wartsila, HHI-EMD, Japan Engine Corporation and WinGD.

While ammonia carriers would be suitable candidates to be the first movers to adopt ammonia as fuel, the use of toxic cargo as fuel is not yet allowed under the provisions of the IGC Code. Subject matter is highlighted at IMO and proposal to exempt anhydrous ammonia from the list of toxic products that can be used as fuels is to be taken into further consideration.

Toxicity of ammonia adds complexity to ship designs. Toxic areas prescriptive requirements are introduced into the interim guidelines and classification rules as outlined in section 2.3. However, actual toxic areas should be a result of ship specific gas dispersion analysis supported by relevant risk assessment covering several scenarios (e.g. loss of containment from storage tank or piping, during bunkering etc.). With the exact toxic areas' determination, the below could be verified:

- Ammonia gas does not reach air intakes, outlets and other openings into the accommodation, service and machinery spaces, control stations, the navigation bridge and other non-toxic areas in the ship.
- Lifesaving appliances (LSA), muster stations and escape routes are not located in toxic areas.
- Decontamination showers and eyewash stations.
- Gas detection requirements and sensors' locations.
- Bunkering safety zones.
- PPE selection according to working area and exposure to ammonia.

An analysis for PPE requirements and standards was conducted. It should be ensured that suitable protective equipment is provided for persons on board, for both routine operations and emergency conditions. Experience from land-based industry shows that the choice of PPE in different areas is subject to the expected concentration and exposure time to ammonia therefore different chemical suits and accessories may be required. Toxic areas determination as described above is a critical step to decide what PPE will be used for each space onboard. This approach with PPE layers is introduced in various publications (SGMF, NTU) and the recent YCA workshop that investigate the safety of ammonia use as fuel.

Classification societies have worked to support the ammonia fuel concept by updating their rules and, through IACS, to feed IMO with useful information. There are still areas where classification rules present minor deviations such as with regards to ammonia detection levels, the lifespan of storage tanks, the ventilation and others indicated in Section 3.3.2. In addition, classification societies have engaged with shipowners, designers, shipyards, engine manufacturers and other stakeholders to conduct feasibility studies for ammonia fuelled vessels including risk assessment workshops and grant approvals in principle for concept designs.

This study is part of a broader planned work that will delve into reliability analysis and risk assessments of ammonia fuelled vessels designs. This first part is relevant for understanding the specific hazards inherent to the nature of ammonia, how such hazards affect the ship and persons onboard, where the regulatory framework development stands and what gaps should be covered to contribute to the adoption of ammonia as a marine fuel.

Building on existing or under development rules and regulations (such as the Guidelines for the use of ammonia as fuels of the IMO) the final objective is the development of Guidance for ships using ammonia as fuel. The preliminary structure for development of such a goal-based Guidance is included in this report.

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List of Abbreviations

ABS	American Bureau of Shipping
ACGIH	American Conference of Governmental Industrial Hygienists
AEGL	Acute exposure guideline levels
AIHA	American Industrial Hygiene Association
ALARP	As Low As Reasonably Practicable
ANSI	American National Standards Institute
AV	Arbetsmiljöverket (Swedish Work Environment Authority)
BLEVE	Boiling Liquid Expanding Vapour Explosion
BOG	Boil Off Gas
CAS RN	Chemical Abstracts Service Registry Number
CCC	Carriage of Cargoes and Containers Sub-Committee (IMO)
CFR	US Code of Federal Regulations
CG	Correspondence Group (IMO CCC Sub-Committee)
CII	Carbon Intensity Indicator (IMO)
DF	Dual Fuel
DFDE	Dual Fuel Diesel Electric
DFG	Deutsche Forschungsgemeinschaft (German Research Foundation)
DOE	U.S. Department of Energy
DOT	Department of Transportation (UN number)
EC	European Commission
ECHA	European Chemical Agency
EEBD	Emergency Escape Breathing Devices
EEDI	Energy Efficiency Design Index (IMO)
EEGL	Emergency Exposure Guidance Level
EEOI	Energy Efficiency Operational Index (IMO)
EEXI	Energy Efficiency Existing Ship Index (IMO)
EINECS	European Inventory of Existing Commercial Chemical Substances
EMSA	European Maritime Safety Agency
EPA	Environmental Protection Agency
ERGP	Emergency Response Planning Guidelines
ESD	Emergency Shutdown
EU	European Union
FGSS	Fuel Gas Supply System

FKM	Fluorocarbon rubber
FMEA	Failure Mode and Effects Analysis
FSS	Fuel Supply System
GCMD	Global Centre for Maritime Decarbonisation
GESAMP	Group of Experts on the Scientific Aspect of Marine Environmental Protection
GHG	Green House Gas
GISIS	Global Integrated Ship Information System (IMO)
GVT	Gas Valve Train
GVU	Gas Valve Unit
GWP	Global Warming Potential
HAZID	Hazard Identification Studies
HAZOP	Hazard and Operability Study
HSE	Health and Safety Executive
IACS	International Association of Classification Societies
ICE	Internal Combustion Engine
IDLH	Immediately Dangerous to Life or Health
IGC	International Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk (IMO)
IGF	International Code of Safety for Ships Using Gases or other Low-Flashpoint Fuels (IMO)
IGO	Intergovernmental Organization
IMO	International Maritime Organization
IRENA	International Renewable Energy Agency
ISO	International Organization for Standardization
LCA	Lifecycle Analysis
LEL	Lower Explosive Limit
LFL	Lower Flammability Limit
LHV	Lower Heating Value
LL	Loading Limit
LNG	Liquefied Natural Gas
LNGC	Liquefied Natural Gas Carrier
LPG	Liquefied Petroleum Gas
LTEL	Long Term Exposure Limit
MAC	Maximum Allowable Concentration
MAK	Maximale Arbeitsplatz Konzentration (Maximal Workplace Concentration)

MARPOL	Marine Pollution (IMO)
MARVS	Maximum Allowable Relief Valve Settings
MEPC	Marine Environment Protection Committee (IMO)
MFV	Master Fuel Valve
MGV	Master Gas Valve
MRV	Monitoring Reporting Verification (EU)
MSC	Maritime Safety Committee (IMO)
MSDS	Material Safety Data Sheet
Mt	Million metric tonnes
MVR	ABS Marine Vessels Rules
N2O	Nitrous Oxide
NASA	National Aeronautics and Space Administration
NFPA	U.S. National Fire Protection Association
NGO	Non-Governmental Organization
NH3	Ammonia
NIOSH	National Institute for Occupational Safety and Health (U.S.)
NO	Nitrogen Oxide
NO2	Nitrogen Dioxide
NOx	Nitrogen Oxides
NRC	National Research Council
NTC	NOx Technical Code
ODP	Ozone Depletion Potential
OEL	Occupational Exposure Limit
OSHA	Occupational Safety and Health Administration
PEL	Permitted Exposure Limit
PGS	Publication series on Dangerous Substances
PM	Particulate Matter
PN	Particle Number
PPM	Parts Per Million
PRV	Pressure Relief Valve
PSC	Port State Control
PWHT	Post Weld Heat Treatment
RA	Risk Assessment

REL	Recommended Exposure Limit
RTK	Righ-to-know (US Department of Transportation number)
SCBA	Self-contained breathing apparatus
SCC	Stress Corrosion Cracking
SCR	Selective Catalytic Reduction
SDS	Safety Data Sheet
SGMF	Society for Gas as a Marine Fuel
SIGTTO	Society of International Tanker and Terminal Operators
SIMOPS	Simultaneous Operations
SMAC	Spacecraft Maximum Allowable Concentration
SO2	Sulphur Dioxide
SO3	Sulphur Trioxide
SOLAS	International Convention for the Safety of Life at Sea, 1974, as amended (IMO)
SOx	Sulphur Oxides
STP	Standard temperature and pressure
STCW	Standards of Training, Certification and Watchkeeping for seafarers
STEL	Short-Term Exposure Limit
SZW	Ministerie van Sociale Zaken en Werkgelegenheid (Ministry of Social Affairs and Employment)
TEEL	Temporary Emergency Exposure Limit
TLV	Thresold Limit Value
TRANSCAER	Transportation Community Awareness and Emergency Response
TRL	Technology Readiness Level
TWA	Time Weighted Average
UEL	Upper Explosive Limit
UFL	Upper Flammability Limit
UI	Unified Interpretation
UN	United Nations
UR	Unified Requirement
USCG	United States Coast Guard
USN	United States Navy
WEL	Workplace Exposure Limits
WtW	Well-to-Wake

1. Introduction

1.1 Background

Among the alternative fuels, anhydrous ammonia has gained a lot of attention within the maritime industry as a long-term solution for decarbonisation. Ammonia is a carbon-free compound and is currently being explored as a potential maritime fuel, to be used either directly by internal combustions engines or in ammonia-based fuel cells. Ship designers, builders, engine manufacturers, owners and operators have shown their interest in investing in ammonia as a fuel through concept designs of ammonia fuelled vessels and ammonia consumers such as marine engines, gensets, boilers and gas turbines.

The revised 2023 IMO Strategy on Reduction of GHG Emissions from Ships (Resolution MEPC.377(80)), approved during the 80th MEPC session, increases the levels of ambition towards decarbonisation compared to the Initial IMO Strategy especially regarding the uptake of zero or near-zero GHG emission technologies, fuels and/or energy sources. These now must represent at least 5%, and striving for 10%, of the energy used by international shipping by 2030.

Ammonia could be an excellent candidate to meet this objective as it can be produced from renewable sources, from the same process as hydrogen, generating almost no greenhouse gas (GHG) emissions on a well-to-wake basis (green ammonia), as illustrated in Figure 1.

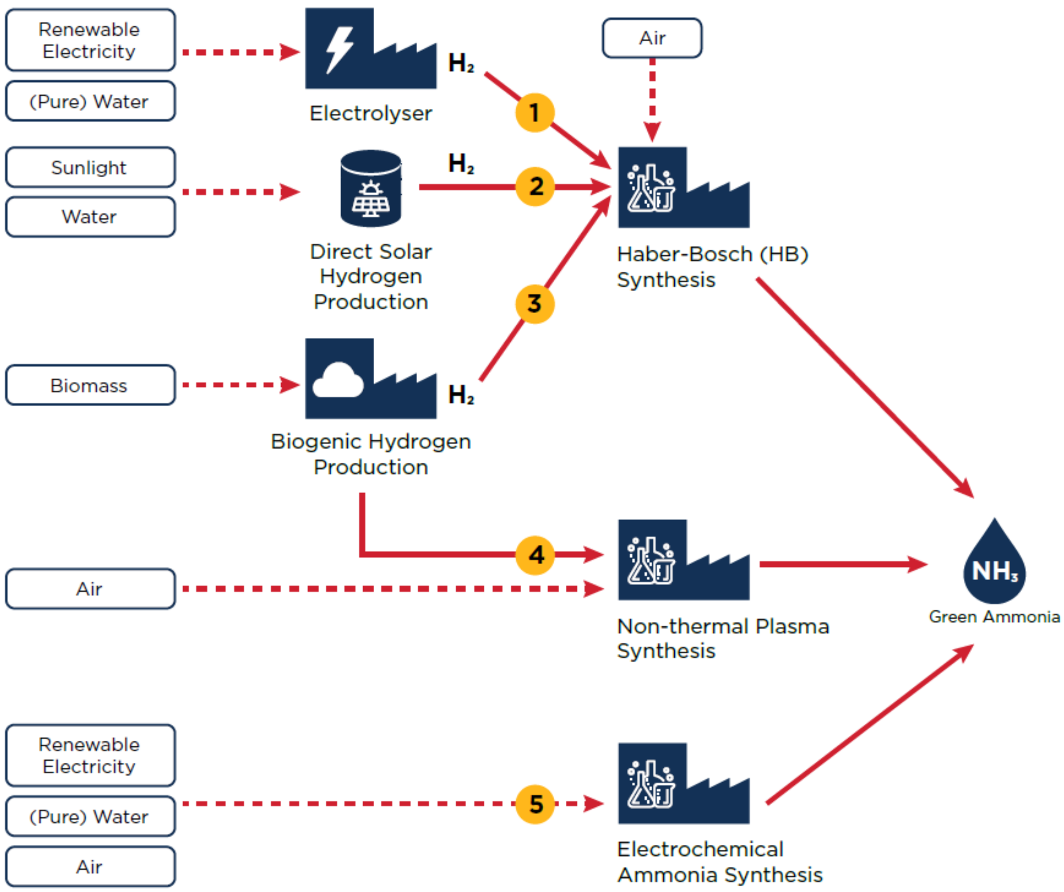

Figure 1: Production process of green ammonia (ABS, 2023c)

Significant efforts are ongoing at the IMO to develop the regulatory framework to cover the use of ammonia as fuel at a time when technology is not mature. Ammonia is a dangerous chemical that poses risks to the crew and the ship during its handling and use onboard that needs to be addressed and regulated. This study will create the foundation for the safe design and use of ammonia as fuel in commercial shipping; the intent is to draw-up a harmonised approach across the shipping industry and to develop a goal-based “Guidance for ships using ammonia as fuel”. This will be achieved through intermediate tasks which include the characterisation of ammonia as chemical and as fuel, reviewing the available rules, regulations and best practices in shipping and land-based industries, undertaking safety and reliability assessments of relevant equipment, systems, and system of systems, and conducting risk assessments for different specific ship types and designs.

The overall study consists of three specific contracts (SC – if all activated) and seven separate tasks as described below and shown in Figure 2:

- The Specific Contract No 1 (SC1) will address the characterisation of the ammonia as fuel (see Task 1);
- The Specific Contract No 2 (SC2) will develop a reliability analysis for equipment and systems and a series of risk assessments for selected ships’ designs (see Task 2 to Task 5);
- The Specific Contract No 3 (SC3) will develop, on the basis of the findings of Task 1 to 5, a goal-based Guidance for ammonia as fuel and the final report (see Task 6 and Task 7).

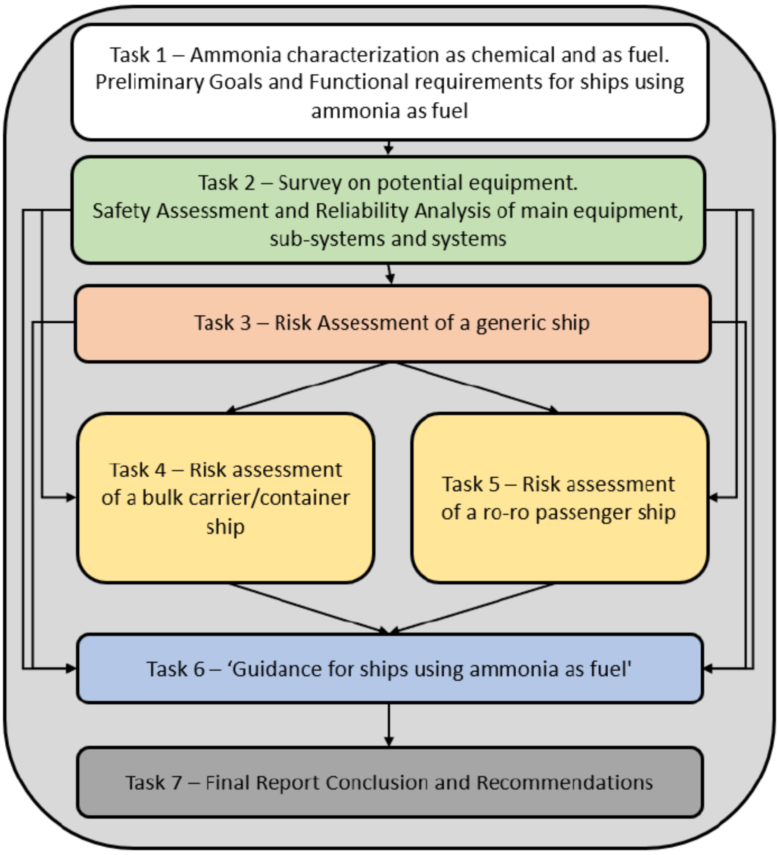

Figure 2: Study logic (Source: EMSA)

1.2 Scope and Objectives

This report serves as the deliverable for Task 1 which is the unique task of the first Specific Contract (SC1) that addresses the characterisation of the ammonia as fuel. This task builds on the results of the previous EMSA study: "Potential of Ammonia as Fuel in Shipping" 2022 by ABS, CE-Delft and Arcsilea (Laursen, et al., 2022), performed as part of EMSA FWC 2021/EMSA/OP/43/2020, further elaborating on the consequences of using ammonia as fuel.

The scope of the first task is to analyse the characteristics of ammonia and the hazards it poses as a potential marine fuel. Special attention is paid to the toxic nature of ammonia analysing the toxicity levels and exposure limits and how these elements affect toxic spaces determination and human activities onboard. This includes an overview of the methodologies and tools used to simulate ammonia gas dispersion, which is a fundamental analysis to determining the toxic areas onboard and bunkering safety zones.

A review of the Personal Protective Equipment (PPE) used in ammonia environments for ordinary and emergency working conditions is carried out based on current experience from onshore industries and shipping. A brief accident review (from land-based production plants, refrigeration facilities, process engineering, etc.) is included in this task to identify the major causes that led to accidents including ammonia. This is a critical step to understand where next tasks of the study, reliability analysis and risk assessments, should be focusing.

This task continues with a review of the existing national and international rules and regulations, classification rules, industrial best practices and identification of conflicts and gaps between them. A similar extensive summary, including a gap analysis, was conducted in the previous EMSA study (Laursen, et al., 2022), so the main intention of this subject task is to identify changes in rules and regulations related to ammonia and to highlight the updates from the latest IMO Sub-Committee on Carriage of Cargo and Containers (CCC), 9th session.

Using the above information, the task concludes by proposing a preliminary structure of how the goal-based EMSA Guidance should be developed; detailed development of Guidance is an objective of Task 6.

2. Ammonia, Toxicity, Health and Protection of Life

Global infrastructure for ammonia is well established. Its widespread use in inorganic fertilisers has provided ample experience in safely handling, transferring and storing this chemical. Figure 3 illustrates ammonia shipping infrastructure, including a traffic heat map of liquefied ammonia carriers and existing port facilities. The red and blue dots represent the ammonia loading and unloading facilities. The figure was plotted with data from 2017, a year when 16 million tonnes (Mt) of ammonia were transported by sea. In 2022, the production of ammonia reached 150 Mt, with 20 Mt transported by sea.

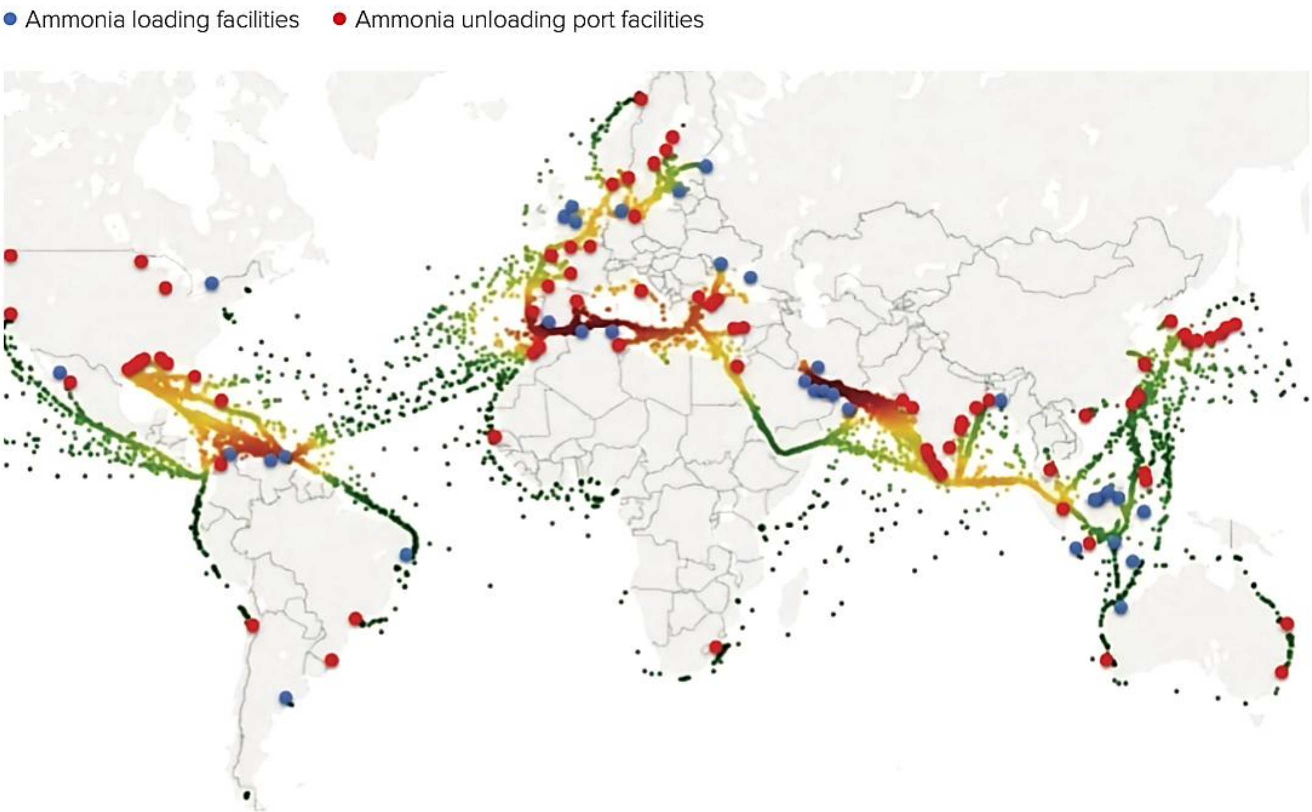

Figure 3: Ammonia shipping infrastructure (The Royal Society, 2020)

Some of the leading ammonia manufacturers include: Yara International ASA, BASF SE, CF Industries Holdings Inc., Nutrien Ltd, SABIC, Eurochem Group, Koch Fertilizer, LLC and China National Petroleum Corporation. In 2022 East Asia produced approximately 87 Mt of ammonia, East Europe and Central Asia 27 Mt, Africa 21 Mt, West and Central Europe 20 Mt and North America 19 Mt whilst the European Union produced 21 Mt.

Ammonia is widely used in industries such as agriculture, textile manufacturing, mining, refrigeration, pharmaceutical, food production and other manufacturing. However, the main use of ammonia is as fertiliser for food production. In households, aqueous ammonia is used as a general-purpose cleaner, in concentrations that range from 5-10%.

The use of ammonia as fuel was first tested in engines during the 19th century. Rudolf Diesel built a steam engine using ammonia vapour, which was the beginning of the Diesel engine invention. During the Second World War, ammonia mixed with coal was used as fuel for some buses and cars in Belgium due to shortages in fossil fuel. During the 1960s, NASA tested an experimental rocket plane -- the North American Aviation X-15 -- which used ammonia as fuel not in an internal combustion engine, but in a rocket as propellant for the XLR99 engine. However, the use of non-fossil fuels was limited to niche applications due to the high price of production compared to the fossil fuels (Lauf, Wsewolod, & Zimmermann, 2021).

The global worldwide fleet currently features no vessels fuelled by ammonia. However, some classification societies already provide “Ammonia Ready” notations for vessels operating on conventional fuels but possessing design features suitable for future conversion to ammonia-propulsion.

According to Clarksons, in June 2023, there were 191 ammonia-ready vessels on order. In January 2022, the first ammonia-ready vessel, the tanker “Kriti Future” was delivered to Avin International, built at New Times Shipbuilding in China and classed by ABS. In May 2023, the first ammonia-ready containership, the CMA CGM “Masai Mara”, was built by Qingdao Beihai Shipbuilding Heavy Industry.

A limited orderbook for ammonia-propelled vessels is beginning to emerge as shown in Table 1 with information collected from different shipowners.

Table 1: Current orders of ammonia-fuelled vessels

Shipowner	Type	Order	Delivery	Shipyard
CMB	Newcastlemax bulk carrier	10	2025	CSSC Qingdao Beihai Shipbuilding
Exmar LPG BV	LPG Carrier (46,000 cbm)	2	2026 (Q1)	Hyundai Mipo Dockyard
Faerder Tankers	Car carrier (7500 ceu)	2	TBC	Undisclosed
Faerder Tankers	Product Tanker (LR2)	2	TBC	Undisclosed
MOL	LPG Carrier (40,000 cbm)	1	2026	Tsuneishi Shipbuilding
North Sea Container Line	Containership	1	2026	Undisclosed
Eastern Pacific Shipping	Very Large Ammonia Carrier (VLAC)	2	2026	Hyundai Heavy Industries
Capital Gas	Very Large Ammonia Carrier (VLAC)	2	2026	Hyundai Heavy Industries

2.1 Ammonia Characterisation

Anhydrous ammonia (NH_3) is a carbon-free compound of nitrogen and hydrogen, a colourless gas with a strong, sharp, irritating odour. It is important to differentiate between anhydrous ammonia and aqueous ammonia. Anhydrous ammonia contains no water; it is 100% pure ammonia. On the other hand, aqueous ammonia is a water-based solution normally having a concentration between 10-35% of ammonia.

2.1.1 Chemical and Physical properties

Anhydrous ammonia has the number 231-634-3 in the EINECS (European Inventory of Existing Commercial Chemical Substances) list. The CAS RN (Chemical Abstracts Service Registry Number) is 7664-41-7, established by the American Chemical Society to identify each chemical compound:

Table 2: Anhydrous ammonia identifier in different organisations

Organization	Identifier
EINECS (EC number)	231-634-3
CAS Number	7664-41-7
RTK substance number	0084
DOT number	UN 1005

The key properties of ammonia are shown below in Table 3:

Table 3: Physical-chemical properties of ammonia

Property	Units	Value
Chemical formula	-	NH_3
Appearance @STP	-	Colourless gas
Odour	-	Strong pungent odour
Liquid density	kg/m^3	682 (at 1,013 bar, -33.5°C)
Gas density	kg/m^3	0.73 (at 1,013 bar, 15°C)
Melting point	°C	−77.73 (at 1 atm)
Boiling point	°C	-33.34 (at 1 atm)
Critical temperature	°C	132.4
Critical pressure	kPa	11,410
Liquid specific gravity	-	0.596 (at 1 atm)
Gas specific gravity	-	0.62
Flammable range in dry air	% vol	15.15 to 27.35
Vapour pressure	kPa	857.3 (at 20ºC)
Magnetic susceptibility	cm^3/mol	$-18.0 \cdot 10^{-6}$
Refractive index	-	1.3327
Viscosity (gas)	μPa	10.07
Energy density (liquid)	MJ/L	15.6
Heat of vaporisation	kJ/kg	1,372
Flash Point	ºC	132
Autoignition temperature	ºC	651
Solubility in water	g/l	51 (20°C, 1 atm, highly soluble)
Solubility	-	chloroform, ether, ethanol, methanol
Dielectric constant		16.9 (liquid, at 25ºC)
Dipolar moment		1,3x10-18 e.s.u
Ionisation potential	volts	11,2
Heat of combustion	Btu/lb	8001

Property	Units	Value
Molar mass	g/mol	17.031
Molar heat of formation	Kcal/mol	-10.96 (at 25ºC)
Free energy of formation	Kcal/mol	-3.903 (at 25ºC)
Acid Dissociation Constant	pKa	32.5 (at 25ºC)
Base Dissociation Constant	pKb	4.75 (at 25ºC)
Conjugate acid	-	Ammonium
Conjugate base	-	Amide
Minimum ignition energy	mJ	40-680[2]
Cetane number		0
Octane number		~130

Depending on pressure and temperature, ammonia can be found as a colourless gas, a colourless liquid and even as a white solid. Ammonia is easily liquefied due to the strong hydrogen bonding between molecules.

At atmospheric temperature and pressure, it has a pungent smell, turns into a liquid below -33.5ºC and freezes to crystals at -77.7ºC. At higher pressures, ammonia easily becomes a liquid, making it easier to transport and store.

Comparing the properties of ammonia with those of LNG, there are some initial observations. Regarding their physical state, ammonia is a colourless gas at standard temperature and pressure (STP), whereas LNG is a cryogenic liquid derived from natural gas. They differ in their chemical composition; ammonia is NH_3, while LNG primarily consists of methane (CH_4) along with other hydrocarbons. Ammonia shows solubility in water and specific organic solvents, whereas LNG is not soluble in water but can dissolve in specific solvents under certain conditions. The densities of liquid and gas for ammonia and LNG differ significantly due to their distinct states at standard conditions. Ammonia has lower boiling (-33.34°C) and melting (-77.73°C) points compared to LNG, which typically liquefies at much lower temperatures (approximately -162°C). Both substances have different flammable ranges and behaviors. Ammonia has a higher flammability range in dry air (15-28% vol), whereas LNG is a highly flammable substance at lower concentrations (5-15% vol).

Regarding energy content, ammonia has a lower energy density (15.6 MJ/L) compared to LNG, which generally has a higher energy density due to the high calorific value of methane.

In summary, from these initial comparisons, it can be concluded that ammonia and LNG differ significantly in their physical states, chemical compositions, energy densities, flammability characteristics, and solubility properties. Each substance has a different behavior in terms of its application as a fuel. Their properties also make a difference in terms of transport, storage and handling (safety).

The different states for ammonia can be easily intercorrelated using the anhydrous ammonia phase diagram found in Figure 4.

[2] Minimum Ignition Energy of Ammonia depends on the type of spark.

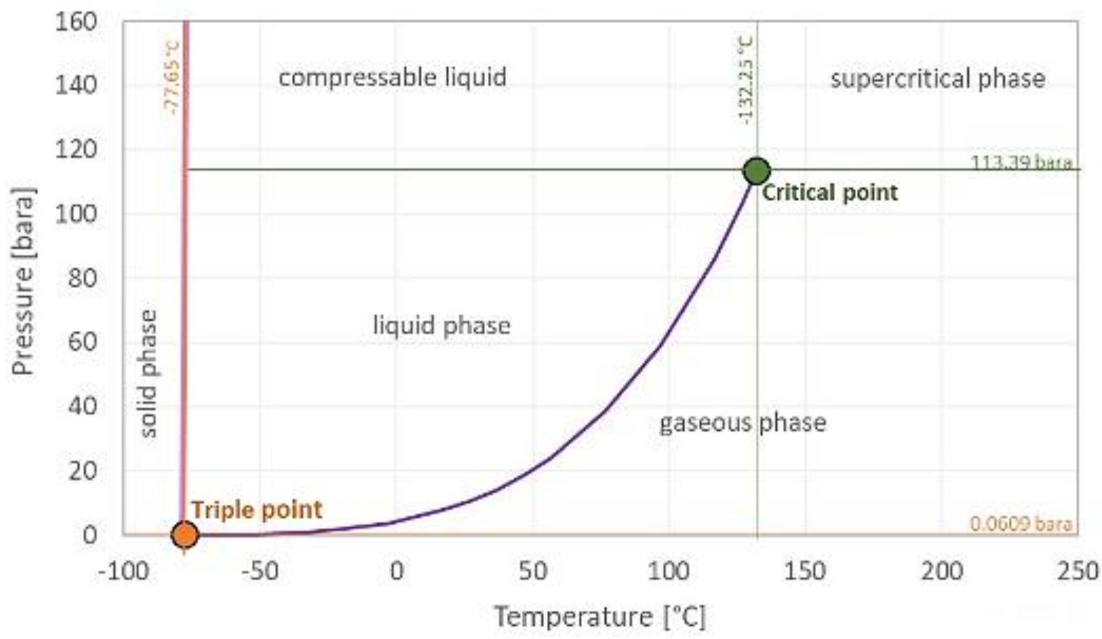

Figure 4: Phase diagram of ammonia (Source: The Engineering ToolBox) [3]

The density of ammonia vapour is lower than air (the relative density of ammonia to dry air is 0.589), so it will tend to move and dissipate in the atmosphere as it rises. However, the density of ammonia vapour depends on the temperature at a certain pressure as represented in Figure 6.

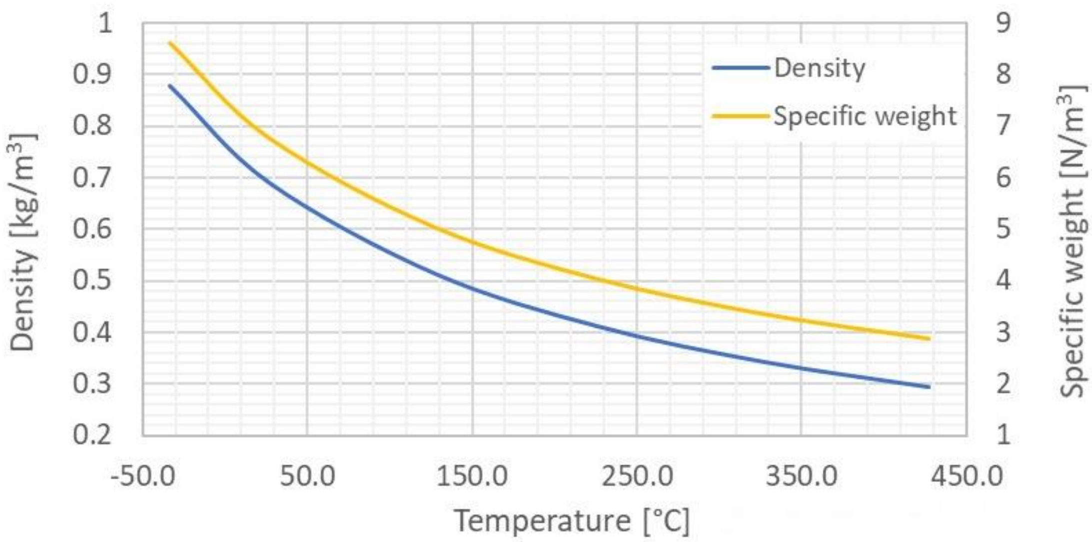

Figure 5: Ammonia gas density and specific weight at 1 bar (Source: The Engineering ToolBox)

[3] Triple point is the temperature and pressure at which the three phases (gas, liquid, and solid) of that substance coexist in thermodynamic equilibrium and critical point or critical state is the point at which two phases of a substance initially become indistinguishable from one another.

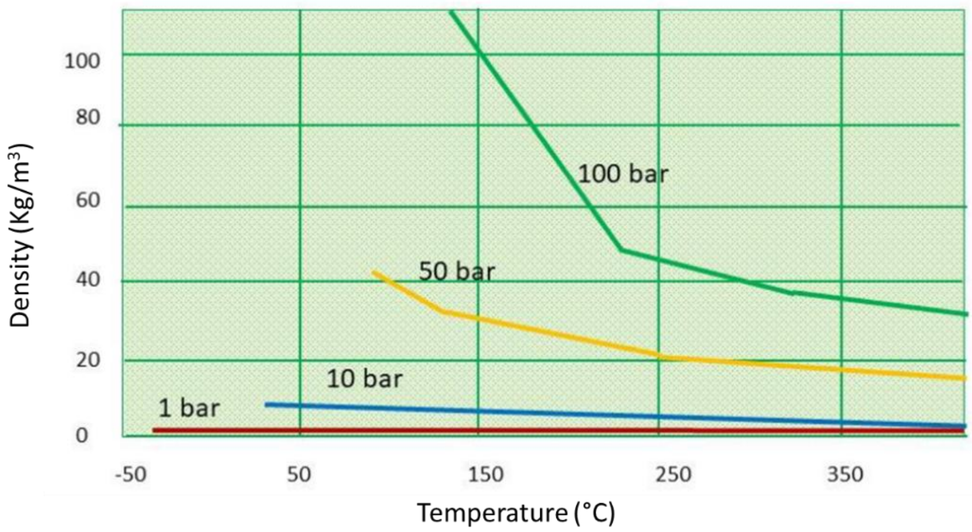

Figure 6: Density of ammonia gas as a function of temperature and pressure (Source: The Engineering ToolBox)

Since there is no water, the pH of pure anhydrous ammonia cannot be measured. When diluted with water, it becomes a strong base and its corrosiveness can cause chemical burns. Ammonia seeks water from the nearest source, including the human body, extracting water from the tissues and causing chemical burns on the skin.

Although ammonia is considered a non-flammable gas by the United Nations, it will ignite at a temperature of 651ºC within concentrations between 15-28% vol. The concentrations required to ignite are very high and its diffusion in the air is very fast, but in closed environments it is dangerous. Its flammability range is wider than those of methane, propane, propylene, gasoline or diesel and butane as shown in Table 4 and a factor to consider in enclosed spaces. Note that the LFL and UFL for MGO and HFO are provided only for reference and depend on the product.

Table 4: LFL and UFL of alternative and conventional fuels

Substance	LFL (%)	UFL (%)
Ammonia	15	28
Hydrogen	4	74
HFO	4.3	45.5
MGO	0.6	7.0
Ethane	3	13
Methane	5	15
Propane	2	10

Anhydrous ammonia, in both gas and liquid phase, has a high thermal conductivity and heat capacity compared to many other substances, which gives very good heat transfer properties. The heat of vaporisation of ammonia at boiling point is 23.4 kJ/mol, which is why it makes it a very good refrigerant, absorbing a large amount of heat when it boils.

Even though ammonia is considered a relatively stable product, it is still capable of creating some dangerous or potentially dangerous reactions. In fact, ammonia reacts dangerously with some products (e.g. chlorine, fluorine, bromine, mercury and hypochlorite).

Ammonia has the “great advantage” of having a very low odour threshold (2-5 ppm), which allows it to be detectable by smell long before the concentration reaches dangerous values (300 ppm, IDLH). In the event of a minor leak, the strong smell combined to the inadequate risk perception could create panic reaction and generate a side accident in the public.

2.1.2 Ammonia-Water solubility

Liquid ammonia is a valuable solvent, better than water for some organic substances. It is a poor conductor of electric current. The properties of ammonia in water can be directly linked to most of the hazards associated with the substance. When it enters the body through breathing, swallowing or skin contact, it reacts with water producing ammonium hydroxide, which is very corrosive and damages cells.

Ammonia solution, also known as ammonia water, ammonium hydroxide or aqueous ammonia is a solution of ammonia in water, denoted as $NH_{3(aq)}$. While ammonia is a gas in standard conditions, it is very soluble in water, attributed to the hydrogen bonding between ammonia and water molecules.

The nitrogen atom is very electronegative. It draws the electrons from the hydrogen atom and creates a slightly negative charge around the nitrogen and a slightly positive around the hydrogen, making it a polar molecule. Water is polar as well. Between the water and the ammonia there is a strong hydrogen bond, due to their mutual attraction.

Due to its hygroscopic property, when anhydrous ammonia reacts with water it deprotonates a small fraction of the water to give ammonium ions (NH4+) and hydroxide ions (OH-), according to the following equilibrium:

$$NH_3 + H_2O \rightleftarrows {NH_4}^+ + OH^- + \text{Heat} \qquad \text{[Eq. 1]}$$

However, it is very difficult to form stoichiometric ammonium hydroxide, as the equilibrium is pushed towards the reactant side. A very small portion of the ammonia in an ammonia solution is converted to ammonium (0.42% in a 1 Molar solution of ammonia). Ammonium hydroxide cannot be isolated because the ion-water attraction overcomes the attraction between ions, so it is dissociated into the ammonium cation and hydroxide anion. The process of ammonia absorbing water is exothermic, meaning it releases heat.

Water has a neutral pH of 7, so the presence of ammonia increases the concentration of hydroxide ions in the solution, which raises the pH of the water, making it slightly alkaline. In the absence of humidity, anhydrous ammonia can be considered a relatively non-corrosive substance, although in the presence of water it forms a strong base with a pH greater than 11. It ionises much less completely in water than in a strong base such as sodium hydroxide. The pH for different concentrations of aqua ammonia is detailed in Table 5.

Table 5: pH of aqueous ammonia at 25ºC

NH_3 weight %	Normality	pH
17.0	10.0	12.1
0.17	0.1	11.1
0.0017	0.001	10.1

As ammonia mixes with water, the density of the mixture decreases because the created ammonium hydroxide solution is lighter than water. Depending on the quantity of ammonia, it may result in a diluted solution, a saturated solution or a supersaturated solution. The maximum concentration of ammonia in water (saturated) at 15.6ºC has a density of 0.880 g/cm^3. It is often known as 880 ammonia and contains 35.6% ammonia by mass (308 grams of ammonia per litre of solution).

As reference, the density of the four elements at standard temperature and pressure (STP) is provided in Table 6.

Table 6: Density of Anhydrous ammonia, Ammonium hydroxide, Water and Dry Air

Element	Formula	Units	Value @ STP
Anhydrous ammonia	NH_3	kg/m^3	0.73
Ammonium hydroxide	NH_4OH	kg/m^3	880
Water	H_2O	kg/m^3	1.000
Dry air	-	kg/m^3	1.293

During the process of mixing ammonia with water, an adsorption, absorption and dilution happen simultaneously according to Figure 7.

- Adsorption: Ammonia adheres to the surface of the droplet
- Absorption: Ammonia is absorbed by the droplet.
- Dilution: Ammonia is diluted in the droplet according to the equilibrium of [Eq. 1]

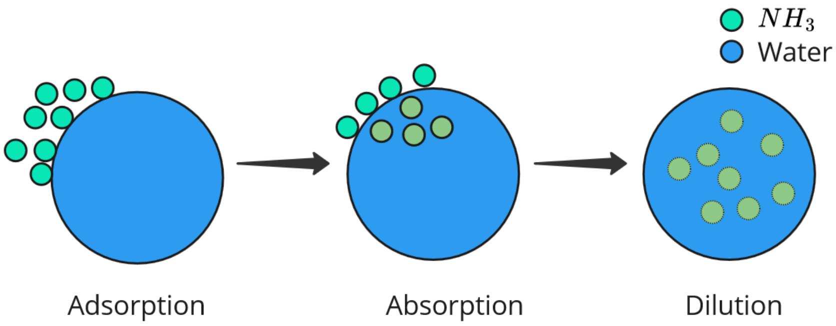

Figure 7: Dilution of ammonia with water droplets

The solubility of ammonia in water is influenced by temperature. When ammonia reacts with water, it generates heat, violently increasing the temperature of the water and reducing the efficiency of solubility: an increase in temperature favours the reverse reaction (un-dissociation of ammonium hydroxide), causing ammonia to become less soluble.

Furthermore, the concentration of ammonia that can be dissolved in water is directly related to the pressure of gaseous ammonia above the solution. Increasing the pressure of gaseous ammonia will lead to more ammonia being dissolved in the water.

Finally, the ease of dilution of ammonia in water may be used in the design of some safety systems to help prevent a leak. When using sprayed water, fine water droplets mix with the vaporised ammonia, facilitating the entry of air into the mixture. Water should never be sprayed directly onto liquefied ammonia because the boiling reaction is very explosive and suddenly generates much more vapours.

Also, water sprayed into a tank containing ammonia vapour will result in a vacuum, so there will be risk of collapsing the tank or, alternatively, a heavy inflow of air into the tank. For big tank volumes, there is risk of dragging people into the tank system.

The use of water curtains as a control measure is intended to prevent the dispersion and movement of the cloud. The position of the curtains and the water flow rate will influence the desired effect, the effectiveness of which is enhanced when multiple curtains are placed in series, according to the direction of the leak. This serves as a defensive measure, while assessing the situation and ultimately taking other control or mitigation measures.

Although at first glance the addition of water to the ammonia cloud would appear to be a good mitigation method, it creates ammonium hydroxide, a substance that is corrosive to the eyes, skin and respiratory tract; the potential side effects on health will depend on the concentration. In enclosed spaces, a specific system should be designed to collect the ammonia water.

To summarise the above, the strong affinity of ammonia for water molecules implies that the following should be considered with respect to risks and safety:

- Ammonia reacts with moisture in the eyes and mucous membranes (the respiratory tract) to form ammonium hydroxide, a substance that causes saponification and liquefaction of the exposed moist epithelial surfaces of the eye and can easily penetrate the cornea and damage the iris and lens. After exposure to high concentrations of liquid ammonia, corneal burns occur and may lead to blindness. Respiratory protection devices must have the appropriate filters with full-face masks.
- Water spray systems, water screens and water curtains can be used as control measures, mitigating the dispersion and advancement of the cloud of ammonia gas. This has been extensively studied in fire codes, which conclude that the use of curtains may scavenge up to 90% of ammonia in certain conditions, using fan-shaped water curtains and with the pressure as high as possible (Hua, Yue, Pi, Pan, & Jiang, 2017).

2.1.3 Ammonia-Air mixture

Anhydrous ammonia is hygroscopic which means it has a strong affinity for water molecules. The air naturally has humidity; thus, it contains water vapour in it. The water moisture in the air can range from trace amounts up to more than 4% in volume, depending on the pressure and the temperature. Once the air is saturated (relative humidity 100%), water droplets can be formed in which ammonia is easily absorbed and diluted. Before saturation, the presence of water vapour enhances the reactivity of ammonia with copper, zinc and many alloys (see reference[4]).

The dispersion model of ammonia is complex and should be simulated in different scenarios. Some companies such as Glexcon, offer specific software to determine the consequences of the accidental release of hazardous chemical substances based on the leakage conditions (pressure, temperature, vapour mass fraction), the characteristics of the leak (hole diameter and height above ground level) and the environmental conditions. In case of a leakage, the dispersion is determined by the location of the leak, the storage conditions, the duration of the release, and the flow rate (Kay Leng Ng, Liu, Siu Lee Lam, & Yang, 2023). The toxic gas cloud from refrigerated atmospheric storage tanks is generally smaller than those from semi-refrigerated ammonia and pressurised ammonia.

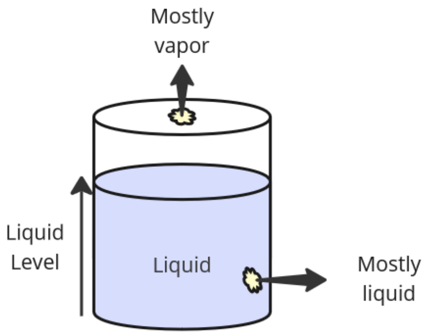

Figure 8: Different positions of the leakage in a tank

If the leakage is below the liquid level, the leak will be mostly liquid; if it happens above the liquid level, it will be mostly vapour as represented in the Figure 8.

The handling of liquefied ammonia during storage and transportation in a cold state is inherently safer than in a high-pressure liquefied state. Recently some ammonia field experiments have been conducted to describe the behavior of cold ammonia liquid spills on dry land and into water such as the Red Squirrel ammonia field experiments.

[4] https://www.osha.gov/etools/ammonia-refrigeration/ammonia

Release of refrigerated ammonia

With leaks of refrigerated ammonia, the general process is outlined in Figure 9. The liquid ammonia pool is initially at its normal boiling temperature (-33ºC). The pool gets energy from the surroundings; air, radiation, ground and precipitation and the balance of energy all determine the temperature of the pool and thereof the boil-off gas, the part of ammonia that evaporates. With the boil-off gas, energy is removed from the pool by vapour generation.

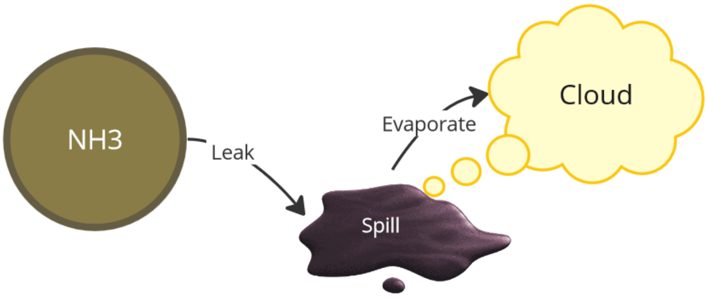

Figure 9: Refrigerated ammonia loss of containment stages

In the air, ammonia is taken up in the form of water droplets. In case of a refrigerated leakage, droplets will appear in the atmosphere due to the temperature decrease and because of the ammonia boil-off gas:

- Ammonia dissolves in the droplets. The quantity mainly depends on the air humidity and the air temperature; with a humidity of 99% and 30ºC the amount of ammonia dissolved is less than 1%.
- Ammonia adsorbs on the surface of the droplet. Only a small percentage of the dissolved ammonia in the droplet remains on the surface.

Pressurised ammonia release

In the case of a pressurised containment, there are primarily three stages that occur during a free dispersion process of ammonia:

1. In a first stage there is a rising with buoyancy of the ammonia, generated at the point closest to the leak source. Most of this aerosol will mix with the ambient humidity, creating a white cloud and behave like a dense gas.
2. In the generated cloud there is an air entrainment, that will heat the vapour cloud, due to the difference between gas cloud and ambient environment temperatures.
3. Vapor cloud dispersion, diluting the concentration of the gas cloud with the upward movement cloud, along with the entrainment and heat transfer processes of the air.

Water curtains

Water curtains may be a way to reduce the dispersion of the cloud, but it should be discussed based on the properties of the ammonia cloud, and the probability for aerosol formation, which is directly related to the ammonia storage conditions. The projection of sprayed water generates a turbulent motion in the cloud that aids in dilution. The dilution effect of ammonia in the air is further complemented by the dilution of ammonia in water, resulting in the creation of a corrosive ammoniacal solution.

Compared with the free dispersion process, the water curtain scavenging ammonia dispersion process can be divided into three regions:

- The free dispersion area (this area refers to the distance between the release source and the water curtain).
- The "NH_3-water curtain" interaction area (when the gas cloud is diffused near the water curtain, the gas cloud touches the water droplets and will perform very complex functions).

- The free dispersion area behind the water curtain (an area in which a part of the gas runs around or through the water curtain and gradually moves away from the water curtain).

If an ammonia leak occurs in an enclosed space and there is no way to contain or confine the gases, dispersion of the gases and dilution into the atmospheric air can be achieved by a forced ventilation that introduces air into the gas mass.

The effects of mixing vapourised ammonia from a refrigerated ammonia spill at -33ºC, and dry or humid air in an isobaric and adiabatic process are summarised in the Figure 10. The density decreases linearly with the increase of ammonia, which means the mixture is always buoyant (Skarsvåg, Bucelli, Aasen, & Spillum Grønli, 2023). In a leak the mixture will tend to ascend.

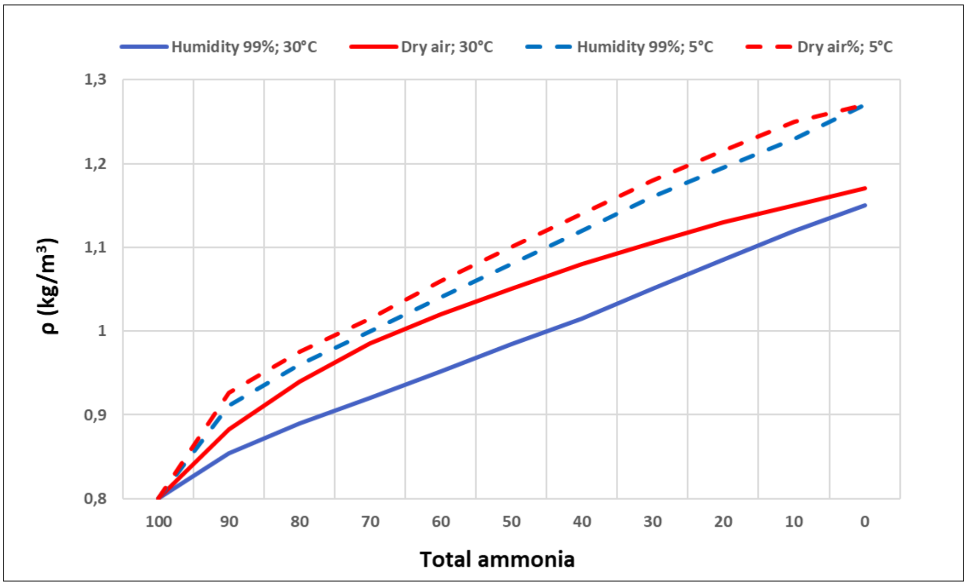

Figure 10: Liquid ammonia mixing with humid air and dry air

Some studies already have demonstrated that water curtains are a very efficient way of diluting and reducing the concentration of ammonia, reaching an efficiency as high as 90% (Hua, Yue, Pi, Pan, & Jiang, 2017). The efficiency and application of the water curtain depends on the properties of the ammonia cloud and the aerosol formation, which is directly related to the ammonia storage conditions. For water curtain solutions in enclosed spaces, specific solutions to collect the ammonia water should be designed.

2.1.4 Material incompatibility and Stress Corrosion Cracking

Ammonia is incompatible with various metals. Its exposure to these metals produces corrosion, converting the metal into a more chemically oxide. The compatibility depends on the dilution level and the temperature of ammonia. In the presence of moisture, it reacts with and corrodes copper, brass, zinc and other alloys, forming a greenish/blue colour.

Ammonia is an alkaline-reducing agent and reacts with acids, halogens and oxidising agents. These properties add challenges related to the selection of materials for onboard equipment and tanks. In this light, any study and selection of materials should be extensive and take into account the metals, rubbers and polymers typically used for gaskets and sealing.

Its compatibility with elastomers used in protective equipment, plugging, valve seals, etc., varies; contact with natural rubber, nitrile, polyurethane, viton (FKM) or silicone is not recommended at low temperatures. In certain temperature ranges, its use with neoprene (-40ºC and 80ºC), butyl (-54ºC and 149ºC), silicone (between -20ºC and 204ºC) is acceptable. Teflon, although technically not an elastomer, is also compatible with ammonia.

Extensive lists of materials compatible with ammonia may be found on the websites of ammonia suppliers such as Airgas Speciality Products. There are several codes of practice related to corrosion (HSE, 1986) which offer advice for the appropriate construction materials for ammonia storage vessels. The American Society for Metals (ASM) has extensive literature studying the corrosion of ammonia in multiple metals (Cramer, Davies, & Covino, 2006).

Stress Corrosion Cracking

The use of ammonia may cause stress corrosion cracking (SCC), cracks formed in carbon steel due to contact with ammonia. The cracks are small at the surface, but can be deep, even going through the entire thickness of the metal. The presence of oxygen and residual stress are the causes for forming SCC cracks.

Ammonia SCC is most prevalent in carbon steels equipment in service or in copper-zinc alloys in aqueous environments. Post weld heat treatment reduces the occurrence of SCC. The areas more susceptible to ammonia SCC are ammonia storage tanks, piping and related components in ammonia refrigeration units. It commonly occurs in brass tubes in cooling water service that have been contaminated with ammonia due to biological growth or other contamination. It also can occur when ammonia is intentionally added to process streams as a neutraliser by someone unaware of its potential effect on brass tubes.

The cracks may be avoided by minimising the oxygen presence by purging with nitrogen, adding 0.2% water to the ammonia or using stainless steel equipment. Ensuring no oxygen presence is the best way to avoid potential issues in the complete supply chain, but it is very difficult to guarantee.

2.1.5 Storage and Transport of Ammonia

Anhydrous ammonia has been widely stored and transported by pipelines, rail, ships and trucks for many years. The storage and transport of ammonia is mainly in liquid state. This can be achieved either by increasing the pressure (pressurised tanks) or reducing the temperature (insulated tanks). As reference, at room temperature (circa 25^{o}C), ammonia becomes liquid at a pressure of approximately 8.5 bar.

The fraction of ammonia liquid and vapour depends directly on pressure and temperature conditions. When ammonia is stored in a tank where there is a gas phase and a liquid phase, the storage pressure is a function of the temperature of the liquid. When the system receives heat, it will generate more boil-off until the system balances the new vapour pressure.

To store ammonia in a liquid state, it must be kept in mind that it has a high expansion coefficient during the transition from gaseous to liquid states (1:850). There are several regulations providing maximum filling levels for stationary and mobile pressurised and refrigerated tanks. In the U.S., the transport of anhydrous ammonia is regulated by the Department of Transportation (DOT) under CFR Title 49. In Figure 11 the most common road trailer (MC 331 high pressure, 11,500 gallons capacity) and rail insulated tank (DOT 105J, 33,500 gallons capacity) are shown.

- For stationary and mobile tanks without reliquefaction the tanks must have a maximum filling limit of 85%
- LPG tankers have reliquefaction plants onboard, allowing filling limits up to 98%

Storage conditions for ammonia are very relevant, because, when leaks occur, those conditions directly affect the behavior of the cloud, as detailed in Ammonia-Air mixture section.

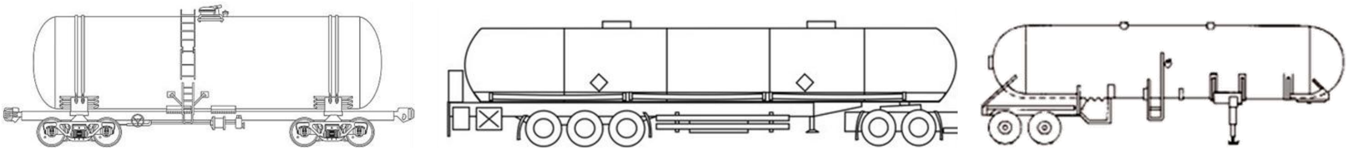

Figure 11: Tanker rail car and tanker trucks

In the maritime industry, ammonia historically has been shipped in three different gas carrier types:

- **Fully refrigerated**: Cargo is carried at pressures close to atmospheric and low temperatures close to cargo's boiling point. Cargo tank design pressure is up to 0.7barg[5]. Total cargo capacity is usually above 20,000 m^3.
- **Semi-pressurised**: A combination of pressurisation and refrigeration. Cargo tank design pressure in the range of 4-8 barg. Total cargo capacities range between 5,000 to 30,000 m^3.
- **Fully pressurised**: Cargo is carried at ambient temperature and high pressure up to approximately 20 barg. The tanks are extremely heavy. They are usually small gas carriers with cargo capacities of about 4,000 m^3.

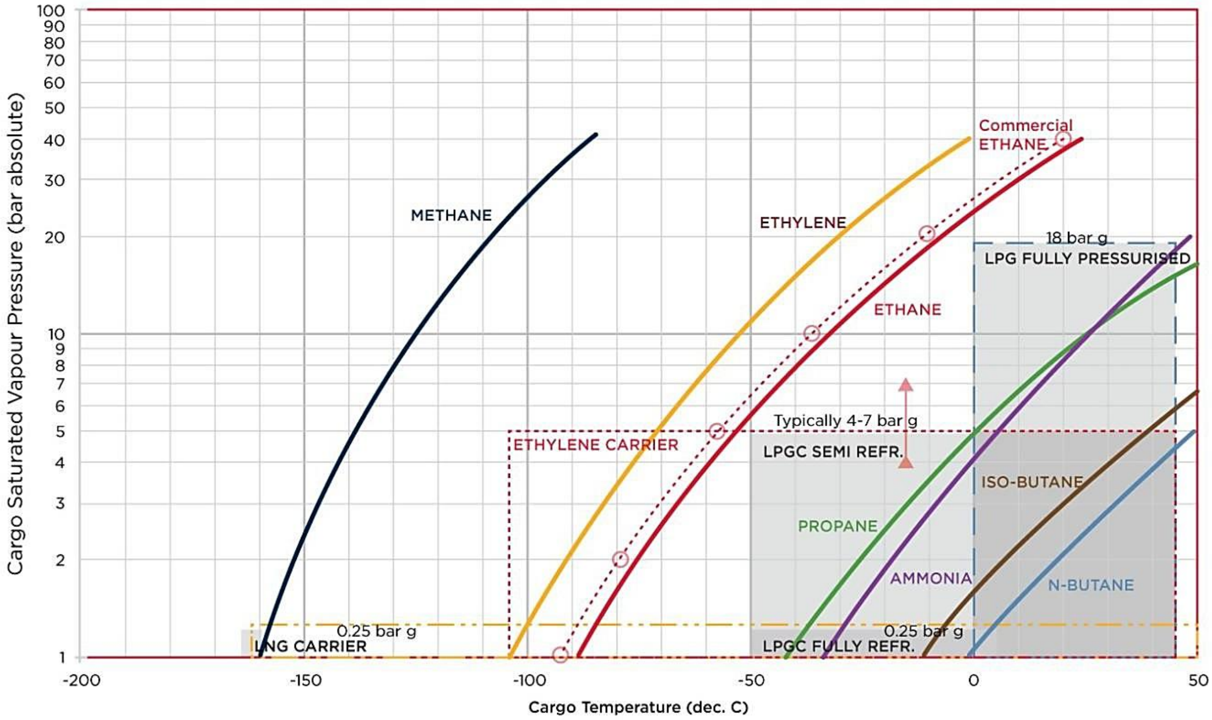

Figure 12: Typical operating range of common types of liquefied gas carriers

Figure 12 shows the saturated vapour pressure curves of the main liquefied gases carried under the IGC Code and the operating range (rectangles) of the most common gas carriers (fully refrigerated, semi-pressurised and fully pressurised).

- **Filling Limit (FL)** Maximum liquid volume in a cargo tank relative to the accepted total tank volume when the liquid cargo has reached the reference temperature.
- **Loading Limit (LL)** Maximum allowable liquid volume relative to the tank volume to which the tank may be loaded.

The Loading Limit is calculated from the Filling Limit with the density of ammonia at reference temperature (ρ_R = 681.97 kg/m^3) and at loading temperature (ρ_R). The reference temperature of ammonia is the temperature that requires no pressure to maintain the liquid state (-33.5ºC). For example, for an extremely warm cargo:

$$LL = FL \frac{\rho_R}{\rho_L} \quad \text{[Eq. 2]}$$

[5] barg unit of gauge pressure, or pressure measured against the ambient pressure.

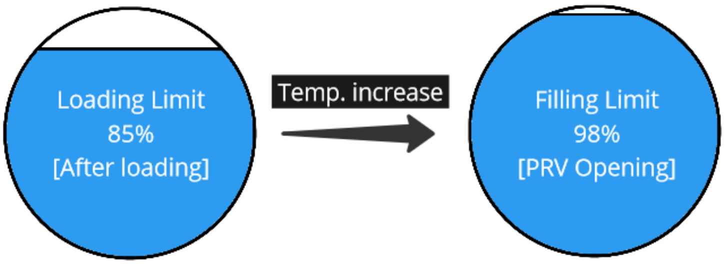

Figure 13: Filling limit and Loading limit

2.2 Toxicity, Exposure limits and Flammability

As can be seen in the safety datasheet for ammonia, the NFPA (U.S National Fire Protection Association) classifies it as a serious hazard to health, a slight hazard due to its flammability and minimally reactive.

The subsequent sections outline the toxicity values of ammonia and the thresholds established by different agencies as the maximum permissible levels of exposure for workers and individuals to ensure their safety and well-being.

2.2.1 Toxicity

There are different values available for the same effect. The exposure to an ammonia atmosphere may induce the following physical effects:

- **Ocular effects**: Ammonia vapour causes irritation to the eyes and respiratory tract. High concentrations can cause conjunctivitis, laryngitis and pulmonary edema, accompanied by a state of suffocation.
- **Skin effects**: Contact with the skin can cause burns and blisters. When it comes into direct contact, liquid ammonia freezes the tissues and causes burns. The eyes are especially sensitive to alkaline products. Ammonia reacts with moisture in the eyes and mucous membranes to form ammonium hydroxide, a substance that causes saponification and liquefaction of the exposed moist epithelial surfaces of the eye and can easily penetrate the cornea and damage the iris and lens. After exposure to high concentrations of liquid ammonia, corneal burns occur and may lead to blindness.
- **Respiratory effects**: The inhalation of ammonia may result in a rise of systemic blood pressure. The most common cause of death in humans exposed to ammonia is pulmonary edema. Contact with liquefied ammonia under pressure may result in frostbite.

As stated above, at room temperature ammonia is a colourless gas with a very sharp odour. In small concentrations the gas is detectable by smell. In high concentrations it is an immediate hazard to life.

Table 7 shows health effects from ammonia exposure based on concentration. Table has been created upon review of safety datasheets provided by public agencies such as the Spanish Ministry of the Interior Civil Protection and health authorities like Public Health England, along with information from manufacturers' associations such as CEFIC (European Chemical Industry Council) and CIAFA (Cámara de la Industria Argentina de Fertilizantes y Agroquímicos), and data obtained from laboratories like Scharlab.

Table 7: Concentration in air of Ammonia and health effects

Concentration (ppm)	Effect
5 – 25	Odour perception
20 - 50	Mild discomfort
50 – 80 (2 hour)	Perceptible eye and throat irritation
100 (2 hour)	Nuisance eye and throat irritation
140 (2 hours min)	Severe eye, nasal, throat and chest irritation. Leave exposure area
300	No scape-impairing symptoms and no irreversible effect
500 (30 min)	Upper respiratory tract irritation, tearing of the eyes
700 – 1,700	Coughing, bronchospasm and chest pain with severe eye irritation and tearing
5,000 – 10,000	Rapidly lethal: Chemical bronchitis and chemical burns of the skin
10,000	Promptly lethal

2.2.2 Exposure limits

Several global agencies and organisations establish exposure limits and guidelines for safe exposure to ammonia due to its toxic properties and potential hazards. These guidelines are critical to ensure the safety of workers and the public who may be exposed to ammonia in various work, industrial, or other settings. Here are some of the prominent organisations and regulations related to ammonia exposure:

- European Chemicals Agency (ECHA): In the European Union, ECHA establishes regulations for chemicals, including ammonia. The agency sets occupational exposure limits and provides information on the classification and labelling of hazardous chemicals.
- Occupational Safety and Health Administration (OSHA): In the U.S., OSHA sets regulations and occupational exposure limits for ammonia.
- National Institute for Occupational Safety and Health (NIOSH): NIOSH, a U.S. federal agency, provides recommendations and safer exposure limits for various substances, including ammonia.
- U.S. Environmental Protection Agency (EPA)
- American Industrial Hygiene Association (AIHA)
- U.S. Department of Energy (DOE)
- Local and regional regulations: In addition to national and international regulations, many local and regional jurisdictions may also establish their own regulations and exposure limits for ammonia.

It is crucial for organisations and employers to adhere to these regulations to protect the health of workers and minimise the risks associated with ammonia exposure. Additionally, providing proper training and PPE to workers who may be exposed to this hazardous chemical is essential.

The Occupational Exposure Limit (OEL) is an upper limit on the acceptable concentration of a hazardous substance in workplace air for a particular substance. It is an important tool in risk assessment and is typically set by competent authorities. Most OELs are developed to protect workers from the development of any adverse effects. OELs do not coincide for all agencies. The easiest way to check OEL in the EU member states is using GESTIS[6]. It is a freely accessible substance database on chemical compounds maintained by the Institut für Arbeitsschutz der Deutschen Gesetzlichen Unfallversicherung (IFA). In Table 8 different Exposure Levels from different agencies have been compiled.

Table 8: Acute ammonia exposure limits

Country	Agency	Guideline	15 min	30 min	1 hour	4 hour	8 hour
European Union	ECHA	EU-OEL	—	—	—	—	20 ppm
European Union	ECHA	EU-OSTEL	50 ppm	—	—	—	—
Canada	NRC	EEGL	—	—	100 ppm	—	100 ppm (24 hour)
Germany	DFG	MAK	—	—	—	—	20 ppm
Sweden	AV	OEL	50 ppm		—	—	25 ppm
The Netherlands	SDU	MAC	—	—	—	—	20 ppm
United Kingdom	HSE	WEL-LTEL	—	—	—	—	25 ppm
United Kingdom	HSE	WEL-STEL	35 ppm	—	—	—	—
United States	ACGIH	TLV-STEL	35 ppm		—	—	—
United States	ACGIH	TLV-TWA	—	—	—	—	25 ppm
United States	AIHA	ERGP-1	—	—	25 ppm	—	—
United States	AIHA	ERGP-2	—	—	150 ppm	—	—
United States	AIHA	ERGP-3	—	—	750 ppm	—	—
United States	DOE	TEEL 1	—	—	20.9 mg/m^3	—	—
United States	DOE	TEEL 2	—	—	110 mg/m^3	—	—
United States	DOE	TEEL 3	—	—	766 mg/m^3	—	—
United States	EPA	AEGL-1	30 ppm (10 min)	30 ppm	30 ppm	30 ppm	30 ppm

[6] https://limitvalue.ifa.dguv.de/

Country	Agency	Guideline	15 min	30 min	1 hour	4 hour	8 hour
United States	EPA	AEGL-2	220 ppm (10 min)	220 ppm	160 ppm	110 ppm	110 ppm
United States	EPA	AEGL-3	2,700 ppm (10 min)	1,600 ppm	1,100 ppm	550 ppm	390 ppm
United States	NASA	SMAC	—	—	20 ppm	—	14 ppm (24 hour)
United States	NIOSH	IDLH	—	300 ppm	—	—	—
United States	NIOSH	REL-STEL	35 ppm		—	—	—
United States	NIOSH	REL-TWA	—	—	—	—	25 ppm (10 hour)
United States	OSHA	PEL-STEL	35 ppm	—	—	—	
United States	OSHA	PEL-TWA	—	—	—	—	50 ppm (10 hour)
United States	USN	MAC	—	—	400 ppm	—	20 ppm (60 days)

The acronym of the agencies and the exposure levels are included in the list of abbreviations. Some of the most important OEL are included into Table 9.

Table 9: Occupational Exposure Levels Health effects

OEL	Health effects
PEL	**Permissible Exposure Limit** is set to protect workers against health effects of exposure to hazardous substances. PEL is enforceable by OSHA. It can be TWA and STEL.
REL	**Recommended Exposure Limit** is set to protect workers against health effects of exposure to hazardous substances. REL is reserved to NIOSH. REL are TWA and STEL.
TLV	**Threshold Limit Values** is set to protect workers against health effects of exposure to hazardous substances. TLV is based on group consensus. TLV can be TWA and STEL.
TWA	**Total Weight Average** exposure to a contaminant to which workers may be exposed without adverse effect over a period such as in an 8-hour day or 40-hour week.
STEL	**Short-Term Exposure Limit** is the exposure to a chemical substance related normally to 15-minute reference period to prevent adverse health effects.
IDLH	**Immediately Dangerous to Life or Health** is the concentration that possess an immediate threat to life or would cause irreversible or delayed adverse effects or would interfere with an individual's ability to escape from a dangerous atmosphere.

There are many other OELs than just those listed above. The following tables identify OELs from U.S. and European references. In the U.S., different Agencies define different limits. The three most important limits for ammonia exposure based on health risks are AEGL, ERGP and TEEL.

- **Acute Exposure Guideline Levels (AEGL)** are developed by the U.S. EPA to provide emergency response planning and risk management guidance for acute exposures to hazardous chemicals. These levels are used to help protect public health in case of accidental chemical releases.

Table 10: AEGL values for ammonia (ppm)

Tier	Health effects
AEGL 1	This is the airborne concentration, expressed as parts per million (ppm) or milligrams per cubic meter (mg/m3), above which it is predicted that the general population, including susceptible individuals, could experience notable discomfort, irritation, or certain asymptomatic no sensory effects. However, the effects are not disabling and are transient and reversible upon cessation of exposure.
AEGL 2	This is the airborne concentration (expressed as ppm or mg/m3) 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	This is the airborne concentration (expressed as ppm or mg/m3) which it is predicted that the general population, including susceptible individuals, could experience life-threatening health effects or death.

- **Emergency Response Planning Guidelines (ERPGs)** are airborne concentrations of chemicals that have been evaluated for three levels of emergency response. These are a nuisance level, level that would affect egress from an exposure or a level that is near, but below a life-threatening concentration. The ERPG is a volunteer committee of the AIHA that is comprised of industrial hygienists and toxicologists.

Table 11: ERPG values for ammonia

Tier	Health effects
ERPG 1	The maximum airborne concentration below which it is estimated that nearly all individuals could be exposed for up to one hour without experiencing other than mild, transient adverse health effects or without perceiving a clearly defined objectionable odour.
ERPG 2	The maximum airborne concentration below which it is estimated that nearly all individuals could be exposed for up to one hour without experiencing or developing irreversible or other serious health effects or symptoms which could impair an individual’s ability to take protective action.
ERPG 3	The maximum airborne concentration below which it is estimated that nearly all individuals could be exposed for up to one hour without experiencing or developing life-threatening health effects.

- The **Temporary Emergency Exposure Limits** for chemicals **(TEEL)** developed by the U.S. DOE.

Table 12: TEEL values for ammonia

Tier	Health effects
TEEL 1	The airborne concentration above which it is predicted that the general population, including susceptible individuals, when exposed for more than one hour, could experience notable discomfort, irritation, or certain asymptomatic, no sensory effects. However, these effects are not disabling and are transient and reversible upon cessation of exposure.

Tier	Health effects
TEEL 2	The airborne concentration above which it is predicted that the general population, including susceptible individuals, when exposed for more than one hour, could experience irreversible or other serious, long-lasting, adverse health effects or an impaired ability to escape.
TEEL 3	The airborne concentration above which it is predicted that the general population, including susceptible individuals, when exposed for more than one hour, could experience life-threatening adverse health effects or death.

2.2.3 Flammability

Ammonia is a flammable gas in the presence of oxygen and a suitable ignition source. It may ignite under the following conditions:

- **Presence of Oxygen (O_2)**: Ammonia requires the presence of oxygen for combustion to occur. In the absence of oxygen, such as in air-deprived environments, it cannot ignite.
- **Source of Ignition**: A source of ignition, such as a spark, an open flame, intense heat, or an electrical discharge, is needed to initiate the combustion of ammonia. Without a source of ignition, ammonia will not ignite spontaneously.
- **Adequate Concentration**: The concentration of ammonia in the air must fall within its flammability range, which generally ranges from 15-28% ammonia in air. Concentrations below or above these values are non-flammable.
- **Adequate Temperature**: Temperature is also an important factor. Ammonia is more likely to ignite at higher temperatures, so an increase in ambient temperature can increase the risk of flammability.

It is essential to consider these factors when working with ammonia, especially in enclosed spaces. Proper safety measures, such as the appropriate storage and handling, as well as the prevention of ignition sources in areas where ammonia is present, should be taken to minimise the risk of fire or explosion.

In literature, various values are reported concerning the Lower and Upper Explosive Limits (LEL and UEL as summarised in Table 13 (Bouet, 2005).

Table 13: Different values of Ammonia Lower and Upper Explosive Limit

Substance	LEL (%)	UEL (%)
TOX 003-06-1998 (French Ministry for Territorial Development)	16	25
NFPA (1994) and Medart (1979)	15	28
Weiss (1985)	15.5	27

The self-ignition temperature of a gas or vapour mixture is the minimum temperature at which the mixture undergoes a rapid chemical reaction, resulting in the appearance and propagation of spontaneous flames. In the literature, ammonia's self-ignition temperature is recorded as 650°C.

The ignition of a flammable mixture necessitates the local introduction of a specific amount of heat. Determining the exact energy required to ignite a mixture poses challenges. Buckley and Husa (1962) determined the minimum ignition energy of ammonia using a capacitive system, yielding a value of 680 millijoules (mJ). On the other hand, Kramer (1985) obtained a lower value of 14 mJ for an ammonia-air mixture, highlighting the difficulty in quantifying ignition energy across different experimental systems (Bouet, 2005). Despite Kramer's lower value, an air-ammonia mixture has a considerably higher minimum ignition energy (1-2 orders of magnitude), when compared to most air-hydrocarbon mixtures.

2.3 Toxic Areas and PPE

The nature of ammonia (its special characteristics are described above) requires special consideration to define the hazardous spaces onboard a ship carrying ammonia as fuel in storage tanks. The use of ammonia as cargo is regulated in the IGC Code. Combined LPG/NH_3 carriers have been operating for several years, so there is already experience in handling ammonia as cargo, and potential presence of ammonia on deck through piping, cargo holds and cargo compressor rooms. The main new hazard from using ammonia as fuel is mainly the introduction of ammonia into the engine room, fuel preparation rooms and bunkering operations. Different kinds of vessels (other than gas carriers) also may have different storage tank configurations and arrangements.

2.3.1 Toxic Areas Onboard

The international regulations (IGC and IGF Codes) refer to the term “Hazardous Area” to identify an area in which an explosive gas atmosphere is or may be expected to be present, in quantities such as to require special precautions for the construction, installation and use of equipment. Any other area is characterised as a “Non-hazardous Area”, or simply stated as gas safe area.

The term “hazardous area” was first introduced in the IGC, then adopted in IGF Code as well. It classifies three Hazardous Area Zones (0, 1, 2) with “0“ defining the most hazardous. The hazardous area considerations are made based on mitigation of fire and explosion risks. According to these, the appropriate electrical equipment (EX rated, intrinsically safe etc.) is selected and airlocks, ventilation and vent outlets are defined.

However, in addition to the hazardous area considerations as derives from a flammability point of view, toxicity is another major hazard from potential release/leak sources. “Toxic areas/zones” definition is introduced in most classification societies rules to reduce the risks from potential releases. Appendix B lists the requirements amongst classification rules for the toxic areas’ determination for reference purposes.

In ammonia fuelled vessels, spaces where ammonia is present, or release could occur would include:

- Ammonia fuel storage tanks and hold spaces.
- Fuel preparation rooms or tank connection spaces (TCS) (including fuel supply system, fuel valve train).
- Engine room due to ammonia fuel consumers failure (main engines, generator engines, gas boilers) or through auxiliary system medium contamination (cooling water, lubricating oil, cooling oil, starting air).
- Pressure Relief Valves (PRVs) from storage tanks or piping.
- Master Gas Valves (MGVs) for ammonia fuel supply system.
- Bunkering stations (enclosed or semi-enclosed).
- Ventilation exits from areas where ammonia release can occur.

The following areas are to be considered as “toxic” and are required to be located at minimum distances from the nearest air intake, outlet or opening to accommodation spaces, service spaces and control stations, or other non-toxic and non-hazardous areas[7]:

i. *B or 25 m, whichever is less, from the vent mast,*

ii. *10 m from,*
   - *Entrances to the spaces containing potential source of ammonia release,*
   - *Ventilation outlets from secondary enclosures around ammonia piping and from the spaces containing potential source of ammonia release,*
   - *Bunker manifold valves and all other flange connections of ammonia fuel piping as well as from the spillage coamings surrounding it,*
   - *Engine exhaust exits, crankcase and sump tank vent outlets, as applicable,*

iii. *5 m from the vent outlets of ammonia drain tank(s) and auxiliary circuits of engines.*

[7] For reference as per ABS “*Requirements for Ammonia Fuelled Vessels*” (ABS, 2023a)

In addition, IMO Sub-Committee on Carriage of Cargoes and Containers has made progress with the Draft Interim Guidelines for Ships Using Ammonia as Fuel making extensive reference to toxic areas. These areas include but are not limited to the following:

1. *the interiors of fuel tanks, any pipework for pressure-relief or other venting systems for fuel tanks, pipes and equipment containing fuel;*
2. *tank connection spaces, inter-barrier spaces and fuel storage hold spaces for tank containment systems requiring secondary barriers;*
3. *fuel preparation rooms;*
4. *annular space of secondary enclosures around fuel pipes;*
5. *enclosed and semi-enclosed bunkering stations and other enclosed and semi-enclosed spaces in which potential sources of release such as single-walled piping containing fuel are located;*
6. *areas on open deck including bunkering stations within 10 m of any flanges, valves, and other potential leakage sources in ammonia fuel systems;*
7. *areas on open deck within B or 25 m, whichever is less, from outlets from the pressure relief valves installed on a liquefied fuel gas tank and all other fuel gas vent outlets;*
8. *areas on open deck within B or 25 m, whichever is less, from outlets from inter-barrier spaces for tanks of IMO type A;*
9. *areas on open deck within 10 m from outlets from inter-barrier spaces for tanks of IMO type B;*
10. *areas on open deck within 10 m from outlets from secondary enclosures around ammonia piping, ventilation outlets from tank connection spaces and fuel preparation rooms and other spaces containing ammonia leakage sources; and*
11. *areas on open deck within 5 m from inlets to secondary enclosures around ammonia piping, ventilation inlets to tank connection spaces and fuel preparation rooms and other spaces containing ammonia leakage sources; and*
12. *areas on open deck within 5 m from entrance openings to spaces containing ammonia leakage sources.*

The above areas are the minimum requirements; the exact determination of toxic areas is subject to a detailed gas dispersion analysis supported by a risk assessment. The purpose of the gas dispersion analysis should be to demonstrate that ammonia gas does not reach air intakes, outlets and other openings into the accommodation, service and machinery spaces, control stations, the navigation bridge and other non-toxic areas in the ship. The acceptable limits need to be defined and agreed at the IMO. Accordingly, lifesaving appliances (LSA), muster stations and escape routes are not to be located in toxic areas. Above should be also verified by a gas dispersion analysis. Operational and emergency response procedures are to consider and to provide guidance for the safe operation and escape of crew from such areas.

Machinery Space Arrangements

For the case of ammonia fuelled vessels, the gas safe machinery seems to be the most appropriate design concept so that a single failure will not lead to release of ammonia gas into machinery space, by using double wall piping.

Most classification societies make reference to the gas-safe concept as well in their rules. In addition, CCC 9/INF.16 submitted by IACS member states that ESD protected concept shall not be permitted to prevent any possible ammonia leakage to engine room for the following reasons:

- Consequence of ammonia leakage (toxicity) in engine room is different than natural gas (flammability).
- Toxicity concentration level is much lower than flammability level.
- Safety measure of ammonia leakage would differ from natural gas leakage.

Therefore, during CCC 9 it was suggested that gas-safe machinery space will be considered the default option in IMO interim guidelines as first step and further investigation should be conducted from Administrations to look into ESD approval through alternative design process. In addition, machinery spaces containing ammonia consumers are to be arranged for remote monitoring.

2.3.2 Safe Haven

The Draft Interim Guidelines for Ships Using Ammonia as Fuel introduced the concept of the "safe haven" providing refuge in case of a major release of ammonia on the vessel. According to the requirement, the "safe haven" should be arranged in an enclosed space, with capacity to accommodate all persons onboard. Even though the requirements in the draft interim guidelines aim to limit the consequences of ammonia discharges, having a well-protected space where the crew can take refuge in a substantial ammonia release scenario will increase the overall safety.

Prescriptive requirements for the "safe haven" covering the location and arrangement of the space in terms of emergency escapes, ventilation inlet and outlets and openings are also included in the draft guidelines.

2.3.3 Bunkering Safety Zones

In addition to the toxic areas that should be defined on ships, bunkering activity is one of the most critical tasks when referring to ammonia fuelled vessels. Different types of bunkering are expected and can be categorised into the four categories below (Duong, et al., 2023). The chosen method depends on the amount of ammonia required, operational circumstances, and time constraints.

- Ship-to-ship (STS)
- Terminal-to-ship (TTS)
- Truck-to-ship (T-TS)
- Ammonia portable tank (APT)

Creating a safety zone and determining the distance between the bunkering vessel and the receiving vessel or terminal are vital for enhancing the safety of ammonia bunkering. Since ammonia bunkering is new, there are currently no clear rules for safety zones. Some of the factors to be taken into consideration include:

- To standardise the effects of an unintended ammonia release, it is important to devise strategies that can decrease both the rate and duration of leakage when bunkering.
- It is important to carefully plan cargo loading during bunkering. The ship's design and environmental factors can impact the spread of gas.
- When determining the safety zone for ammonia bunkering, it is important to consider the direction and speed of the wind.
- Local regulations can complicate the creation of a safety zone for ammonia bunkering. This is because zoning laws, environmental regulations, and safety standards can all have an impact. However, the inconsistency of these regulations across different regions can present a challenge when trying to establish a standardised safety zone for ammonia bunkering.

Again, gas dispersion simulations would be essential to determine the bunkering safety zones. Relevant studies have already been conducted while others are underway to address different bunkering release scenarios (NTU, 2022), especially in the area of Singapore where the demand forecast for ammonia bunkering is expected to reach 20% of the global demand for ammonia by 2045 (GCMD , 2023).

2.3.4 Gas Dispersion Analysis Tools

Gas dispersion modelling, as part of a consequence analysis, has been conducted for decades, owing to the long-standing need for predicting air quality. The use of Computational Fluid Dynamics (CFD) has also become feasible. Several tools are reviewed here[8]:

- **PHAST (Process Hazard Analysis Tool)**: developed by DNV; according to its website, it is "a globally adopted solution for modelling discharge, dispersion, fires, explosions and toxic effects of a wide range of loss of containment scenarios"; it was not developed specially for ammonia dispersion but can be applied to ammonia. PHAST adopts a Unified Dispersion Model (UDM) framework in integrating different prediction modules. PHAST determines the plume dynamics by solving a set of ordinary differential equations in the downwind direction, considering the momentum, mass, heat sources along the central trajectory as well as the environmental forcing

[8] Review is conducted for information purposes only.

such as the winds. Along the central trajectory, the transverse concentration distribution depends on a similarity profile so that the plume properties in the transverse dimensions are primarily assumed rather than solved. The UDM framework is so-called the Lagrangian type of modelling, in that the model focuses on a specific fluid element and its momentum, mass, and heat balances with the ambient. The model equations are only solved along the central trajectory of the plume instead of in a large space. Within this framework, both steady and unsteady releases can be solved. PHAST also has the strength of providing detailed formulae for a wide variety of source terms. The weakness is apparent: the solution is only accurate in one dimension, which is the downwind direction. The solution is only approximate or nominal in the transverse directions.

- **ALOHA (Areal Locations Of Hazardous Atmospheres)**: developed by the U.S. National Oceanic and Atmospheric Administration (NOAA) and is maintained by the U.S. Environmental Protection Agency. ALOHA "is the hazard modelling program for the CAMEO® software suite (Computer-Aided Management of Emergency Operations), which is used widely to plan for and respond to chemical emergencies". ALOHA relies primarily on empirical or theoretical formulas in calculating plume trajectory and concentration profiles. In other words, it is more like a "calculator" than a simulator. For example, it uses the Gaussian model for the chemical dispersion in a neutrally buoyant ambient. It uses the ALOHA-DEGADIS model for dispersion of a heavy-gas plume (buoyant), which is applicable to ammonia released at a low temperature. In either case, some level of unsteadiness due to a time-varying source can be handled by compositing up to five stages, each of which is steady-state. The strengths of this software, on the other hand, include a wealth of formulas or empirical relations that can be used to set up ambient conditions, a broad coverage of different kinds of chemicals, and the fast calculation speed.
- **FLACS-CFD**: developed by GexCon AS; the "software simulates the dispersion of hazardous materials, fire and explosion with precise accuracy for in-depth safety studies". FLACS-CFD is a specialised CFD package based on the three-dimensional Reynolds-Averaged Navier-Stokes framework with the k-ε turbulence model. This framework is different from that of PHAST, in that it solves a set of partial differential equations in the three-dimensional space. The solution at all grid points will be solved for, whether the plume will pass by or not. This type of model is so-called Eulerian, focusing on all field points rather than only the points along the plume trajectory. In fact, general-purpose CFD codes, such as Simcenter Star-CCM+ (Siemens), OpenFOAM (OpenCFD), and Fluent (Ansys), are all Eulerian type of models. FLACS-CFD is more user-friendly than general-purpose CFD software packages for pre-defined analyses but may not be able to handle complex obstructions in way of the plume. Compared to PHAST, FLACS-CFD has higher fidelity because 1) it does not rely on assumed cross-sectional profiles of the plume and 2) it does not require as many empirical source terms as PHAST.

Table 14 shows a simple comparison of these tools based on the information from their websites and user's manuals.

Table 14: Comparison of different commercial software packages that can be used for ammonia gas dispersion modelling

	PHAST	ALOHA	FLACS-CFD
Developer	DNV	NOAA	GexCon AS
Software cost	Paid software	Free software	Paid software
Model type	Trajectory-tracing	Formula-based	Domain-based
2D or 3D modelling	2D	2D	3D
Can handle both liquid and gaseous phases?	Yes	Yes	Yes
Can consider rainout?	Yes	No	Yes
Can consider liquid pool as a source?	Yes	Yes	Yes
Can handle interaction liquid ammonia and water (spill)?	Yes	No	No
Can consider humidity in the ambient air?	Yes	Yes	Yes
Can handle complex obstacles in way of plume?	No	No	Simple
Can add atmospheric boundary layer for wind profile?	Yes	Yes	Yes
Can handle large-scale dispersion?	Yes	Yes	Yes

The most flexible tool for modelling ammonia dispersion is the generic CFD software. The model could have different levels of fidelity. The CFD model with the highest fidelity will include all key physical factors for ammonia such as fluid (both gas and liquid droplets) dynamics, heat transfer, evaporation, condensation, and complex interaction with water. Most general CFD software packages, such as OpenFOAM, Simcenter Star-CCM+, or Fluent, have solvers developed to address these factors. However, including all those solvers in the same CFD model would be very challenging. For example, ammonia phase change and large-scale plume tracing will require multiscale modelling both in time and in space. To date, most CFD simulation efforts for ammonia dispersion are still focused on gaseous ammonia released into the ambient air (Yadav & Jeong, 2022). This simplification is believed to be more conservative than considering a two-phase release which would usually incur some losses to the spill (such as loss of liquid ammonia mass to the soil) and thus have a reduced impact on the environment. Some temporary solutions can be adopted. For example, in order to take the liquid ammonia pool from rainout into account, an area source for the pool can be applied to the same CFD model which has a gaseous release as its primary source. Nevertheless, the long-term goal of general CFD is still to address all key physical factors in the same model. In what follows, we only focus on the simplification where all released ammonia becomes gaseous upon exiting the release point; in other words, even if there is liquid ammonia, flash boiling of the liquid part will occur immediately.

The CFD simulation of a gaseous release has been quite mature. While there have not been many applications to ammonia particularly, the methodology has been well applied to other gases. A typical CFD model will solve the conservation equations of mass, momentum, gas species, energy, and turbulence quantities in both near and far fields. The model is typically based on the 3D Navier-Stokes equations supplemented by proper multi-component gas representations, a proper turbulence model (such as the k-ε, k-ω, the Detached Eddy Simulation family, or the Large Eddy Simulation), and the equation of state. It is reasonable to use the ideal gas law for the gaseous ammonia for simplicity.

The dimensions of the computational domain depend on the expected extent of the gas plume. It is common for a maritime safety assessment to simulate the entire life of the plume from the release through the moment when the concentration levels such as 25 or 30 ppm have completely disappeared. Some trial and error could be needed to determine the size of the computational domain. For cases with complex structures or obstructions in way of the plume, the domain would need to be sufficiently larger in order for the turbulent flow to be fully developed around the structures. It is well-known that turbulence would increase the total diffusivity of the dispersed materials and therefore would have a strong impact on the rate of dilution. Figure 14 shows an example of an ammonia dispersion simulation around a segment of a containership close to the accommodations. The domain is long and narrow with the expectation that the plume will be mostly confined in this long channel. Figure 15 shows another ammonia gas dispersion simulation that is intended to cover the full lengths of two ships, an ammonia bunkering vessel and a bunkering receiving vessel. With no strong symmetry in the geometrical setup, the computational domain has to cover a wider range in all directions. Such a large domain would also be convenient when the setup is modified for different wind directions.

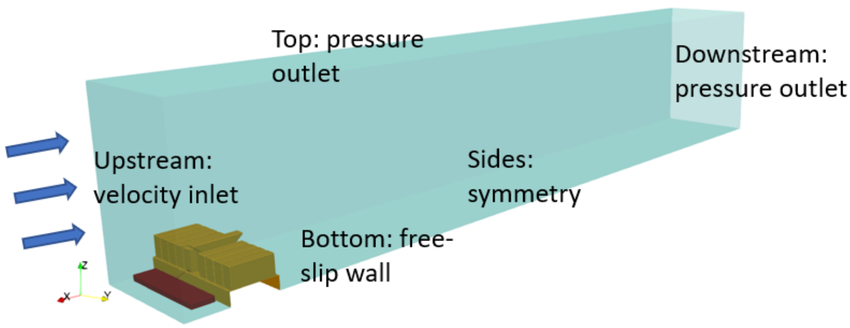

Figure 14: Computational domain for an ammonia leakage analysis around a segment of a containership; the boundary condition types are indicated for each boundary

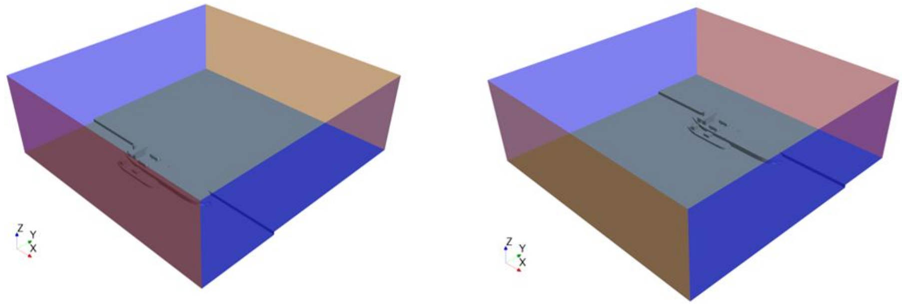

Figure 15: Computational domain for an ammonia leak analysis around an ammonia bunkering vessel (the smaller one) and a containership (the larger one): left: with wind direction from the ammonia bunkering vessel to the containership; the inlet boundary is the face with the smallest Y value; right: with wind direction from the containership to the ammonia bunkering vessel; the inlet boundary is the face with the largest Y value; the domain size is 250 x 700 x 700 m in the X, Y, and Z directions, respectively

Boundary conditions should be chosen to properly represent the ambient conditions. In open-air dispersion scenarios such as ship-to-ship ammonia bunkering, one could choose to apply an inlet wind profile in accordance with an atmospheric boundary layer. The top and the far-downstream boundaries could be set to pressure outlets.

Computational mesh should be designed to reflect the key features of the flow field. The computational mesh should be refined where the ambient flow or the plume patterns is expected to change rapidly, for example, around blunt obstructions where there are vortex shedding or separation. Figure 16 shows a typical mesh configuration for a ship-to-ship bunkering scenario between an ammonia bunkering vessel and a tanker, i.e., the receiving vessel. The computational mesh has hierarchically refined mesh zones closer and closer to the release point and gradually coarser meshes away from the two vessels. Figure 17 shows another example for ammonia dispersion resulting from an accidental leakage from the fuel line in a vessel engine room. There are many structures and equipment included in this three-deck high engine room. Computational mesh needs to be carefully designed along the plume trajectory and around the structures.

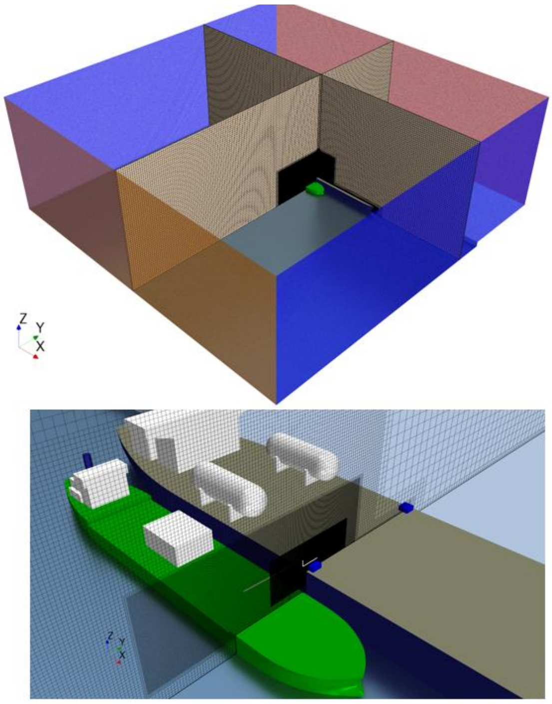

Figure 16: Example of computational mesh setup for an ammonia leakage simulation during ship-to-ship bunkering; the hypothetical gas release point is at the bunkering station of the tanker (the grey-blue vessel). The green one is the ammonia bunkering vessel. Upper: a general view of the mesh setup; lower: close-up view on the area around the ammonia release point.

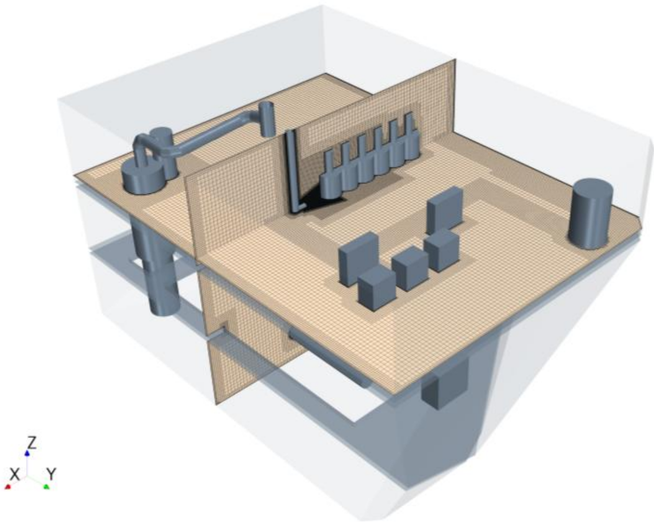

Figure 17: Example of computational mesh setup for an ammonia leakage simulation in a vessel engine room

A gas release should always start with a well-established steady-state ambient air flow, except for some oscillatory unsteadiness resulting from vortex shedding from the bluff obstructions. It takes some trial and error to determine as to how much time lead time will be needed to establish such a steady state background flow. Some computation time can be saved when the steady state background flow can be reused for similar release scenarios.

General CFD packages have the superior capability to reveal 3D plume patterns for user-specified concentration levels. The graphical rendering of general CFD software is much more sophisticated than special tools as reviewed in Table 14. Figure 18 shows a sample flow pattern in a cut plane across an ammonia bunkering vessel and a receiving tanker using Star-CCM+. The vortical structures shed from the sharp corners of the structures (e.g., the vessel deck edges) can be readily observed.

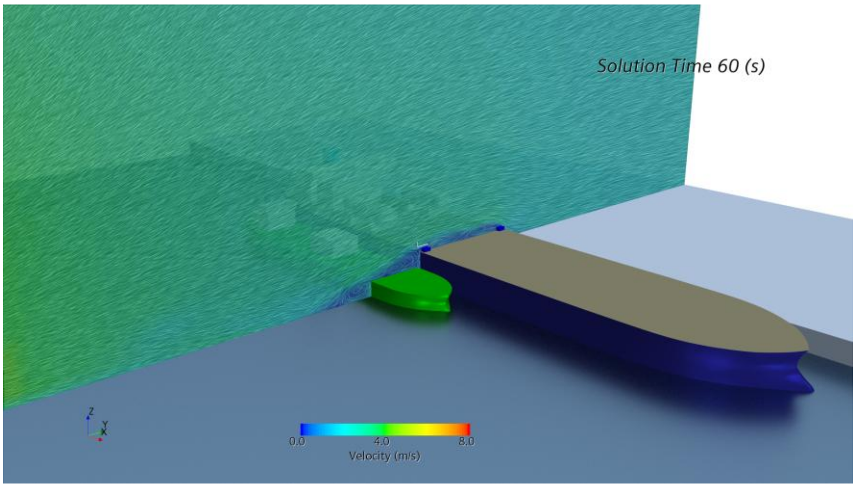

Figure 18: Velocity field in the plane cutting through the ammonia release point. Colours represent the velocity magnitude; the fine traces in the plane show the velocity vector directions. Wind direction is from the land to the sea (from the tanker towards the ammonia bunkering vessel)

The ammonia plume pattern can be shown for user-specified concentration values. The impact of different concentration levels can be inspected from different perspectives within the CFD software. This will be a necessary step in defining the safety zones for a risk factor.

Figure 19: Top view of the 3D concentration contours of ammonia released from the bunkering vessel (represented by the maroon block on the left side) toward the midbody of a containership; wind direction is from the ammonia bunkering vessel to the containership; the contour colours: grey for 30 ppm, green for 160 ppm, and blue for 1,100 ppm

Figure 19 shows the 3D concentration contours at 30, 160 and 1,100 ppm at a given time using OpenFOAM for the same case as shown in Figure 14. Figure 20 shows the 3D concentration contour surfaces for an ammonia plume in the engine room using Star-CCM+. The release is due to an accidental rupture of a fuel line near the main engine. The ammonia plume is strongly affected by the main direction of ventilation in the engine room as well as its initial momentum.

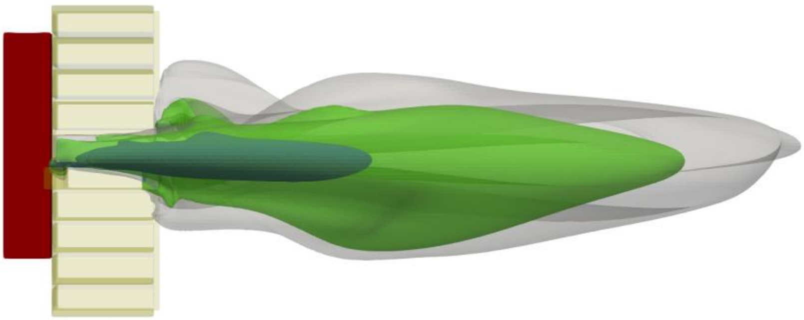

Figure 19: Top view of the 3D concentration contours of ammonia released from the bunkering vessel (represented by the maroon block on the left side) toward the midbody of a containership; wind direction is from the ammonia bunkering vessel to the containership; the contour colours: grey for 30 ppm, green for 160 ppm, and blue for 1,100 ppm

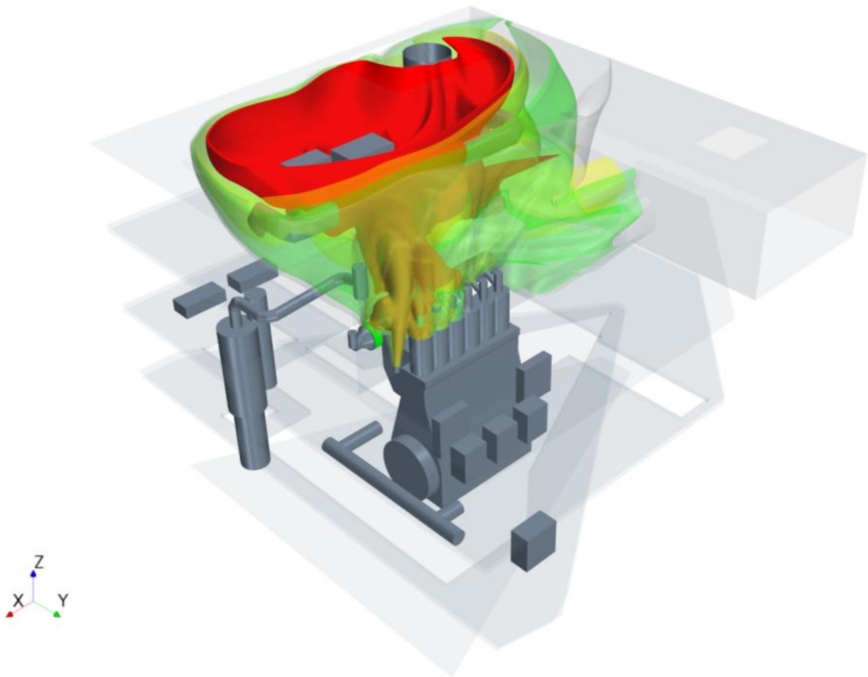

Figure 20: 3D concentration contours of released ammonia due to an accidental leakage from a fuel line near the main engine; the main ventilation direction is from lower to higher decks; the contour colours: grey for 30 ppm, green for 160 ppm, yellow for 1,000 ppm, and red for 15,000 ppm

Clearly, the three commercial tools, i.e., PHAST, ALOHA, FLACS-CFD, and the two general CFD software, i.e., OpenFOAM, Star-CCM+, as reviewed here, all have different strengths and weaknesses. For example, the specialised tools can address more physical aspects for ammonia gas dispersion than general CFD software currently can because they can easily adopt empirical formulas or assumptions. On the other hand, the general CFD packages are more flexible, more suitable for addressing complex gas-environment interactions than the specialised tools. They also provide more sophisticated rendering for 3D views of the flow field.

The results of risk assessments that will be undertaken during the following tasks may require conducting gas dispersion analysis for certain scenarios (bunkering, vent mast, loss of containment etc.) to determine:

- Toxic areas onboard the ship.
- Gas detection requirements and sensors' locations.
- Bunkering safety zones.
- PPE and LSA requirements.

2.3.5 Personal Protective Equipment (PPE)

The Draft Interim Guidelines for Ships Using Ammonia as Fuel as presented in CCC 9, include a dedicated section to address on-board personnel protection in both normal and emergency situations. Similar requirements exist in IGC Code Chapter 14.4 applicable to gas carriers intending to carry specific individual products such as anhydrous ammonia. The requirements in the draft interim guidelines are listed below:

Protective equipment

- *Suitable protective equipment, including eye protection, to a recognized national or international standard should be provided for protection of crew members engaged in normal operations related to the ammonia fuel system.*
- *Personal protective and safety equipment required in this section should be kept in suitable, clearly marked lockers located in readily accessible places.*

Emergency equipment

- *Suitably marked decontamination showers and eyewashes should be available in convenient locations:*
  - *close to bunkering stations;*
  - *close to exit from tank connection spaces;*
  - *close to exit from fuel preparation rooms; and*
  - *in machinery spaces for ammonia fuelled consumers.*
- *The showers and eyewashes should be operable in all ambient conditions. A heating system with temperature control is required if pipe routeing of the water supply exposes the piping to freezing conditions. Water supply capacity should be sufficient for simultaneous use of at least two units. Thermal insulation is not considered as an alternative to a system with temperature control.*
- *A stretcher that is suitable for hoisting an injured person from spaces such as tank hold spaces should be kept in a readily accessible location.*
- *The ship should have onboard medical first aid equipment, including oxygen resuscitation equipment, based on the requirements of the Medical First Aid Guide (MFAG) for ammonia.*
- *Suitable respiratory and eye protection for emergency escape purposes should be provided for every person on board, subject to the following:*
  1. *filter-type respiratory protection is unacceptable; and*
  2. *self-contained breathing apparatus should have at least 15 minutes of service time; and*
  3. *emergency escape respiratory protection should not be used for fire-fighting or cargo-handling purposes and should be marked to that effect.*

In addition to the protective and emergency equipment, the guideline also includes specific requirements for the safety equipment available on the vessels. These are listed below:

Safety equipment

- *Sufficient, but not less than three complete sets of safety equipment should be provided in addition to fire-fighter's outfits required by SOLAS regulation II-2/10.10. Each set should provide adequate personal protection to permit entry and work in a gas-filled space. This equipment should consider the nature of ammonia.*
- *Each complete set of safety equipment should consist of:*
  1. *one self-contained positive pressure air-breathing apparatus incorporating full face mask not using stored oxygen and having a capacity of at least 1,200 litres of free air. Each set should be compatible with that required by SOLAS regulation II-2/10.10;*
  2. *gastight protective clothing, boots, and gloves to a recognized standard;*
  3. *steel-cored rescue line with belt; and*
  4. *explosion-proof lamp.*
- *An adequate supply of compressed air should be provided and should consist of:*
  1. *at least one fully charged spare air bottle for each breathing apparatus required above;*
  2. *an air compressor of adequate capacity capable of continuous operation, suitable for the supply of high-pressure air of breathable quality; and*
  3. *a charging manifold capable of dealing with sufficient spare breathing apparatus air bottles for the breathing apparatus required above.*

ABS, in its "*Requirements for Ammonia Fuelled Vessels*" (ABS, 2023a), has already developed PPE requirements that should consist of large aprons, special gloves with long sleeves, suitable footwear, coveralls made of chemical-resistant material and face shields manufactured to a recognised national or international standard. These are to be provided for protection of crew members engaged in normal bunkering operations or fuel system maintenance and operation. The protective clothing and equipment should cover the crew's entire body without any exposed skin.

Apart from the fixed gas detection system at certain locations around the ship, personnel should be provided with personal and portable gas detectors, designed and tested in accordance with recognised standards for toxicity and suitable for ammonia service. All of them should be also EX proof rated. Where the ammonia gas detector range of operation cannot cover the ppm levels required for toxicity detection and the percentage (%) level required for fire and explosion detection, separate gas detectors covering each range of operation are required at each detector location. Personal gas detector should be used by personnel at all times while regular calibration is required as per manufacturer's recommendations. Portable gas detectors are used to check atmosphere before entering an enclosed space. Indicative gas detection equipment is shown in below figures.

PPE Standards

Regulation (EU) 2016/425 sets the requirements for the design and manufacture of PPE. As per European legislation, all types of respiratory protective equipment must be tested and certified. European standards (EN) have been developed for almost every type of protective and respiratory equipment to set performance requirements and test methods. Some common EN standards applicable to PPE intended for ammonia use are listed in Table 15.

Table 15: PPE standards

Standard	Description
EN 136 – Full face masks	The standard specifies the requirements for full face masks. These masks can be used in negative pressure systems, powered or supplied air systems. According to the standard there are three classes of full face masks: ■ Class 1 – Light duty and low maintenance ■ Class 2 – General duty, with maintainable parts ■ Class 3 – Heavy duty, fire fighters
EN 14387 – Mask filters	Filters for the masks are certified against EN 14387 standard and classified based on product use: ■ Type A: Organic gases and vapours with boiling point higher that 65°C, as specified by manufacturer. Brown colour code. ■ Type B: Inorganic gases and vapours as specified by manufacturer, excluding CO. Grey colour code. ■ Type E: Sulphur dioxide and other acidic gases and vapours, as specified by manufacturer. Yellow colour code. ■ **Type K: Ammonia and organic ammonia derivatives, as specified by manufacturer. Green colour code.** Filters are also categorised according to their capacity to: ■ Class 1: low capacity, up to 1000ppm ■ Class 2: medium capacity, up to 5000ppm ■ Class 3: high capacity, up to 10,000ppm
EN137 – Self-contained breathing apparatus (SCBA)	Respiratory protective devices – Self-contained open-circuit compressed air breathing apparatus with full face mask – Requirements, testing, marking
EN 943	Protective clothing against dangerous solid, liquid and gaseous chemicals, including liquid and solid aerosols – Part 2: Performance requirements for Type 1 (gas-tight) chemical protective suits for emergency teams (ET)
EN 374 – Gloves	Modified standard for chemical protective gloves
EN 166 – Eye protection	Personal eye-protection – Specifications
EN 13832 – Footwear	Footwear protecting against chemicals

Chemical protection suits certification is very important for use in a hazardous substances environment. Their mechanical and chemical resistance should be verified against the applicable standards shown in Table 16.

- Mechanical resistance: anti-abrasive, crack proof and puncture proof
- Chemical resistance: resistant against hazardous materials penetration.

Table 16: Chemical protection suits standards

Standard	Description
EN 943-1: Type 1a, 1b, 1c and 2	Protective clothing against liquid and gaseous chemicals, including liquid aerosols and solid particles – Part 1: Performance requirements for ventilated and non-ventilated 'gas-tight' (type 1) and 'non-gas-tight' (type 2) chemical protection suits.
EN 943-2: Type 1a ET and type 1b ET (for emergency teams)	Protective clothing against liquid and gaseous chemicals, including liquid aerosols and solid particles – Part 2: performance requirements for gas-tight (type 1) chemical protective suits for emergency teams (ET)
EN 14605: Type 3 and 4	Protective clothing against liquid chemicals – performance requirements for clothing with liquid-tight (type 3) or spray-tight (type 4) connections, including items providing protection to parts of the body only (types PB [3] and PB [4])
EN ISO 13 982-1:2005	Protective clothing for use against solid particulates – Part 1: performance requirements for chemical protective clothing providing protection to the full body against airborne solid particulates (type 5 clothing)
EN 13 034:2005: Type 6	Protective clothing against liquid chemicals – performance requirements for chemical protective clothing offering limited protective performance against liquid chemicals (type 6 and type PB [6] equipment)
EN ISO 6529:2003	Protective clothing – protection against chemicals – determination of resistance of protective clothing materials to permeation by liquids and gases.
EN 1149-1	Protective clothing – electrostatic properties
ASTM F739: 2012	American society testing & materials test method for the permeation of liquids and gases through protective clothing materials under conditions of continuous contact.
EN ISO 16602:2007	Protective clothing for protection against chemicals – classification, labelling and performance requirements.

PPE levels

SGMF publication distinguishes and suggests three roles/levels of PPE depending on the expected exposure time to ammonia vapour and liquid. As stated in their publication "*Ammonia as a marine fuel*" (SGMF, 2023) these are:

1. ***Emergency responders*** *who need to access contaminated areas to make the system safe, for example by closing valves which requires a long time, will need a* ***gas-tight suit****. This should cover the whole body, be impermeable to ammonia and provide some protection in cold environments. Self-contained breathing apparatus (SCBA) is also likely to be required.*

2. *For* ***operators*** *dealing with ammonia, for example connecting the bunkering system, a* ***lighter chemical suit*** *should be sufficient to guard against ammonia leaks and splashes. A full-face mask with ammonia removal cartridge is likely to be sufficient for an operator to escape quickly, within seconds, to a safe area.*

3. *Other staff may need to carry cartridge type gas masks to allow them to escape to a place of safety/gas protection room should an ammonia leak occur.*

Similar approach suggesting three levels is followed in NTU's (Nanyang Technological University, Singapore) latest study about bunkering, safety and release simulations (NTU, 2022). Publication states:

- ***Level A** – Fully covered and sealed, pressurised chemical suit capable of temperatures down to -40°C, and complete with large flexible front window, integral booties and gloves. Under gloves and booties shall be donned along with Self-Contained Breathing Apparatus (SCBA), followed by the level A suit donned over the outside. Usually, it takes 15 to 20 minutes with help to don the level A ensemble. A dense gas ammonia cloud can be as cold as -65°C which could cause the standard level A suit to crack if the wearer was caught in a very dense cloud or was sprayed with liquid. Low temperature level A suits are also available, suitable for temperatures down to -70°C. However, they are very expensive.*
- ***Level B** – Chemical splash suit with a hood that seals around the SCBA face mask, with boots and gloves taped or an O-ring sealed to the suit. The SCBA is donned over the top of the level B suit. The level B ensemble can be donned without help in 5 to 10 minutes.*
- ***Level C** – Fully equipped Hi-Vis vest placed over long trousers and long-sleeved workwear with industrial footwear. The level C ensemble is also known as the ASTI vest and includes the following items carried in the vest:*
  - *Lapel-mounted personal ammonia detector*
  - *Full face compact Air Purifying Respirator complete with K2 filter*
  - *Nomex hood*
  - *LED right angle vest mounted flashlight*
  - *Safety goggles with anti-fog spray for Air Purification Respirator (APR)*
  - *Elbow-length chemical safety gloves*
  - *Chemical break open eyewash*

A recent ammonia emergency workshop was conducted in September 2023 in Le Havre, France where ammonia Emergency Response Practice specialists from Yara Clean Ammonia (YCA) met with key maritime stakeholders to promote knowledge transfer from Yara's experience to the maritime sector (YCA, 2023). Among discussions, PPE characteristics were suggested to follow four-level classification as indicated in Table 17. All levels, from A to D, require a specific training for proper use.

The multiple PPE approaches provided in presented regulations, publications and studies make it obvious that not a single PPE standard can be used in all locations and for all activities onboard an ammonia fuelled ship, but this should be based on toxic areas definition, concentrations and exposure durations. A gas dispersions analysis supplemented by a risk assessment will be required to define the exact PPE levels in corresponding locations.

Table 17: PPE layers derived from ammonia emergency response workshop (Source: YCA[9])

Level	Areas / Conditions	PPE	Photos	Remarks
A	Can be used against liquid projection, inside aerosol, and dense gas releases.	■ Fully encapsulated suit ■ SCBA (Self Contained Breathing Apparatus) or Air Line with pass through. ■ Nitrile inner gloves for protection upon exiting suit to prevent possible contamination. ■ Chemical gloves & outer gloves for thermal protection and abrasion resistance ■ Chemical over boots		The suit can be for a one time use with normally a maximum exposure time of about 400min. It can also have a 10-year lifetime, but in this case the complete equipment must by yearly inspected by the OEM, the exposure duration must be recorded, and specific decontamination and storage procedure must be in place.
B	Can not be used against liquid projection nor aerosol/dense gas exposure. Can only be used against gas exposure when IDLH is reached (300ppm) and up to a few thousands' ppm (2000 to 3000).	■ Chemical suit with acid hood ■ SCBA (Self-contained breathing apparatus or air line) ■ Nitrile inner gloves for protection upon exiting suit to prevent possible contamination. ■ Outer gloves for thermal protection and abrasion resistance ■ Chemical boots ■ Gloves and pant legs taped to prevent skin exposure as applicable to type of suit.		To use this suit, the ammonia concentration level must be controlled and constantly monitored to evacuate the area when it reaches defined upper limit.

[9] YCA: *"PPE characteristics and standards can vary in some countries. The local environment can also influence the choice of type of equipment. The following PPE description can only be considered as example of existing solutions. For safe use of this type of equipment as it relates to NH3 response more advanced and practical training is required."*

Level	Areas / Conditions	PPE	Photos	Remarks
C	Can be used against liquid projection, inside aerosol, and dense gas releases. For specific maintenance and operation activities where the risk of liquid/aerosol/dense cloud cannot be discarded (loading/unloading activities, sampling, line breaking, equipment opening, etc…)	■ Chemical suit with acid hood ■ Full face respirator with chemical cartridges-Coverage to IDLH only ■ Nitrile inner gloves for protection upon exiting suit ■ Outer gloves for thermal protection and abrasion resistance ■ Chemical boots		This level could be used for prolongated exposure during special activities where the gas concentration cannot be lowered to less than 25ppm, is constantly monitored, not exceeding IDLH 300ppm and the risk of prolongated liquid exposure is null.
D	Can not be used against liquid projection, inside aerosol, and dense gas releases. Can be used by all personal present in a location where ammonia is handled and, only if their activity does not involve ammonia direct handling.	■ Hardhat ■ Safety glasses ■ Long sleeve shirts and pants ■ Safety footwear ■ Gloves ■ Escape mask at the waist		This minimum set shall be sufficient to enable any employee “surprised” by an ammonia leak to escape and shelter in dedicated place safely. The escape mask is there to help in case the only escape route available is exposed to the vapour cloud.

2.4 Accidents Review

Incident reporting is legally enforced to inform the relevant authorities at international, national and local level about deaths, injuries, occupational diseases, spills and dangerous occurrences. This facilitates the discernment of the origin and nature of risks, thereby determining whether they need to be investigated. Incident reporting serves multifaceted purposes, enhancing overall safety by capturing and applying lessons learned, facilitating the continuous improvement of legislation, fostering the advancement of new technology and industry best practices, contributing to hazard identification through statistical data analysis and monitoring the environmental impact of such incidents.

Establishing strong safety cultures for the maritime sector is needed to navigate the big transformations safely. Although regulation may help, the maritime industry needs to embrace a top-to-bottom safety culture.

A good example would be the "HOT-fit" strategy, which focus on the interdependencies between the human (H), organisational (O) and technological (T) dimensions to optimize management performance. "HOT-fit" requires organisations to implement a continuous learning methodology to improve internal best practices and this daily real operation may be used by the industry to set new regulations and standards. It is comprised of:

- a reporting culture
- a fair culture
- a learning culture
- a flexible culture

To evaluate the risks associated with ammonia-fuelled ships, it would be ideal to analyse the existing cases of the same type of ship (ammonia fuelled ship) accidents and therefore, the target ship should be evaluated based on this. Currently there are no ammonia fuelled ships, but ammonia has been transported for decades and used as a refrigerant onboard the vessels. Although there is insufficient accident data that can be used to evaluate the safety of the target ship, the evaluation of the potential risk of ammonia fuelled ships could be done by expanding the scope of analysis to onshore ammonia production/consumption plants and gaining experience by analysing what accidents have occurred in the industry related to ammonia and onboard of the vessels. A review of known accidents related to ammonia has been conducted, considering on-land plants, refrigeration facilities, process engineering, land transportation of ammonia.

There have been countless reports of accidents on land related to ammonia since it is widely used in the fertiliser and food industry. As an example, according to the Canadian government report, between 2007 and 2017 in British Columbia, western Canada, there were a total of 59 ammonia leak incidents recorded, 14 of which resulted in casualties (Table 18). The table shows the total number of ammonia accident classified into three major groups (excluding unidentified cases), along with their corresponding sub-category "contents". Among them, it shows that accidents due to operating problems were quite high while accidents due to component failure/wear in the equipment damage group occur most frequently.

Table 18: Main causes of accidents in ammonia facilities in British Columbia

Cause of accident	Number of causes	Accident failure
Equipment damage	15	Component failure
Operating problem	4	System control failure of monitoring
	1	Breakdown of worker tools
	2	Incorrect use of component
	9	Lack or inadequate preventive maintenance programs
Installation	5	Improper operating procedures
	4	Operating environment
	2	Operator error

Cause of accident	Number of causes	Accident failure
	1	Access to restrict areas surrounding maintenance
	3	System component compatibility issues
Unidentified	1	Missing isolation
	1	Missing component
	1	Improper installation
	1	Inadequate protective equipment for components
	4	Not recorded

These results also suggest that the ship's ammonia fuel system may be exposed to dangers resulting from mechanical issues, such as component failure or wear, or from incorrect operating practices.

Understanding the gap between how crew manage vessel operations now and what will be required of them in the future will become critical to ensuring competence throughout the transformation to advanced technologies.

2.4.1 eMARS

eMARS is owned and operated by the European Commission. The database was created in 1982 as part of the Seveso Directive, which is European legislation that regulates the management of risks in industrial establishments that handle large quantities of hazardous substances. It is a collaborative database of incidents and accidents related to hazardous substances. Anyone can submit an incident or accident report and the data is publicly accessible and can be used for research, education, and accident prevention purposes. The data collected in eMARS is the most complete database in the review conducted. It includes multiple details for each accident (ID, title, start and finish date, event type, industry type, etc), damages (property or environment), injuries to persons, lessons learned, emergency response and remedial measures.

From November 1979 to November 2023, eMARS reported 1,198 accidents of which 69 are related to ammonia. The first ammonia accident is from October 1985 and the last one from February 2023. The breakdown of the cause of accident is compiled in Table 19. There is still a relevant percentage of accidents due to component failure and operator error. The component failure may be improved with redundant systems and increased monitoring of the most relevant items. The operator error may be improved by intensifying the training of the operators and their engagement with the procedures.

Table 19: eMARS main causes of accidents related to ammonia

Cause of accident	Number of causes	Accident failure
Equipment damage	21	Component failure
Explosion	3	Unknown
Fire	8	Multiple
Operating problem	4	System control failure of monitoring
	1	Incorrect use of component
	2	Lack or inadequate preventive maintenance programs
Installation	4	Improper operating procedures
	9	Operator error
	17	Unidentified

Conducting a thorough examination of this accident database facilitates the discernment of recurrent patterns, thereby pinpointing crucial focal points where preventive or corrective measures should be strategically concentrated. These measures encompass enhancing maintenance protocols, imparting comprehensive training to personnel in emergency procedures, and ensuring the continuous update and alignment of safety protocols and technical specifications in accordance with evolving regulatory framework and recommended industry practices.

Valve failures is the most common cause among the reviewed accidents. Failure in valves, seals, or equipment connections leads to ammonia dispersion, resulting in some cases in severe or fatal injuries and environmental damage; as example can be mentioned the incident in an ammonia tank storage installation on the January 4, 2005. In this event, due to the complete opening of the ammonia storage tank drainage valve, there was a sudden and violent release of ammonia. This incident resulted in serious injuries to the personnel. Additionally, it caused the formation of an additional leak near the drainage point, releasing significant amounts of liquid ammonia that evaporated and dispersed in the surrounding area. Sometimes, automatic shut-off valves did not operate properly.

Another recurrent cause of accidents is **electrical problems and power failures**, triggering critical events that lead to explosions or failures in safety systems. As an example, on June 26, 2009, a violent storm led to the stop with a total blowoff of the installation for ammonia production in an ammonia plant. The thunderstorm caused a complete power failure as well on the high voltage as on the low-tension grid. There was consequently a stop of all the electrical motors and an explosion occurred in this furnace.

A third cause of accidents is corrosion in pipes, valves, and equipment due to prolonged exposure to chemicals and lack of proper maintenance. On occasion, the causes of the accidents were identified as design failures and technical specifications errors, such as mistakes in material selection, pipes unsuitable for certain temperatures and pressures, lack of adherence to technical specifications during installation and operation, and problems in the design of critical systems. On April 2, 2011, there was an ammonia leak from high-pressure section of urea plant caused by the corrosion of a section of pipeline.

Finally, some accidents are caused by human errors, **misuse of alarm systems, errors in operating procedures, communication failures, and lack of training**, especially regarding the operation of critical equipment. In some incidents, the emergency response was delayed or not carried out efficiently, resulting in more serious consequences. On May 31, 2019, there was an ammonia release in a chemical plant that caused the death of a worker, another one was critically injured, and another worker was mildly injured. In addition, emergency personnel had to be treated. Operators did not follow the right working procedure for valves operations. Therefore, an automatically operated valve opened, causing a release of ammonia that directly affected them.

Drawing insights from these incidents is essential to strengthen industrial safety protocols and protect the health of workers and the environment.

2.4.2 Occupation Safety and Health Administration

The U.S. Department of Labor uses an OSHA database that encompasses ammonia leakage accidents reported since 1984. There have been 243 reported incidents during storage and handling of ammonia. Among these cases, 58 have resulted in fatalities, while a significant portion of these incidents involves injuries like chemical burns and respiratory issues. The summaries currently available include completed investigations from 1984 through 1 year earlier than the day the report is checked online. Summaries for later dates are not available, to provide time for OSHA staff to complete the investigation and revise the summary. The data has been collected from the official website[10].

The data reported includes information about the accident (e.g. Summary Nr, Report ID, event date, etc.) or the employee's details (age, sex, nature of injury etc.). There is a short event description of the consequences of the accident described. To have further information on the accidents, each one can be duly accessed through the summary number for further investigation.

[10] https://www.osha.gov/ords/imis/accidentsearch.html

2.4.3 Offshore accident statistics

Insights can be gained from accidents involving ships carrying ammonia as cargo. Table 20 lists all 12 worldwide accidents obtained from the IHS Seaweb database recorded for the period 1978–2021, with most of them being classified as serious accidents (approximately 66%) and involving LPG tankers. There were no reports of environmental pollution nor major harm to the ship structure. However, in most cases, there were fatalities, with the most severe incident being an explosion in the engine room of an LPG tanker caused by a rupture in the ammonia storage tank, which led to 6 fatalities. These events indicated the need for caution when handling ammonia at all stages of its operations, as ammonia transportation is expected to increase in the future, and there is presently a lack of effective regulation, operational experience and training. In conclusion, although ammonia has been typically transported as a ship's cargo or used as a refrigerant in a refrigeration plant, it has not been utilised yet as a ship fuel. This is a major concern due to sufficiently high safety implications and the clear risks related to bunkering, storage, supply and use of ammonia on board ships; the potential impact is not small enough to be considered as negligible. Ensuring its safe use as a fuel for ships is seen as a very urgent matter.

Table 20: Seaweb accidents compilation related to ammonia

Year	Ship type	Accident type	Fatal	Cause
1978	LPG Tanker	Hull/Machinery Damage	0	Vessel adrift and ammonia leak in a storm
1981	Oil Products Tanker	Hull/Machinery Damage	0	Leak in refrigeration system
1982	Fishing Vessel	Hull/Machinery Damage	7	Leakage of ammonia cargo because a net hit a pipeline
1982	Fish Factory Ship	Fire/Explosion	0	Explosion of canister of ammonia due to the fire
1983	LPG Tanker	Hull/Machinery Damage	6	Hose bursts whilst discharging anhydrous ammonia
1996	LPG Tanker	Hull/Machinery Damage	1	Leakage of ammonia from loading arm
1999	LPG Tanker	Hull/Machinery Damage	0	Leakage of ammonia due to a mis-operation of a valve
2005	Container ship	Hull/Machinery Damage	0	Leakage of ammonia from one container
2007	Fishing vessel	Fire/Explosion	6	Explosion in engine room caused rupture of ammonia storage tank
2014	Chemical Tanker	Collision	0	Collision
2014	Fishing vessel	Hull/Machinery Damage	6	Leak of ammonia in refrigeration system
2021	LPG Tankers	Illness/Fatality/Injury	1	Ammonia leakage

3. Ammonia Regulatory Framework

3.1 International Regulations in Shipping

The safe transport of ammonia on ships is covered in specific codes. For aqueous ammonia, the International Code for the Construction and Equipment of Ships Carrying Dangerous Chemicals in Bulk (IBC Code) is applicable. Similarly, for anhydrous ammonia, the International Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk (IGC Code) applies.

However, for the purpose of using ammonia as a fuel in shipping, there are no specific international regulations. The use of ammonia as a marine fuel is in the early stages of development and it is essential for ammonia specific hazards to be addressed in future legislation.

The most relevant code that addresses all areas that need special consideration for the ammonia fuelled vessels is the International Code of Safety for Ships Using Gases or other Low-Flashpoint Fuels (IGF Code), which provides general requirements for low-flashpoint fuels, but prescriptive requirements only for natural gas. Adopted in 2017, the code outlines general requirements for low-flashpoint fuels (in Part A) and specific requirements for natural gas (in Part A-1). In 2020, the IMO approved the “Interim Guidelines for the Safety of Ships Using Methyl/Ethyl Alcohol as Fuel” (MSC.1/Circ.1621) that aim to ensure the safety of ships that use methyl/ethyl alcohol as a fuel.

International organisations such as the IMO, IACS and Classification Societies, SGMF and SIGTTO have been working to develop and update the rules and regulations specific to ammonia fuelled ships. During the latest IMO Sub-Committee on Carriage of Cargo and Containers (CCC), 9th session, in September 2023 the development of the Draft Interim Guidelines for Ships Using Ammonia as Fuel progressed and are expected to be finalised in 2024.

The previous EMSA study (Laursen, et al., 2022) includes an extensive summary of the ammonia applicable regulatory framework; the purpose of this study is to provide an update on the progress made since the 2022 EMSA study was completed. This mainly derives from the conclusions of CCC 9.

3.1.1 Sub-Committee on Carriage of Cargo and Containers (CCC)

The CCC 9 session focused on crucial discussions related to the development of guidelines on the use of ammonia and hydrogen as fuels, guidelines for the use of LPG cargo as fuel, and updated requirements for the carriage of bulk cargoes and dangerous goods. A comprehensive review of the CCC's activities can provide valuable insights into potential future regulatory developments.

With regards to ammonia specifically, Sub-Committee discussed overarching principles and directions for the further development of the interim guidelines for ships using ammonia as fuel and agreed that the following principles should be taken into account by the correspondence group:

- Ships using ammonia as fuel shall be subject to a holistic risk assessment.
- Interim Guidelines shall consider refrigerated and semi-refrigerated ammonia storage options as a first stage; Pressurised ammonia will be covered through alternative design process.
- Portable tank provisions for ammonia shall not be specifically developed but covered through alternative design process.
- Guidelines will not consider Emergency Shut Down (ESD) machinery space concept. Administrations will need to go through the alternative design process. Gas-safe machinery space will be the default option.
- Consideration of safe refuge (safe haven) on board ships using ammonia as fuel in case of ammonia contamination/leaks based on ship type and number of people onboard; application of the interim guidelines could exclude specific ship types.
- Provisions for personnel safety and PPE, recognised as a last line of defence, shall be developed considering class rules and shore-based industry practice.
- Regarding concentration limits for ammonia exposure for personnel, during normal operations there shall be no ammonia present.
- Regarding release of ammonia for safety reasons, release mitigating measures shall be considered in the guidelines.

Work on this subject will continue intersessionally with further discussion during CCC 10 (September 2024).

To support discussions during CCC 9 several informative documents had been submitted in advance are listed in Table 21. These can be found in IMO's library and downloaded through IMODOCS.

Table 21: CCC 9 documents related to ammonia fuel

Reference No.	Submitted By	Document Title
AMENDMENTS TO THE IGF CODE AND DEVELOPMENT OF GUIDELINES FOR ALTERNATIVE FUELS AND RELATED TECHNOLOGIES		
CCC 9/3	Germany	Report of the Correspondence Group
CCC 9/3/1	ITF and Republic of Korea	Proposal for Safety Principles and Draft Safety Provision against Toxicity for Development of Guidelines for Ships Using Ammonia as Fuel
CCC 9/3/2	Republic of Korea	Study on Safety Assessment of Ammonia Toxicity
CCC 9/3/13	Japan	Comments on annexes 4, 5 and 6 to document CCC 9/3
CCC 9/3/14	IACS	Comments on document CCC 9/3 pertaining to the use of ammonia as fuel
CCC 9/INF.7	Denmark, Finland, Norway and Sweden	Supporting information to the draft interim guidelines for the safety of ships using ammonia as fuel
CCC 9/INF.16	IACS	Gap analysis between ammonia as fuel and the IGF Code
CCC 9/INF.27	Environmental Defense Fund	Study on Impacts of Ammonia Spills on Marine Ecosystems
REVIEW OF THE IGC CODE		
CCC 9/4/1	Republic of Korea	Proposed amendments to MSC.1/Circ.1599/Rev.2 and MSC.1/Circ.1622 to quality high manganese austenitic steel for ammonia service and to revise additional compatibility test requirements for ammonia service
CCC 9/4/9	Belgium, Canada, Japan and Liberia	Comments on the report from the Correspondence Group on Amendments to the IGF Code and Review of the IGC Code
CCC 9/INF.19	Republic of Korea	Technical information on the ammonia compatibility test of high manganese austenitic steel

The background of the CCC 9 outcome also has been based on several discussions around ammonia as fuel that were held in previous CCC, MSC, and MEPC meetings with several submissions as listed in Table 22 in chronological order.

Table 22: CCC, MSC, MEPC submissions related to ammonia as fuel

Reference No.	Submitted By	Document Title
CCC 7, 6-10 September 2021		
CCC 7/3/9	Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden and European Commission	Comments on CCC 7/3/Rev.1 Report from the Correspondence Group and proposal for developing guidelines for the use of ammonia and hydrogen as a fuel
MSC 104, 4-8 October 2021		
MSC 104/15/9	Japan, Singapore, ICS and INTERCARGO	Development of non-mandatory guidelines for safety of ships using ammonia as fuel
MSC 104/15/10	Japan	Hazard Identification of ships using ammonia as fuel
MSC 104/15/30	Japan	Necessity of deliberations on operational safety measures and fire safety measures
CCC 8, 14-23 September, 2022		
CCC 8/13	Japan	Report of the Correspondence Group (safety information for the use of ammonia)
CCC 8/13/1	Japan, Singapore, ICS and INTERCARGO	Issues to be considered and possible way forward for the development of guidelines for the safety of ships using ammonia as fuel
CCC 8/13/2	Republic of Korea	Comments on document CCC 8/13
CCC 8/INF.10	Japan	Summary of comments provided to the Correspondence Group (safety information for the use of ammonia)
MEPC 79, 12-16 December 2022		
MEPC 79/INF.26	Republic of Korea	Development of a fuel supply system and re-liquefaction system for LPG/Ammonia carriers

3.1.2 IGC Code

Transportation of anhydrous ammonia by gas carriers is covered under the IGC Code. Note, the IBC Code contains only the requirements for carriage of aqueous ammonia up to 28% in water. Therefore, IGC code is the basic reference for ammonia storage and should be taken into consideration for ammonia fuelled vessels.

Anhydrous ammonia is listed as toxic cargo in Chapter 19 of the IGC Code that includes the list of products that can be carried under the code.

Table 23: IGC Code Chapter 19, Anhydrous Ammonia

Product Name	Ship Type	Vapour Detection	Gauging	Special requirements
Ammonia, anhydrous	2G/2PG	T[11]	C[12]	14.4, 17.2.1, 17.12

Special requirements for carrying anhydrous ammonia are included in the IGC Chapter 19 referring to specific chapters of the code.

Chapter 17.12 contains the main requirements for carrying ammonia with focus on risk mitigation against stress corrosion cracking in containment and process systems made of carbon manganese or nickel steels. These requirements are applicable to cargo tanks, pressure vessels and cargo piping systems and include these constructional or operational measures to limit stress corrosion cracking.

Carbon Manganese Steel

Where carbon manganese steel is used this should be fine grained steel with a specified minimum yield strength of 355 N/mm^2 and with maximum yield strength not exceeding 440 N/mm^2. In addition, one of the following constructional or operational measures are also to be taken:

- Lower strength material with specified minimum tensile strength not exceeding 410 N/mm^2; or
- Post weld stress relief heat treatment (PWHT); or
- Carriage temperature to be maintained close to the boiling point of -33˚C, but in no case at a temperature above -20˚C; or
- The ammonia shall contain not less than 0.1% w/w water, and as documented.

Nickel Steel

Nickel steels containing more than 5% nickel are not suitable for storing anhydrous ammonia. Therefore, the typical nickel steel materials used for LNG storage, which contain 9% nickel, cannot be used for this purpose. Nickel steels containing not more than 5% nickel may be used, provided the ammonia is carried below -20˚C.

The IGC Code requirements also recommend keeping the dissolved oxygen content below 2.5 ppm w/w, driving operational measures to reduce oxygen content in tanks before loading ammonia.

There are other IGC Code requirements driven by the toxic and corrosive nature of the carriage of ammonia including:

- Gas and vapour detection to be suitable for toxicity.
- Cargo tank gauging instrumentation to be of indirect or closed type.
- Materials to be resistant to the corrosive nature of ammonia.
- Mercury, copper, copper bearing alloys and zinc materials are not to be used for cargo tanks, piping, valves, fittings, etc. that are normally in direct contact with the ammonia liquid or vapour (IGC 17.2.1).
- In addition to the standard personnel protective equipment for gas carriers, including aprons, eye protection, first-aid equipment and full protective safety outfits and air sets, the carriage of ammonia also requires

[11] Toxic vapour detection
[12] Indirect or closed gauging

respiratory and eye protection for the emergency escape of every person onboard (IGC 14.4) subject to the following:
1. filter-type respiratory protection is unacceptable;
2. self-contained breathing apparatus shall have at least a duration of service of 15 min; and
3. emergency escape respiratory protection shall not be used for firefighting or cargo-handling purposes and shall be marked to that effect.
- Protective clothing should be gastight and approved for ammonia use to a recognised standard.
- One or more suitably marked decontamination showers and eyewash stations shall be available on deck, taking into account the size and layout of the ship. The showers and eyewashes shall be operable in all ambient conditions.

High Manganese Austenitic Steel

The CCC 9 reviewed the results of the completed test of high manganese austenitic steel for ammonia service, which ensured that high manganese steel plate and weldment without post-weld heat treatment was resistant to ammonia stress corrosion cracking (SCC). In addition, post-weld heat treatment – which can affect material properties - considered as a mitigation against SCC showed no significant improvement. Therefore, high manganese austenitic steel can be considered resistant to ammonia SCC and therefore can be used for ammonia cargo and/or fuel tanks containing ammonia.

Noting the above and based on submitted documents CCC 9/4/1 and CCC 9/INF.19 (Republic of Korea), modifications to revised guidelines on the application of high manganese austenitic steel for cryogenic service (MSC.1/Circ.1599/Rev.2) were agreed, accepting high-manganese austenitic steel as being suitable for ammonia service, and waived the post-weld stress relief heat treatment in 17.12.2.2 of the IGC Code for ammonia cargo and/or fuel, as contained in draft circular MSC.1/Circ.1599/Rev.3.

In addition, CCC 9 considered proposed modifications to the Guidelines for the acceptance of alternative metallic materials for cryogenic service in ships carrying liquefied gases in bulk and ships using gases or other low-flashpoint fuels (MSC.1/Circ.1622), containing additional compatibility test procedures for ammonia service, as contained in draft circular MSC.1/Circ.1622/Rev.1.

Toxic products as fuel

Prohibition of using toxic products as fuel remains the main obstacle in IGC Code. IGC 16.9.2 states: "*The use of cargoes identified as toxic products shall not be permitted.*". The IGF Code, though, does not prohibit the use of ammonia as fuel but allows equivalents to be applied. During CCC 9, this issue was taken into consideration as discussion focused on toxic products as fuel, noting the proposal to exempt anhydrous ammonia from the list of toxic products that can be used as fuels, modifying 16.9.2 of the IGC Code (CCC 9/4/9 (Belgium, Canada, Japan and Liberia)).

As per IGC Code Chapter 16, methane (LNG) is the only cargo that can be used as fuel; other cargo gases may be used, if acceptable to the Administration, providing the same level of safety as natural gas is ensured. LPG and ethane are an example as they are used as fuel mostly in LPG carriers and ethane carriers respectively. Additional guidelines shall be developed to ensure the same level of safety as natural gas (methane) for the use of cargoes identified as toxic products which are required to be carried in type 2G/2PG ships, as fuel.

An amendment to the IGC Code allowing ammonia as fuel would be a big step forward. Ammonia carriers would be excellent candidates as first movers on the ammonia fuel pathway. There is extensive experience with carrying and handling ammonia as cargo in ammonia gas carriers. Crews already have the appropriate knowledge and certification to handle flammable and toxic gases. Therefore, the transition to ammonia fuel would be easier for gas carriers that already handle ammonia as cargo.

A similar approach was followed with natural gas as fuel, as LNG carriers were the first vessels to use their cargo as fuel. Regardless of IGC Code amendments, the development of the guidelines will provide valuable guidance for any vessels intending to use ammonia as fuel, including gas carriers. Provided CCC 9 agrees on amendment of paragraph 16.9.2 of the IGC code, the adoption could be in December 2024 at the earliest (MSC 109) therefore interim guidelines would have been finalised by that time given current work plan.

3.1.3 IGF Code

Historically, SOLAS has prohibited the use of low-flashpoint fuel oils less than 60˚C, except for use in emergency generators, where the limit is 43˚C and subject to several additional requirements detailed under SOLAS II-2 Regulation 4.2.1. In parallel, the IMO adopted the IGF Code, which serves as an international standard for ships operating with gas or low-flashpoint liquids as fuel, other than those ships covered by the IGC Code.

The IGF Code is mandatory by SOLAS II-1 Part G. The adoption of the IGF Code introduced a framework and requirements under SOLAS for burning fuels with a flashpoint less than 60˚C.

With the adoption of the IGF Code and 2016 IGC Code, the IMO has established the regulatory safety requirements and framework for using natural gas and other low flashpoint fuels on all ship types. In all cases, the prescriptive and goal-based objectives apply the following three safety principles, and general arrangements, to mitigate the risks of using low flashpoint fuels:

- Prevention of leakage, e.g. double barriers, sealing systems, protective locations, cofferdams, air locks;
- Prevention of explosive or toxic atmosphere, e.g. ventilation, gas detection, hazardous area classification, master gas fuel valves, fuel block and bleed valves, inert gas barriers, and fuel purge systems; and
- Explosion mitigation, e.g. explosion relief valves, pressure vent systems, design for worst case pressure rise, specialised fire detection and firefighting equipment.

Although the IGF Code has been developed for the use of fuels with low flash point, prescriptive requirements are currently applicable to natural gas only. Other low flashpoint fuels may also be used as marine fuels, provided they meet the intent of the goals and functional requirements of the IGF Code and provide an equivalent level of safety. This approval process is by application of the "alternative design" criteria under 2.3 of the IGF Code and equivalency shall be demonstrated as specified in SOLAS II-1/55, which refers to the engineering analyses submitted for approval (by the Administration) to be based on the MSC.1/Circ.1212/Rev.1 guidelines.

CCC 9 agreed to the timelines below (Table 24) for the development of several standards for alternative fuels through the IGF Code. The scope of remaining work extends to 2026 and includes development of standards for low-flashpoint oil fuels, hydrogen, ammonia, fuel cells, and methyl/ethyl alcohol fuel standards, and may extend to the development of a mandatory instrument for the use of fuel cells and methyl/ethyl alcohols.

Recognising the urgent need to provide guidance to Administrations, shipowners and industry on the safe use of hydrogen and ammonia as fuel, the Sub-Committee agreed on the establishment of an intersessional working group to advance the development of these guidelines. The approval of the guidelines for ships using ammonia as fuel is planned approximately end of 2024 during the MSC 109 meeting (Table 24).

Table 24: CCC 9 work plan for the development of safety provisions for Alternative Fuels

Meeting	Objectives	Year
ISWG-AF 1	- Further develop/finalise guidelines for ships using hydrogen as fuel **- Further develop/finalise guidelines for ships using ammonia as fuel**	9 – 13 Sep 2024
CCC 10	- Prepare amendments to the IGF Code →Natural Gas - Finalise guidelines for ships using hydrogen as fuel **- Finalise guidelines for ships using ammonia as fuel** - If time permits, further develop guidelines for low flashpoint oil fuels - If time permits, start to discuss the development of mandatory instruments regarding methyl/ethyl alcohols	16 – 20 Sep 2024
MSC 109	- Approval of the guidelines for ships using hydrogen as fuel **- Approval of the guidelines for ships using ammonia as fuel**	2 – 6 Dec 2024
CCC 11	- Further develop/finalise guidelines for low flashpoint oil fuels - If time permits, develop mandatory instruments regarding methyl/ethyl alcohols - If time permits, start to discuss the development of mandatory instruments regarding fuel cells	Sep 2025
MSC 111	- Approval of the guidelines for low flashpoint oil fuels	May 2026
CCC 12	- Further develop/finalise mandatory instruments regarding methyl/ethyl alcohols - Further consider the development of mandatory instruments regarding fuel cells	Sep 2026

3.1.4 Classification Societies & IACS

Since 2021, most classification societies have published either separate guidelines for ammonia fuelled vessels or incorporated these into their existing rules and requirements. Revised editions have been published to catch up with the latest developments (Table 25).

Table 25: Classification Guides/Rules for ammonia fuelled vessels

Classification Society	Rule / Requirement	Published Date
American Bureau of Shipping (ABS)	*Requirements for Ammonia Fuelled Vessels*	September 2023
Bureau Veritas (BV)	*Ammonia-Fuelled Ships – Tentative Rules. NR671*	July 2022
China Classification Society (CCS)	*Guidelines for Ships Using Ammonia Fuel*	November 2022
Det Norske Veritas (DNV)	*Rules for Ammonia in Part 6 Chapter 2 Section 14*	July 2023
Indian Register of Shipping (IR)	*Guidelines on Ammonia Fuelled Vessels*	December 2022
Korean Register (KR)	*Guidelines for Ships Using Ammonia as Fuels*	2023
Lloyd's Register (LR)	*Rules and Regulations for the Classification of Ships using Gases or other Low-flashpoint Fuels - Appendix LR2 - Requirements for Ships Using Ammonia as Fuel*	July 2023
Nippon Kaiji Kyokai (NK/ClassNK)	*Guidelines for Ships Using Alternative Fuels (Edition 2.0) (Methyl / Ethyl Alcohol / LPG / Ammonia)*	June 2022
Registro Italiano Navale (RINA)	*Rules for the classification of ships (REP) Part C Machinery, Systems and Fire Protection – Appendix 13 LPG or NH3 Fuelled Ships*	July 2023

Although the classification guidelines follow the IGF Code structure there are minor differences between them and gaps regarding the use of ammonia as fuel. Section 3.3.3 highlights the areas where these guidelines differ between each other and the IGF Code, and where extra emphasis is needed to cover adequately the use of ammonia as fuel.

Most classification societies have actively worked with designers and shipyards to issue "Approval in Principle" (AIP) of pioneering designs of ammonia fuelled vessels and to address how the specific hazards of ammonia can be practically mitigated onboard various kinds of ships. In addition, "ammonia fuel ready" notations are being used to already built vessels to promote the future use of ammonia fuel when technology and regulatory framework matures.

In 2022, IACS Council launched a new Safe Decarbonisation Panel (SP) in recognition of the challenge of meeting ambitious decarbonisation targets and to safely aim to support the implementation of new fuels and technologies. The SP is currently working on new Unified Requirements for the Control of Ammonia releases in Ammonia fuelled vessels.

3.1.5 Society of International Gas Tankers and Terminal Operators (SIGTTO)

The Society of International Gas Tankers and Terminal Operators (SIGTTO) has been supporting industry with committees and working group activities to promote industry safety. The Working Groups are developing publication procedures in the key cargo transportations aspects of LNG, LPG, ammonia, methanol, hydrogen and CO_2 to fulfil their safety mission.

SIGTTO already has a working group to address the practicalities of establishing the bunker arrangements required for ammonia's use in liquefied form. The working group includes work on the IGC Code, the Energy Efficiency Design Index (EEDI), the Energy Efficiency Existing Ship Index (EEXI) and lessons learnt from incidents. According to SIGTTO's 2022 annual report (SIGTTO, 2022) the working group has made good progress on addressing the safety, environmental and operational issues associated with gas carrier propulsion systems.

SIGTTO members have extensive experience with shipping bulk ammonia cargoes in LPG/Ammonia carriers on behalf of the fertiliser industry for many decades, and this experience will be invaluable in establishing industry best practice guidelines for handling this product as a marine fuel.

Operational guidelines with regards to ammonia are included in their *"Liquefied Gas Handling Principles on Ships and in Terminals"* (SIGTTO, 2016) to supplement IGC Code with regards to:

- Carbamates creation prevention. It is highlighted that ammonia should never be loaded into a tank that contains an atmosphere of combustion generated inert gas. Ammonia reacts with the carbon dioxide in the inert gas and produces carbamates that can potentially block pipelines and pumps. Nitrogen should be used for inerting.
- Mitigation of stress corrosion cracking by reducing oxygen levels prior introducing ammonia. Additionally, an older information paper "*Avoidance of Stress Corrosion Cracking (SCC) in Cargo Tanks, Reliquefaction Condensers and Condensate Return Pipework With Liquefied Ammonia Cargoes*" (SIGTTO, 1988) has been issued.
- Cargo changeover and difficulties to remove ammonia traces. Fresh water washing can be considered an effective way.

SIGTTO also has published several other publications and recommendations that may be used as reference for the development of specific ammonia guidelines, highlighting the below:

- ESD Systems – Recommendations for Emergency Shutdown and Related Safety Systems
- Recommendations for Relief Valves on Gas Carriers
- Ship/Shore interface for LPG/Chemical Gas Carriers and Terminals
- Guidelines for the Alleviation of Excessive Surge Pressures on ESD for Liquefied Gas Transfer Systems
- Recommendations for Liquefied Gas Carrier Manifolds
- Ship to Ship transfer Guide for Petroleum, Chemicals and Liquefied Gases
- Liquified Petroleum Gas Sampling Procedures

3.1.6 Society for Gas as a Marine Fuel (SGMF)

The Society for Gas as a Marine Fuel (SGMF) released the document "*Ammonia as a marine fuel – an introduction*" in February 2023 (SGMF, 2023). The document provides information and guidance based on industry practice and relevant information. It covers various aspects such as the definition and usage of ammonia, its safety and environmental profile, technical considerations for ammonia fuelled ships, system designs, bunkering facilities and processes, and the training of personnel involved in handling ammonia. Also, highlights the strengths and weaknesses of ammonia as a marine fuel, including its low greenhouse gas emissions potential, usability in internal combustion engines, and its wide availability. The challenges related to ammonia's toxicity, potentially higher combustion emissions, and the need for addressing greenhouse gas emissions throughout its lifecycle are highlighted. The document acknowledges that current regulations do not permit the use of ammonia as a marine fuel due to its toxicity, and port procedures and risk mitigation measures need to be developed for safe bunkering operations. SGMF continues towards this path by organising a working group to discuss and address ammonia bunkering and safety and provide guidance/recommendations to support the safe adoption of ammonia as fuel.

3.2 Land-based Industry Regulations

3.2.1 ISO Standards

The International Organization for Standardization (ISO) has published a range of standards related to the use of anhydrous ammonia in industrial or land-based sectors that also may be suitable for marine applications. The previous EMSA study (Laursen, et al., 2022) included an extensive analysis of those standards, which are briefly listed in Table 26; there were no further updates from the ISO at the time this study was published. Although mentioned ISO standards are not directly related to ammonia as fuel, they can provide a robust foundation for the ammonia behaviour, risks, storage and transferring conditions.

Table 26: ISO standards related to ammonia from land-based industry

Document	Title
ISO 5771:2008	Rubber hoses and hose assemblies for transferring anhydrous ammonia
ISO 7103:1982	Liquefied anhydrous ammonia for industrial use – Sampling – Taking a laboratory sample
ISO 7105:1985	Liquefied anhydrous ammonia for industrial use – Determination of water content – Karl Fischer method
ISO 7106:1985	Liquefied anhydrous ammonia for industrial use – Determination of oil content – Gravimetric and infra-red spectrometric methods
ISO 7108:1985	Ammonia solution for industrial use – Determination of ammonia content – Titrimetric method
ISO 6957:1988	Copper alloys – Ammonia test for stress corrosion resistance
ISO 17179:2016	Stationary source emissions – Determination of the mass concentration of ammonia in flue gas – Performance characteristics of automated measuring systems
ISO 21877:2019	Stationary source emissions – Determination of the mass concentration of ammonia – Manual method

The use of ammonia as fuel has yet to mature and has not been addressed at the ISO level. On the other hand, LNG is well covered by ISO standards in marine industry in response to growing interest and applications for LNG as a marine fuel and demand for an internationally recognised marine fuel standard. Table 27 lists the ISO standards that are applicable to LNG with particular focus on bunkering operations, an area where standardisation is essential.

Table 27: ISO standards related to natural gas as marine fuel

Document	Title
ISO 23306:2020	Specification of liquefied natural gas as a fuel for marine applications
ISO 21593:2019	Ships and marine technology – Technical requirements for dry-disconnect/connect couplings for bunkering liquefied natural gas
ISO 20159:2021	Ships and marine technology – Specification for bunkering of liquefied natural gas fuelled vessels
ISO/TS 18683:2021	Guidelines for safety and risk assessment of LNG fuel bunkering operations

The ISO is also working towards standardisation of methanol as marine fuel; the standards seen below are under development:

- ISO/CD 6583 Specification of methanol as a fuel for marine applications
- ISO/AWI 22120 Ships and marine technology – Specification for bunkering of methanol fuelled vessels

From these precedents, it can be concluded that an ISO standard for marine fuel covering the specification for anhydrous ammonia will be developed, given the interest from the marine industry and CCC 9 progress within IMO. This, of course, would require a collaboration between the IMO and the ISO.

Industry experience with the contamination of LNG and ethane also suggests that a marine fuel specification will be required to document critical fuel properties and limitations. These include properties such as ammonia, water, oxygen, debris, etc., which may be relevant to the tank material and the ability to document the sulphur content and the fuel property test standards for each fuel parameter. For some of these emerging fuels, industrial specifications are sufficient; the products are not subject to the same variations in fuel properties as conventional residual fuel oils. However, the lack of a marine fuel standard is often cited as a barrier to adoption.

3.2.2 National Standards and Guidelines

Individual governments have developed their own national regulations related to the production, transport, storage and application of anhydrous ammonia. The table below offers a list of the most cited regulations from various countries.

European Union

The EU uses specific directives (ATEX, PED, and Seveso-III) to provide guidance for storage, handling, and use of ammonia. Table 28 below summarises the various EU regulations and documents.

Table 28: European Regulations and Guidance Documents

Document	Title
ATEX 94/9/EC	Equipment Directive - Equipment and protective systems intended for use in potentially explosive atmospheres
ATEX 99/92/EC	Workplace Directive - Minimum requirements for improving the safety and health protection of workers potentially at risk from explosive atmospheres
EN 378	Refrigerating systems and heat pumps. Safety and environmental requirements. Basic requirements, definitions, classification and selection criteria
EN 60079	Explosive atmospheres. Electrical installations inspection and maintenance
IEC 60335-2-40	Household and similar electrical appliances - Safety – Part 2-40: Particular requirements for electrical heat pumps, air-conditioners and dehumidifiers
PED 97/23/EC	The Pressure Equipment Directive

In the Netherlands, there are national guidelines for the onshore storage and handling of ammonia. These guidelines are covered by the Publication series on Dangerous Substances (PGS).

- PGS 12 – Ammonia - Storage and Offloading (PGS, 2020a)
- PGS 13 – Ammonia as a refrigerant in cooling systems and heat pumps (PGS, 2020b)

United States

In the U.S., several agencies and organisations (mentioned in Section 2.2.2) have established exposure limits and guidelines for safe exposure to ammonia. OSHA, the U.S. government’s national safety body, sets regulations and occupational exposure limits for ammonia. NIOSH, a U.S. federal agency, provides recommendations and safer exposure limits for various substances, including ammonia. Other agencies are the U.S. EPA, American Industrial Hygiene Association, the U.S. DOE. ANSI standards also have been issued to support the storage and handling of ammonia and mainly its use in refrigerating systems.

Table 29: U.S. Regulations and Guidance Documents

Document	Title
ANSI K61 / CGA 2.1 – 2014	American National Standard Safety Requirement for the Storage and Handling of Anhydrous Ammonia
ANSI/IIAR 2-2008	American National Standard for Equipment, Design and Installation of Closed-Circuit Ammonia Mechanical Refrigerating System
ANSI/IIAR 3-2012	American National Standard for Ammonia Refrigeration Valves
ANSI/IIAR 4-2015	Installation of Closed-Circuit Ammonia Refrigeration Systems
ANSI/IIAR 5-2013	Start-up and Commissioning of Closed-Circuit Ammonia Refrigeration Systems
ANSI/IIAR 7-2013	Developing Operating Procedures for Closed-Circuit Ammonia Mechanical Refrigerating Systems
U.S. 33 U.S.C §1251	Clean Water Act. The U.S. Clean Water Act (CWA)
U.S. EPA 822-R-18-002	Aquatic Life Ambient Water Quality Criteria for Ammonia – Freshwater 2013
U.S. e-CFR 29 1910.111	Occupational Safety and Health Standards: Storage and handling of anhydrous ammonia
U.S. e-CFR 40 Chapter I Subchapter J Part 372	U.S. EPA Toxic Chemical Release Reporting: Community Right-To-Know

The U.S. Code of Federal Regulations (CFR) also include regulations for ammonia transportation in shipping:

- **U.S. e-CFR 46 98.25 Shipping**: **Anhydrous Ammonia in Bulk**. This Code applies to self-propelled vessels carrying anhydrous ammonia onboard as cargo, cargo residue, or vapour that is not regulated under Title 46 Part 154 (Certain Bulk Dangerous Cargos).
- **U.S. e-CFR 46 151.50-32 Shipping – Barges Carrying Bulk Liquid Hazardous Material Cargoes: Ammonia, Anhydrous**. This Code covers requirements for specific cargoes, including the location of anhydrous ammonia tanks, and related materials, designs, valves, flanges and pipe fittings.
- **U.S. e-CFR 46 130.230 – Protection from Refrigerants**. This USCG regulation requires the provision of a self- contained breathing apparatus to be stowed outside OSV spaces containing refrigeration equipment that exceeds 0.6 m^3 of ammonia.

Australia

Australia follows a similar approach to the U.S. with federal and state government regulations for the safe handling, storage and use of ammonia, highlighting the Model Work Health and Safety Regulations and the Work Health Safety Act. Table 30 below summarises the various Australian regulations and documents.

Table 30: Australian Regulations and Guidance Documents

Document	Title
Act No. 137, 2011	Work Health Safety Act No. 137, 2011
AS/NZS 2022:2003	Anhydrous ammonia—Storage and handling
AS/NZS 60079.10.1:2009	Explosive atmospheres - Classification of areas - Explosive gas atmospheres
Model Work Health and Safety Regulations 9 January 2014	Model Work Health and Safety Regulations

China

In China, ammonia is also listed as a hazardous chemical within the 2015 Catalogue of Hazardous Chemicals by the Chinese government and specific regulations apply (Table 31).

Table 31: Chinese Regulations and Guidance Documents

Document	Title
Decree - 591	Regulations on Safe Management of Hazardous Chemicals in China
GB 28009-2011	Safety code for cold store
GB 38400-2019	Limit requirements for toxic and harmful substances in fertilizers
GB 50072-2010	Code for design of cold storage
Order of the President No.70 of 29 June 2002	Production safety law of the people's Republic of China

Fertilisers are subject to the control of many regulations and standards in China. Below are the main regulations applicable to fertilisers and indirectly related to ammonia.

- Regulations on the Management of Fertilizers (Draft 2008)
- Measures on the Management of Fertilizer Registration (Decree 8 of the Ministry of Agriculture and Rural Affairs of China, effective on November 30, 2017)
- Fertilizer Data requirements (Decree 8 of the Ministry of Agriculture and Rural Affairs of China, effective on November 30, 2017)
- GB 178382-2021 Fertilizer Marking—Presentation and declaration

India

In India, there are federal regulations and acts that mandate facilities that handle ammonia to identify major accident hazards and take action to prevent such accidents, limiting their potential consequences to people and the environment. Currently, it appears that national standards for risk assessment and management are not in place. Table 32 below summarises the relevant Indian regulations and documents.

Table 32: Indian Regulations and Guidance Documents

Document	Title
The Factories Act, Act 20 of 1987	The Factories Act
Disaster Management Act, 2005	
IS 4544 (2000), ICS 71.060;13.300	Ammonia - Code of Safety [CHD 8: Occupational Safety, Health and Chemical Hazards]
National Policy on Safety, Health and Environment at Work Place	
IS 660 (1963)	Safety code for mechanical refrigeration
IS 732-2274	Code of Practice for Electrical Wiring Installations

3.3 Gap Analysis

The previous EMSA study (Laursen, et al., 2022) included a gap analysis (Appendix C) that highlighted the areas where the existing publications contribute to, or restrain, the adoption of ammonia as a marine fuel. The analysis included an extensive list of regulations that should be updated to support the use of ammonia as fuel. Based on the analysis, updates have been noted in some regulations that are highlighted in the additional column.

Practically, progress has been noted mainly during CCC 9 with the interim guidelines for ships using ammonia as fuel in line with IGF Code and potential amendments to the IGC Code prohibition on the use of toxic products as fuel. The subsections below include two analyses conducted examining the gap between the IGF Code and ammonia as fuel and classification rules as they exist today.

3.3.1 IGF Code and Ammonia as Fuel

During the CCC 9, IACS provided an information document (CCC 9-INF.16) about a gap analysis conducted between ammonia as fuel and the IGF Code, taking into account the different properties, behaviors and hazards/risks. Since development of interim guidelines will be done in line with the IGF Code some gaps identified and not applicable for ammonia should be modified or deleted accordingly. From the list of gaps summarised in the CCC 9 information documents below are some of the highlighted ones:

- Ammonia is not a low-flashpoint fuel therefore any statement or reference should be revised to read as “gases and low-flashpoint fuel”.
- Ammonia fuel definition and specifications should be developed. Cooperation with ISO would help set standards.
- The risk assessment of ammonia fuel should address all relevant hazards. The toxicity of ammonia is a health risk to individuals onboard, however, the flammability and explosivity hazards should also be considered.
- ESD machinery space is not accepted for ammonia. Gas-safe machinery concept will be followed.
- Arrangements to maintain or treat ammonia in case discharge overboard is prohibited should be developed. Dedicated holding tanks, ammonia treatment systems and other options to be considered for the guidelines.
- Ammonia may be stored under high pressure and ambient temperature condition. The limitation of MARVS of type C tank should be modified accordingly. Currently, IGF code allows MARVS up to 1.0 MPa.
- Storage of ammonia fuel in gaseous form may not be considered.
- Materials, welding and post-weld heat treatment requirements should be developed considering the corrosive characteristics and stress corrosion cracking property of ammonia. IGC code chapter 17.12 can be consulted for this reason.
- PRVs vent outlets distances should be further investigated and supported by gas dispersion analysis and risk assessment.
- As anhydrous ammonia may react with carbon dioxide, inert gas using combustion gases is limited for purging and gas-free applications.
- Safety measures are to be developed to prevent the vapour generation during bunkering. Design the system with a vapour return line to be considered.
- Unburnt ammonia emissions, returns from engines, fuel supply systems should not be vented to atmosphere during normal operation. Options to mitigate this should be offered in the guidelines (ammonia treatments systems e.g. knock-out drum, gas absorber and/or holding tanks).
- Toxic area classification (similar to the hazardous areas) is defined.
- Increased ventilation rates (catastrophe ventilation) in the event of gas detection in enclosed spaces is introduced.
- Water mist system or other water-based safety system in ventilation system to bind to toxic ammonia gas in the event of a leak is introduced.
- Ammonia detection levels should be defined. Alarms and safety functions need to be established on these.
- Requirements for gas dispersion analysis and risk assessment to be included for toxic areas definition.

3.3.2 Rules for ammonia fuelled vessels between Classification Societies

ABS carried out a gap analysis beginning of 2023 to identify the differences between the classification requirements for ammonia fuelled vessels. In general, classification societies rules follow the same safety philosophy between them and are in alignment with IGF Code's structure. A brief list of some deviations identified are shown below:

- Extent of operational releases of ammonia
- Handling, storage and disposal of bilge water
- Lifespan of ammonia fuel storage tanks
- Arrangement of bunkering station; open, enclosed or semi-enclosed
- Provision of vapor return manifold to use during bunkering operations
- Limitation of using CO_2 as inert media for ammonia fuel supply systems
- Extent of hazardous areas, in particular consideration of hazardous areas on open decks
- Toxic area definitions and relevant safe distances
- Safe ammonia concentration limit (ppm) to release to atmosphere
- Alarm and safety/automatic shut-down points for ammonia gas detectors

The requirements as stated in classification societies rules, for some of the above points where deviations found, are presented in Table 33 for reference purposes.

Table 33: Deviations between classification societies rules[13]

Classification Society	ABS	DNV	LR	BV	NK	KR
Lifespan of ammonia fuel storage tanks (years)	20	25	20	20	20	20
Arrangement of bunkering station preference	Open (allows natural ventilation)	Open (allows natural ventilation)	Enclosed or semi-enclosed	Enclosed	Open (allows natural ventilation)	Open (allows natural ventilation)
Provision of vapor return to use during bunkering	Yes	No	No	Yes	No	Yes
Limitation of using CO2 as inert media for ammonia fuel supply systems	Yes	No	No	Yes	No	No
Hazardous area consideration on open deck	Yes	No	Yes	Yes	No	No
Ammonia limit to release from the treatment system (ppm)	25	30	25	30	25	25
Gas detection locations in spaces	Ventilation outlets	Ventilation outlets	Not specified	Top and bottom	Ventilation outlets	Ventilation outlets
Alarm / Safety shut-down points for gas detectors (ppm)	25 / 300	150 / 350	25 / 220	30 / N/A	25 / 300	25 / 300

[13] Table is created for information purposes.

3.3.3 IGF Code and Classification Rules

Another regulatory gap analysis between IGF Code and classification rules for ammonia fuelled vessels has been conducted in a recent research paper (Jang, et al., 2023) to analyse hazards, namely toxicity, chemical corrosion, fire and explosion and their potential impact on the human, environment and ship in the event of ammonia leakage. Most critical findings are shown below:

Ship design and arrangement

- Gas-safe machinery space. The ESD machinery space is not applicable and gas-safe machinery space should be applied that is not incorporated in all classification rules.
- Location of fuel preparation and specific requirements:
  1. Open deck or in dedicated spaces below deck
  2. Gastight bulkheads
  3. Water screen or mist system
  4. Means of escape
- Consideration should be made for having tank connection spaces covering connections of tanks located on open deck.
- Bilge system, draining capacity and discharge to dedicated holding tanks. Avoid direct discharge into seawater.
- Some classification rules refer to MARPOL Annex II requirements to follow for the ammonia bilge discharge at sea, as it is covered in the IBC Code as aqueous ammonia (concentration 28% or less).
- Drip trays required locations, material and capacity.
- Airlock arrangements in case access between hazardous/toxic and safe areas is necessary.
- Location of the fuel valve train (FVT) on the vessel either inside the fuel preparation room or within the machinery space as a gastight enclosure needs further consideration.
- Specific ammonia personnel protection equipment consisting of large aprons, special long sleeve gloves, face shields, etc. is required by all classification rules.

Fuel containment system

- Different MARVS limits are set for the fuel storage tanks.
- Filling and loading limits should be defined.
- The lifespan of a fuel storage tank typically does not exceed 20 years, but some classification society has given 25 years of lifespan in their requirements.

Material

- In general, there is consistency regarding material requirements to mitigate stress corrosion cracking as requirements are based on existing IGC Code requirements.
- More specific guidelines should be developed for the use of non-metal materials, rubber or plastics.

Bunkering

- Open deck with natural ventilation. Special consideration for enclosed or semi-enclosed through risk assessment.
- Bunkering safety needs to be developed further for ammonia case. Measures to control spills, drip trays, firefighting requirements are some of the requirements that are not adequately defined in classification rules.
- Some classification rules require the bunkering manifold valve position to be at least 10 m apart, while it is not specified in the IGF Code.
- It was not mandated by IGF Code, but some classification rules require a vapour return line for pressure management during bunkering operation.

Fuel supply systems

- For fuel supply systems, different from IGF Code, classification rules require:
  1. the fuel supply systems are to be designed to prevent venting atmosphere of any ammonia release during normal operation,
  2. each consumer is to be provided with "double block and bleed" valves arrangement not only for the ammonia fuel supply lines but also at the fuel return lines, and
  3. only fully welded bunkering lines are allowed with single wall construction on open deck.

Fire safety

- Tank connection spaces containing fuel pump electric motors, or any other associated rotating parts are to be provided with a fixed fire-extinguishing system.
- Water spray system arrangement for the ammonia fuel piping with source of release to be provided.

Ventilation

- Required ventilation system capacity varies across classification societies, concerning the number and power of ventilation fans in the fuel preparation room and ducts and double pipes.

Explosion Prevention, Area Classification and Toxic Areas

- The distance from the vent mast (or PRV outlet) to the air intake and outlet leading to accommodation, service, and control spaces, as well as other non-hazardous areas, varies significantly across IGF Code and classifications. The IGF Code specifies a minimum distance of 10 m, whereas different requirements from classification one mandates minimum of 15 m and some other either breadth (B) or 25 m.

Control, Monitoring and Safety Systems

- Due to the high toxicity of ammonia which is different from low flash point fuels such as LNG, it was found that different classification societies have slightly different tolerances for ammonia, and there are varying choices and requirements for preventing ammonia leaks. For instance, the IGF Code does not cover any acceptable limits for ammonia leakage, while different approaches exist across various classification societies mandating the ammonia release limits between 25 to 50 ppm for normal operation of the vessel and set various limits between 150 to 300 ppm for the shutdown of the system.

4. EMSA Guidance Development

During CCC 9, the Sub-Committee noted the discussions and progress made by the group on the development of interim guidelines for ships using ammonia as fuel. The draft interim guidelines follow the generic guidelines for developing IMO goal-based standards (MSC.1/Circ.1394/Rev.2) by specifying goals and functional requirements for each section forming the basis for the design, construction and operation of ships using ammonia as fuel. The guidelines will follow, in principle, the structure of IGF Code with the addition of Section 20 – Personnel protection. The expanded table of contents is shown in Table 34.

Table 34: Table of contents of Interim Guidelines for Ships Using Ammonia as Fuel and ABS Requirements for Ammonia Fuelled Vessels

	Draft Interim IMO Guidelines for Ships Using Ammonia as Fuel
1	Introduction
2	General
3	Goal and Functional Requirements
4	General Provisions
5	Ship Design and Arrangement
6	Fuel Containment System
7	Material and general pipe design
8	Bunkering
9	Fuel Supply to Consumers
10	Power generation including propulsion and other fuel consumers
11	Fire Safety
12	Explosion protection
13	Ventilation
14	Electrical installations
15	Control, monitoring and safety systems
16	Manufacture, Workmanship and Testing
17	Drills and emergency exercises
18	Operation
19	Training
20	Personnel protection

4.1 Recommendations for EMSA Guidance Development

The final purpose of the EMSA study, after completion of the intermediate tasks, is to draw-up a goal-based Guidance addressing ships using ammonia as fuel; this will be developed and presented in deliverable of Task 6.

The structure of the Guidance will follow MSC.1/Circ.1394/Rev.2 "*Generic Guidelines for Developing IMO Goal-Based Standards*" up to Tier IV (Figure 21).

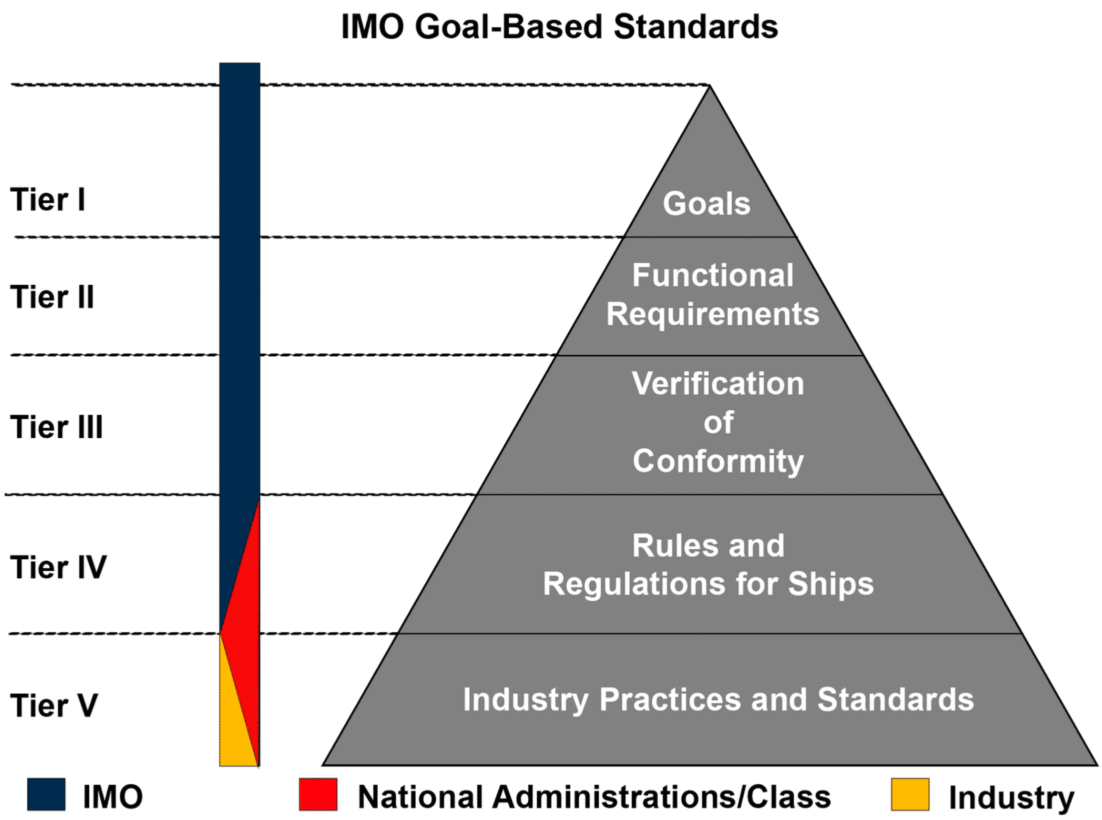

Figure 21: IMO Goal-Based Standards Framework

For the development of EMSA Guidance, it is recommended that chapters should follow the same philosophy as provided in the interim guidelines for ships using ammonia as fuel so that it remains harmonised with on-going work in IMO CCC Sub-Committee.

Each chapter will have the following structure:

1. **Hazards (1)**: each chapter to be identified with relevant hazard category such as, health, fire, explosion, corrosion that are indicated in column (1).
2. **Goals (2)**: are high-level objectives to be met and are indicated in column (2) of the table. Goals are already defined in interim guidelines and ABS Requirements (ABS, 2023a) therefore similar approach is followed.
3. **System / Equipment / Component (3)**: includes all associated equipment and systems relevant to each chapter.
4. **Functional Requirements**: Functional requirements are risk-mitigating measures or criteria to be complied with to meet the goals. Purpose of mitigation measures (4) and actions is to reduce and/or compensate the adverse effects of the hazards and risks relevant to each item. Functional requirements should be able to mitigate the hazards listed in column (1) for the relevant components in column (3). For the functional requirements to be developed in detail, risk ranking from the subsequent risk assessments and mitigation measures will be used along with the reliability analysis results.

5. **Technical Requirements (5):** shall be accompanied by a brief justification explaining the reasons why such a technical requirement is needed (e.g. based on the actual status of the technology, experience with other similar equipment or systems, best engineering practices, etc).
6. **Validation and Verification (6):** establishes methods and criteria to demonstrate and verify that the Guidance's goals and functional requirements and technical requirements are achieved. It is important to note that verification criteria of subject Guidance are not intended to verify the existing international regulations or classification rules. Tier IV of the goal-based standards will not be the test and validation layer.

The content of the Guidance will be developed in detail upon completion of next tasks based on the outcomes of the reliability analysis and risk assessments.

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IMO MSC Circulars

- MSC.1/Circ.1212/Rev.1 Revised Guidelines on Alternative Design and Arrangements for SOLAS Chapters II-1 and III
- MSC.1/Circ.1394/Rev.2 Generic guidelines for developing IMO goal-based standards
- MSC.1/Circ.1455 Guidelines for the Approval of Alternatives and Equivalents as Provided for in Various IMO Instruments
- MSC.1/Circ.1599/Rev.2 Revised guidelines on the application of high manganese austenitic steel for cryogenic service
- MSC.1/Circ.1599/Rev.3 Draft Revised guidelines on the application of high manganese austenitic steel for cryogenic service
- MSC.1/Circ.1621 Interim Guidelines for the Safety of Ships Using Methyl/Ethyl Alcohol as Fuel
- MSC.1/Circ.1622/Rev.1 Guidelines for the acceptance of alternative metallic materials for cryogenic service in ships carrying liquefied gases in bulk and ships using gases or other low-flashpoint fuels

Appendix A Ammonia Combustion and presence in the environment

Ammonia Combustion and Emissions

Using ammonia in internal combustion engines is an area of research and development that holds promise for reducing greenhouse gas emissions and promoting cleaner energy.

Ammonia can be burned either in an internal combustion engine (compression ignition with pilot fuel/spark ignition), or used in fuel cells. Currently, there is no chemical kinetic mechanism to accurately predict the behaviour of ammonia flames for a range of conditions. Slow flame velocity, high auto-ignition temperature, narrow flammability range and lower heat of combustion are issues for ammonia ignition. For ammonia to ignite, it requires a high-ignition energy in the form of either a pilot fuel or another "hot" source to ignite it. However, many different fuels can be used as pilot fuels. The best "igniters" are fuels with a high cetane number such as marine gas oil (MGO), marine diesel oil (MDO) and dimethyl ether (DME); different types of biofuels and very low sulphur oils (VLSFO) also can be used. Therefore, although ammonia is a carbon-free compound, CO_2 emissions arise from the pilot fuel.

Table 35: Key properties of ammonia in comparison to MGO

Item	Ammonia	MGO
Energy density (MJ/L)	12.9	35.95
Latent heat of vapourisation (LHV) (MJ/kg)	18.8	42.8
Heat of vapourisation (kJ/kg)	1371	250-450
Flash point (ºC)	132	65-850
Autoignition temperature (ºC)	651	250
Liquid density (kg/m3)	696 (at -33 ºC)	840 (at 15 ºC)
Adiabatic flame temperature at 1 bar (ºC)	1,800	2,000
Molecular weight (g/mol)	17.031	54
Melting point (ºC)	-77.7	-26
Boiling point (ºC)	-33	154
Flash point (ºC)	132	60
Critical temperature (ºC)	132.25	654.85
Critical pressure (bar)	113	30
Flammable range in dry air (%)	15.15 to 27.35	0.7 - 5
Minimum ignition energy (mJ)	8	0.23
Cetane number	0	40
Octane number	~130	15-25

The comprehensive combustion of ammonia is delineated by the ensuing generalised equation:

$$4NH_3(g) + 3O_2 \longrightarrow 2N_2(g) + 6H_2O(g) \qquad \text{[Eq. 3]}$$

In practical combustion scenarios, numerous byproducts emerge. Various research methodologies and approaches have investigated the reaction pathway of ammonia oxidation, culminating in proposed kinetics. For instance, Figure 22 illustrates a comprehensive model encompassing 98 elementary reactions and 22 distinct species. The use of pilot fuel increases the complexity of the combustion kinetics and the posterior reduction of multiple subproducts.

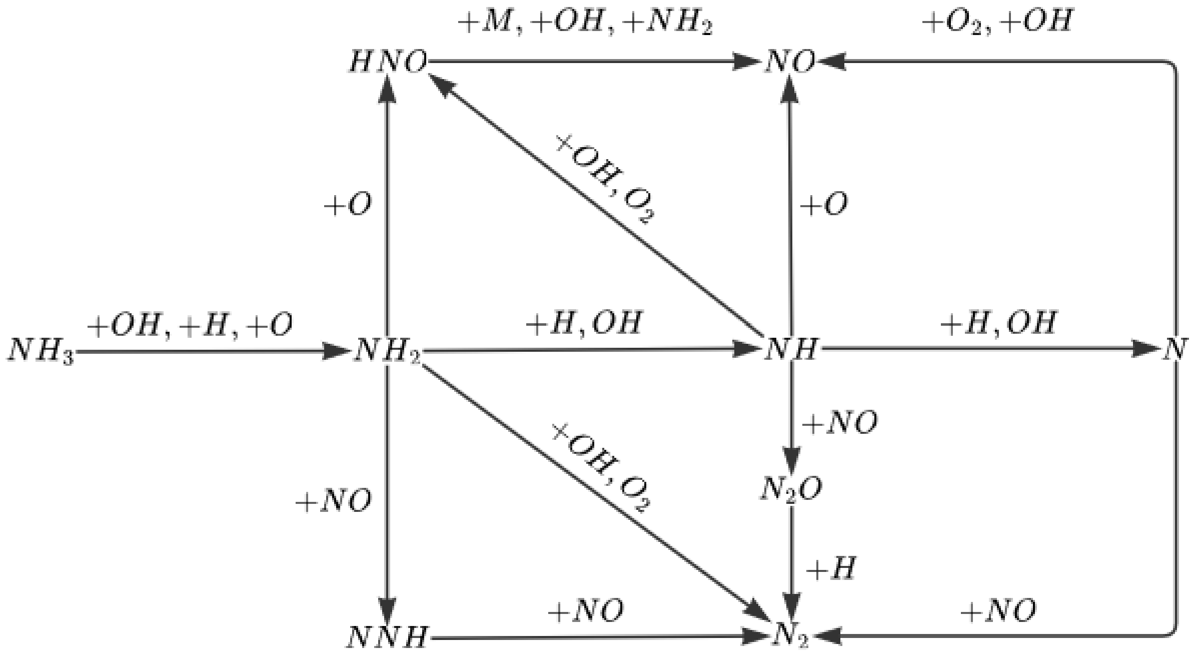

Figure 22: Diagram of ammonia oxidation pathway, Source: (Li, et al., 2021)

According to the U.S. EPA, ammonia is not considered a GHG nor a pollutant. GHG are the gases in the atmosphere that have an influence on the earth's energy balance. According to the EPA, those GHG are carbon dioxide, methane, nitrous oxide and fluorinated gases (hydrochlorofluorocarbons and hydrofluorocarbons).

Nitrous Oxides (N_2O)

When ammonia is combusted in compression ignition engines, significant amounts of NOx are generated due to the high temperatures and pressures. The latest test results from ammonia combustion using diesel cycle show a reduction of 60-70% in NOx compared to MDO, due to ammonia's high cooling effect on the combustion process. If the combustion temperature can be kept below approximately 1,300°C in the diesel process, NOx are not produced, and this seems to be the case when burning ammonia.

Nitrous oxide (N_2O) is a potent GHG with a greenhouse warming potential about 273 times greater than CO_2 for a 100-year period (Intergovernmental Panel on Climate Change, 2021). Therefore, research and development for ammonia-fuelled engines will need to deliver appropriate combustion technologies and also evaluate the exhaust emissions to ensure NOx compliance with the regulatory limits, investigate possible issues with N_2O and control unburnt ammonia to levels deemed acceptable for land-based ICEs fitted with SCR systems.

The U.S. EPA considers NO_2 as primary and secondary "criteria air pollutant" and has set National Ambient Air Quality Standards (NAAQS) for NO_2 to specify maximum amounts of NO_2 to be present in outdoor air.

Currently MAN Energy Solutions, Wärtsila, Japan Engine Corporation and WinGD are working on the final stages of the first ammonia engines with tests up to 90% ammonia and the first deliveries expected in 2024/2025. Although there is different control equipment to reduce the nitrous oxides from the exhaust gas, including electrostatic precipitator, selective catalytic reduction (SCR) and selective non-catalytic reduction, the engine manufacturers have decided to integrate an SCR system to remove the NOx formed during the combustion from the exhaust gas due to higher efficiencies compared to the other technologies. Normally the ammonia required is added by injecting a urea solution into the exhaust gas as represented in Figure 23.

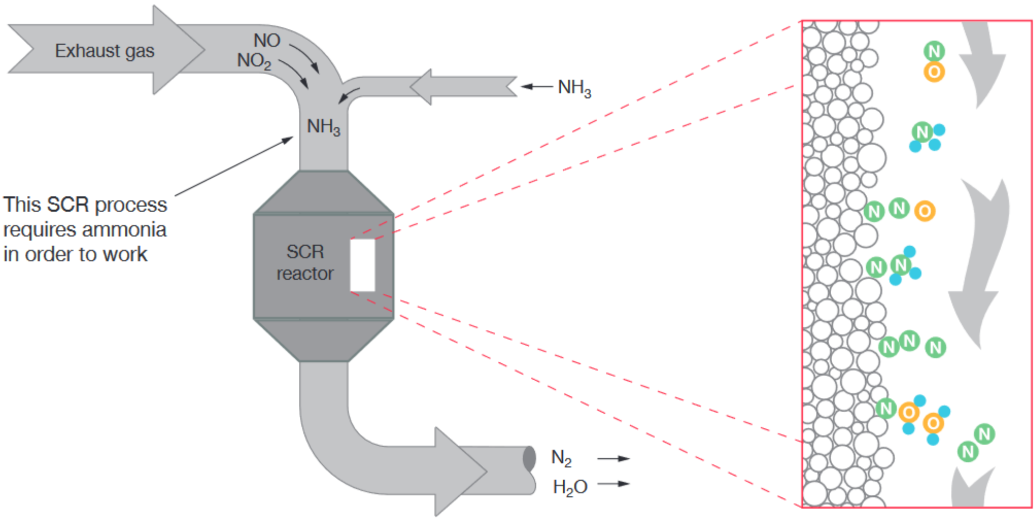

Figure 23: Selective catalytic reduction process (MAN Energy Solutions, 2023)

In the catalytic reaction, NH_3 and NO_x is converted to nitrogen and water, in accordance with the equation below:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \qquad \text{[Eq. 4]}$$

$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O \qquad \text{[Eq. 5]}$$

The reaction between NOx and NH_3 is never perfect, although the current state of the art allows efficiencies higher than 95%. This value is affected by the engine load, the ammonia injection, the droplet breakup, ammonia distribution and the exhaust temperature. The excess of ammonia that goes into the atmosphere is known as “ammonia slip”.

Ammonia Slip

Ammonia slip refers to the emissions of unreacted ammonia that result from incomplete reaction of the NOx and the reagent. Ammonia has zero Ozone Depletion Potential (ODP) and zero Global Warming Potential (GWP). ODP is the relative amount of degradation to the ozone layer it can cause, and GWP is a measure of how much infrared thermal radiation a GHG added to the atmosphere would absorb over a given time frame, compared to the same mass of added carbon dioxide. Nevertheless, ammonia’s presence in the water contributes to excessive nitrogen and leads to the eutrophication; it is also a precursor to PM 2.5. Ammonia slip can shorten the life of the reactor, cause increased corrosion, contaminate the flu ash, increase the build-up of ammonia salts in the preheater and increase ammonia release into the atmosphere, which is undesirable due to the toxicity already described.

There are two major ways to monitor ammonia slip:

- Differential Chemiluminescece with ammonia conversion. It uses two NOx monitoring analysers to measure the difference between total Nitrides and the Nitrogen Oxides (NO and NO_2)
- Tunable Diode Laser uses absorption spectroscopy for a direct concentration measurement of the ammonia.

Despite the fact that ammonia slip not yet regulated by the IMO or any other maritime regulatory body, a 10 ppm limit for ammonia slip has been set for the land-based industries by US EPA (refer to their Air Pollution Control Technology Fact Sheet; EPA-452/F-03-032).

Ammonia in the Environment

Ammonia’s presence in the atmosphere should be considered in terms of safety and environmental impacts. Once released, it often can travel in a gaseous form through the atmosphere for short or long distances. It adheres to the surfaces and can be deposited by rainfall.

Specifically, particulate matter (PM), also known as particle pollution, is a complex mixture of small solid particles and liquid droplets in the air. It is produced by primary (emitted directly) and secondary (in the atmosphere through chemical reactions) sources and separated into three main groupings based on the diameter (in microns): coarse particles (PM10), fine particles (PM2.5) and ultrafine particles (PM0.1). Ammonia contributes to 50% of PM2.5 air pollution in Europe and 30% in the U.S., which causes chronic respiratory illnesses. However, 81% of global ammonia emissions are generated from agriculture. Some of the main chemical reactions in the atmosphere involving ammonia are described below (Wyer, Kelleghan, Blanes-Vidal, Schlauberger, & Curran, 2023):

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4 \quad \text{Ammonium sulfate} \quad \text{[Eq. 6]}$$
$$NH_3 + H_2SO_4 \longrightarrow (NH_4)HSO_4 \quad \text{Ammonium bisulfate} \quad \text{[Eq. 7]}$$
$$NH_3 + HNO_3 \rightleftarrows (NH_4)NO_3 \quad \text{Ammonium nitrate} \quad \text{[Eq. 8]}$$

Ammonia is naturally introduced into water by the breakdown of waste such as food, excrement or plants. Normally, it is broken down by the biological filtration of bacteria in the nitrogen cycle.

An ammonia spill at sea can have significant negative effects on algae and marine animals due to its toxicity and ability to disrupt aquatic ecosystems. The magnitude of the impact will depend on factors such as the concentration of ammonia spill, the duration of the exposure and the sensitivity of the species in the affected area.

The toxicity of ammonia differs in humans and other mammals compared to fish and amphibians due to differences in ammonia metabolism between these categories of organisms. In humans and other mammals, ammonia is converted into urea through the urea cycle, a process known as ureagenesis. Urea is less toxic than ammonia and can be efficiently excreted through urine. Therefore, mammals have an effective mechanism for detoxifying and eliminating ammonia from the body. Fish and amphibians do not have a similar ureagenesis mechanism. Instead, they tend to primarily eliminate ammonia from their bodies by direct excretion via their gills (in fish) or skin (in some amphibians), with relatively little being lost through urine and faeces. Due to this difference in ammonia handling, they are much more sensitive to the toxicity of dissolved ammonia in the water.

Therefore, even dilute concentrations of ammonia in the water can be highly toxic to fish and other aquatic organisms. This is why ammonia is classified as “hazardous to the environment” and it is important to monitor and minimise ammonia discharges into bodies of water to protect aquatic life and maintain healthy aquatic ecosystems.

Non-ionised ammonia in surface water is toxic for fish, but ammonium ions are not. Free ammonia if formed for pH values greater than 7.5-8. On another note, ammonia may be toxic to fish and aquatic plants at levels as low as 0.2 mg/L. These values depend on the species, as represented in Table 36.

Table 36: Lethal concentrations (LC50) for some species (Bouet, 2005)

Species	Threshold	Exposure time	Concentration
Daphnids	LC50	24 hrs	27 mg.l-1
Fish	LC50	24 hrs	182 mg.l-1
Algae	LC50	5 days	185 mg.l-1

Although ammonia under suitable conditions can serve as a source of nitrogen for plants and phytoplankton and promote their growth and reproduction, when it is found at elevated levels along with other nutrients such as phosphate, it can contribute to the excessive growth of algae, often referred to as “algae blooms” or “eutrophication”. Eutrophication is more likely to occur in bodies of water with favourable environmental conditions, such as warm water, high sunlight and thermal stability. These conditions can favour the rapid growth of algae with negative impacts on aquatic ecosystems. They can deplete oxygen in the water during the decomposition of dead algae, leading to hypoxia and the mortality of fish and other organisms. Additionally, the proliferation of cyanobacteria may occur, producing toxins harmful to aquatic life and human health. In open sea waters, ammonia is quickly diluted and the polluted part can immediately start to recover.

Appendix B Toxic Areas

Table 37: Classification societies rules for toxic areas[14]

Classification Society	Rules
ABS	Consideration of toxic areas separately than hazardous areas. Gas dispersion analysis and risk assessment required to validate arrangements. Toxic areas: *To reduce the risks from potential toxic releases (generally from PRVs, hazardous space ventilation exits, bunker stations and other potential release sources protected by drip trays), the following areas are to be considered as toxic areas and are required to be located at the following minimum distances from the nearest air intake, outlet or opening to accommodation spaces, service spaces and control stations, or other non-toxic and non-hazardous areas:* *i. B or 25 m, whichever is less, from the vent mast,* *ii. 10 m from,* ■ *Entrances to the spaces containing potential source of ammonia release,* ■ *Ventilation outlets from secondary enclosures around ammonia piping and from the spaces containing potential source of ammonia release,* ■ *Bunker manifold valves and all other flange connections of ammonia fuel piping as well as from the spillage coamings surrounding it,* ■ *Engine exhaust exits, crankcase and sump tank vent outlets, as applicable,* *iii. 5 m from the vent outlets of ammonia drain tank(s) and auxiliary circuits of engines.* *Vent mast is to be arranged at least B/3 or 6 m, whichever is greater, above the open deck and 6 m from working areas and gangways. In addition, all other vent and ventilation pipes listed in 12/6.4 are to be arranged at least 4 m above the open decks, working areas, walkways and/or gangways.*
BV	Require specific drawings to be submitted for dangerous areas with respect to ammonia toxicity (apart from hazardous areas) but do not include prescribed requirements and distances. Dispersion analysis is required for the definition of dangerous areas around bunkering connections.

[14] Table is created for information purposes.

Classification Society	Rules
DNV	Separate definition for toxic zones Gas dispersion analysis required Safe distances: ■ *The outlet from the vent mast shall be located at least B (greatest moulded breadth) or 25 m, whichever is less, from the nearest air intake, air outlet or opening to enclosed spaces on the vessel.* ■ *Safety distances for vent systems fitted with arrangements to reduce the amount of ammonia being discharged to open air will be evaluated on a case-by-case basis.* ■ *Vent outlets from secondary enclosures around ammonia piping shall discharge at least 10 m away from the nearest air intake, air outlet or opening to enclosed spaces on the vessel.* ■ *All ventilation outlets from spaces designed to safely contain potential ammonia leakages shall discharge at least 10 m away from the nearest air intake, air outlet or opening to other enclosed spaces on the vessel.* ■ *Air intakes to the same space shall be arranged to prevent recycling of ventilation air. The ventilation system exhaust ducts shall discharge at least 4 m away from decks and gangways.* ■ *For ammonia fuel tanks arranged on open deck and not fitted with tank connection spaces, the drip tray covering the tank valves and the tank hatch shall be at least 10 m away from the nearest air intake, air outlet or opening to enclosed spaces on the vessel.* ■ *Spillage coamings surrounding gas bunker manifold valves shall be located at least 10 m away from the nearest air intake, air outlet or opening to enclosed spaces on the vessel.* ■ *Fuel preparation room and tank connection space entrances on open deck shall be located at least 5 m away from the nearest air intake, air outlet or opening to enclosed spaces on the vessel.* ■ *Where single-walled bunkering pipes are applied, drip trays below flanges shall be located at least 10 m away from the nearest air intake, air outlet or opening to enclosed spaces on the vessel.* ■ *The outlet from the fuel tank pressure relief valves shall be located at least B/3 or 6 m, whichever is greater, above the weather deck and 6 m above the working area and gangways, where B is the greatest moulded breadth of the ship in meters.*

Classification Society	Rules
KR	Specific requirements for toxic zones The toxic zone is defined as the area where the concentration of ammonia gas can be maintained up to 25 ppm. *Toxic zone includes, but is not limited to:* *1. Enclosed and semi-enclosed areas where gas leak sources are installed* *2. the following areas on open dock where gas leak sources are installed* *(1) area within 10 m from the ventilation outlet of the area specified in Para1* *(2) area within 6 m from other openings in spaces specified in Para 1.* *(3) area within 25 m from vent mast outlet, however, in case of emergency, the toxic zone is determined in accordance with Para 3.* *(4) area within 10 m from coaming surrounding bunkering manifold* *(5) area within 10 m from release sources such as valves, flanges, etc. of fuel piping on open deck* *3. As an alternative to the definition in Para 2, the area on the open deck where the concentration of ammonia gas is greater than 25 ppm from the following gas release sources through gas dispersion analysis based on the most stringent boundary conditions.* *(1) ventilation outlet or other openings of the spaces specified in Para 1* *(2) vent mast exit* *(3) bunkering manifold* *(4) release sources such as valves, flanges, etc. fuel piping on open deck*

Classification Society	Rules
LR	Separate classification of toxic areas *LR 12.6-01 Toxic area zones shall be specially considered in accordance with the risk assessment required by 4.2 Risk assessment and Risk Based Certification (RBC) in Part A of this Appendix, and the safeguards considered necessary to prevent toxic injury are to be established.* *LR 12.6-02 Zone A toxic areas include the interiors of fuel tanks, equipment and pipework containing fuel, and any pipework for pressure-relief or other venting systems for fuel tanks, pipes and equipment containing fuel.* *LR 12.6-03 Zone B toxic areas include areas or spaces in which potential leak sources are located, including the interiors of ducts and double pipes and areas in the vicinity of openings and outlets from such areas and spaces.* *LR 12.6-04 Vent mast outlets shall be arranged according to the following:* *1. equal to B or 25 m, whichever is less, from the nearest air intake, outlet or opening to accommodation spaces, service spaces, control stations and other non-toxic and non-hazardous areas, exhaust outlets from machinery installations, or areas where unprotected persons may be present; and,* *2. at least B/3 or 6 m, whichever is the greater, above the open deck, working areas, walkways and access gangways or areas where unprotected persons may be present.* *LR 12.6-05 All other vent outlets shall be arranged according to the following:* *1. at least 15 m from the nearest air intake, outlet or opening to accommodation spaces, service spaces, control stations and other non-toxic and non-hazardous areas, exhaust outlets from machinery installations, or areas where unprotected persons may be present; and,* *2. at least 6 m above working areas, walkways and access gangways.* *LR 12.6-06 All ventilation outlets from toxic areas shall be arranged according to the following:* *1. at least 15 m from the nearest air intake, outlet or opening to accommodation spaces, service spaces, control stations and other non-toxic and non-hazardous areas, exhaust outlets from machinery installations, or areas where unprotected persons may be present; and,* *2. at least 6 m above working areas, walkways and access gangways.* *LR 12.6-07 Bunkering manifolds shall be arranged according to the following:* *1. at least 15 m from the nearest air intake, outlet or opening to accommodation spaces, service spaces and control stations, exhaust outlets from machinery installations, or areas where unprotected persons may be present.*
NK	No separate toxic areas/zones classification. One common definition for hazardous areas to minimize the impact of toxicity on ships and people.

Classification Society	Rules
RINA	No reference to toxic areas/zones.

Table 38: Comparative table for toxic areas requirements between classification societies[15]

EXTENT OF TOXIC AREAS (in meters)							
Point of potential ammonia occurrence		Classification Society					
		ABS	DNV	LR	KR	BV	NK
1	Vent mast	B or 25	B or 25	B or 25	25	B or 25	B or 25
2	Vent pipe from fuel piping/system	-	-	-	-	-	10
3	Space entrances	10	5	-	6	-	-
4	Ventilation outlets of the space	10	10	15	10	-	10
5	Ventilation outlet from the secondary enclosure of double-wall piping system	10	10	15	-	-	10
6	Ventilation inlets to the space	-	-	-	6	-	-
7	Bunker manifold valves and flanges	10	10	15	10	-	-
8	Bunkering coaming	10	10	-	10	-	-
9	Engine exhaust, crankcase/sump tank vent	10	-	15	-	-	-
10	Vent pipe from bilge/drain tank or auxiliary system expansion tank	5	-	-	-	-	-
11	Other opening of the space	-	-	-	6	-	-
12	Drip trays covering pipe flanges, tank valves and tank hatch on open deck	-	10	-	10	-	-

NOTES:

1. Lengths in meters in the table are the extent of toxic areas and demonstrate the minimum distances required from the nearest air intake, outlet or opening to accommodation spaces, service spaces and control stations, or other non-toxic and non-hazardous areas.
2. Similar requirements exist between Class Societies for distances of ammonia releases above the weather deck, working areas and walkways; B/3 or 6 meter, whichever is greater, for the vent mast and 4 meter for all other ventilation and vent outlets.

DEFINITIONS:

1. Space: Space means enclosed or semi-enclosed spaces with source of ammonia release/leakage
2. B: Breadth of the vessel

[15] Table is created for information purposes.

Appendix C Gap Analysis (Laursen, et al., 2022)

No Gap or Changes needed to address ammonia
Small Gap or Minor Change to address ammonia
Medium Gap or Some Challenging Change to address ammonia
Large Gap or Many Challenging Changes to address ammonia

Subject	Rule/Guidance	Comment on Code/Standard – Gaps (2022)	Updates (2023)
Sustainability and Emissions Regulations	EU 'Fit-for-55' Fuel EU Maritime	– Focus is only on decarbonised (green) ammonia produced from hydrogen – Focus is on well-to-wake emissions	– Includes also ammonia from natural gas – For green ammonia there are no well to tank values, they are not available – Methane and nitrous oxide are not available yet for ammonia produced by fossil or e-ammonia
	EU Emissions Trading System (ETS)	– Not directly applicable to shipping industry (until 2023 adoption of the 'Fit-for-55' package) – Only focused on tank-to-wake emissions, does not incorporate emissions from consumption	– ETS has not defined the treatment of RFNBOs whether the CF_CO2 will be zero
	EU Energy Taxation Directive	– Maritime sector fully exempt – Member states independently implement national policy	– There is the intention to offer incentives for e-fuels/alternative fuels – Increase the taxation of fossil – However the subject is paused for the moment
	EU RED III	– Divided incentives for shipowners and operators do not stimulate the deployment of renewable fuels – Member states independently implement national policy	– EU RED III will set the regulatory framework for the e-fuels
	MARPOL Annex VI EEDI, EEXI, CII & DCS	– No explicit provision in the IMO regulations and guidelines for the direct use of an ammonia carbon factor in EEDI, EEXI, CII and DCS – Provision for well-to-wake emissions considerations should be considered in these instruments	MEPC 80 adopted the Resolution MEPC.376(80) "Guidelines on Life Cycle GHG Intensity of Marine Fuels (LCA Guidelines)". LCA Guidelines are to address: – Well-to-Tank (WtT), Tank-to Wake (TtW), and Well-to-Wake (WtW) GHG intensity and sustainability aspects for marine fuels/energy carriers for ship propulsion/power generation. LCA Guidelines are to cover: – Complete fuel life cycle from feedstock, extraction, conversion to a fuel product, transportation to fuel utilization by the ship, – Specify sustainability themes/aspects for marine fuels and define a Fuel Lifecycle Label (FLL), – GHG emission factors, information on fuel blends and sustainability themes/aspects, – Elements of the FLL subject to verification/certification, and certification standards and procedures. LCA Guidelines specified carbon factor for synthetic ammonia
	MARPOL Annex VI and NOx Technical Code (NTC)	– Requires NTC amendment to include NH_3 analysers, measurement and calculation provisions for ammonia as fuel to enable NOx certification to regulation 13. – Air emissions limits for NH_3 and N_2O from marine engines, and associated measurement and calculation procedures, are missing from Annex VI and the NTC. – Regulation 18 of Annex VI would benefit from clarification on BDN and fuel sampling obligations for ammonia as fuel. – Application of ammonia as fuel (particularly for retrofits) would benefit from clarification on application of regulation 18.3.2.2 for NOx implications where ammonia is derived from methods other than petroleum refining. – No limits or guidelines exist for environmental impacts of potential NH_3 emissions to water in normal or emergency operations from exhaust cleaning or fuel-system cleaning systems. Precedent exists for water quality limits for SOx EGCS under Annex VI but unclear which.	No updates noted related to ammonia.

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Subject	Rule/Guidance	Comment on Code/Standard – Gaps (2022)	Updates (2023)
	ISO 17179:2016 - Stationary source emissions - Determination of the mass concentration of ammonia in flue gas - Performance characteristics of automated measuring systems	– May be considered or referenced in development of IMO marine standards.	No updates noted related to ammonia.
	ISO 21877:2019 - Stationary source emissions - Determination of the mass concentration of ammonia – Manual method		
Storage – Land	ANSI K61.1-1999 / CGA G-2.1 Requirements for the Storage and Handling of Anhydrous Ammonia	– Not applicable to ammonia storage on ships.	No updates noted related to ammonia.
	U.S. 33 U.S.C. §1251 – Clean Water Act	– No significant gaps for supporting the application of ammonia.	No updates noted related to ammonia.
	U.S. EPA 822-R-18-002 - Aquatic Life Ambient Water Quality Criteria for Ammonia - Freshwater 2013		
	U.S. 40 CFR Ch. I Subchapter J Part 372 - Toxic Chemical Release Reporting: Community Right-To-Know		
Storage – Onboard	IMO IGF Code	– IGF Code Part A-1 prescriptive provisions are specifically for natural gas (methane). Alternative Design process enables approval of other gases and low-flashpoint fuels but could be revised to include specific provisions for ammonia in the longer term. Development of interim guidelines for ammonia is now added to the CCC workplan, commencing CCC 8 in September 2022.	– CCC 9 held in September 2023, decision made that the prepared draft interim guidelines to be further developed. – Amendments to the IGF Code for the introduction of the high manganese austenitic steel have been adopted and added as a new construction material to construct fuel containment and piping systems in addition to corrosion test for ammonia compatibility, subject to requirements specified in MSC.1/Circ.1599/Rev.2, and guideline MSC.1/Circ.1622 as amended by MSC.1/Circ.1648.
	IMO IGC Code	– Provisions could be added to allow toxic anhydrous ammonia to be used as fuel. Review of IGC Code is now added to the CCC workplan, commencing CCC 8 in September 2022.	– CCC 9 Group considered modification to 16.9.2 of the IGC Code on exemption of "Ammonia, anhydrous" from the toxic products. In this respect, the Group felt the need to develop guidelines for ensuring the same level of safety as natural gas (methane) for the use of cargoes identified as toxic products which are required to be carried in type 2G/2PG ships, as fuel. – CCC 9 Group agreed with the modifications accepting high-manganese austenitic steel as being suitable for ammonia service and, in particular, that the post-weld stress relief heat treatment specified as an option in 17.12.2.2 of the IGC Code should be waived for the use of this material with ammonia on IGC Code ships. Revised Guidelines MSC.1/Circ.1599/Rev.2 with a view to approval by MSC 108 and circulation as MSC.1/Circ.1599/Rev.3.
	U.S. CFR 46 98.25 Shipping: Anhydrous Ammonia in Bulk	– No details of anhydrous ammonia as marine fuel. – National regulation not applicable to international vessels.	No updates noted related to ammonia.
	U.S. CFR 46 151.50-32 Shipping: Barges Carrying Bulk Liquid Hazardous Material Cargoes: Ammonia, Anhydrous	– No details of anhydrous ammonia as marine fuel. – National regulation not applicable to international vessels.	No updates noted related to ammonia.
Quality	International Bunker Industry Association	– No specific guidance for ammonia. Missing ISO fuel quality standard together with missing BDN and sampling requirements under Annex VI Regulation 18 hinders consistent implementation.	No updates noted related to ammonia.
	ISO 8217:2017 Petroleum Products - Fuels (class F) - Specifications of Marine Fuels	– Not applicable to and does not discuss ammonia marine fuel. – Additional provisions for ammonia as marine fuel could be developed as a new standard.	No updates noted related to ammonia.

Subject	Rule/Guidance	Comment on Code/Standard – Gaps (2022)	Updates (2023)
	ISO 7103:1982 - Liquefied anhydrous ammonia for industrial use – Sampling - Taking a laboratory sample	– May be referenced in marine standards.	No updates noted related to ammonia.
	ISO 7106:1985 - Liquefied anhydrous ammonia for industrial use - Determination of oil content - Gravimetric and infra-red spectrometric Methods	– May be referenced in marine standards.	No updates noted related to ammonia.
	ISO 7105:1985 - Liquefied anhydrous ammonia for industrial use - Determination of water content – Karl Fischer method	– May be referenced in marine standards.	No updates noted related to ammonia.
	IMO MARPOL Annex VI	– Regulation 18 for fuel oil availability and quality requires onboard fuel to be tested for sulphur content and seal-fuel samples for the record. While regulation 18.4 exempts gas fuels from BDN and fuel sample requirements, regulation 18 would benefit from explicit clarification on BDN and fuel-sampling obligations for ammonia as fuel.	No updates noted related to ammonia.
Transportation & Handling	ASME B31.3-2020 Process Piping	– Not specific to marine, may be referenced in marine standards.	No updates noted related to ammonia.
	ISO 6957:1988 - Copper alloys - Ammonia test for stress corrosion resistance	– May be referenced in marine standards.	No updates noted related to ammonia.
	ISO 5771:2008 - Rubber hoses and hose assemblies for transferring anhydrous ammonia	– Subject limited to hose performance and hose assemblies, may be referenced in marine standards.	No updates noted related to ammonia.
	SIGTTO Liquefied Gas Sampling Procedures	– Not applicable to ammonia. SIGTTO could produce similar recommendations for ammonia gas cargo or fuel.	No updates noted related to ammonia.
	U.S. CFR § 130.230 – Protection from Refrigerants	– National regulation not applicable to international vessels – Not specific or considering marine applications.	No updates noted related to ammonia.
	U.S. CFR 29 1910.111 Occupational Safety and Health Standards: Storage and Handling of anhydrous ammonia	– Not specific to marine, may be referenced in marine standards.	No updates noted related to ammonia.
Bunkering	ISO 20159:2021 - Ships and Marine Technology - Specification for bunkering of liquefied natural gas fuelled vessels	– Not applicable to liquefied anhydrous ammonia. Could be modified or used to develop liquefied ammonia bunkering guidelines.	No updates noted related to ammonia.
	ISO/TS 18683:2021 - Guidelines for safety and risk assessment of LNG fuel bunkering operations		No updates noted related to ammonia.
	ISO 21593:2019 - Ships and Marine Technology - Technical requirements for dry-disconnect/connect couplings for bunkering liquefied natural gas	– Not applicable to liquefied anhydrous ammonia. Could be modified or used to develop liquefied ammonia bunkering coupling standard.	No updates noted related to ammonia.
	IBIA Future Fuels Working Group	– Currently undertaking the assessment of ammonia fuel and associated technologies; results to be released.	No updates noted related to ammonia.
	SIGTTO Ship/Shore Interface for LPG/Chemical Gas Carriers and Terminals	– SIGTTO publications address liquefied gases including anhydrous ammonia, so no big gaps, but it could provide specific guidance for ammonia gas cargo or fuel.	No updates noted related to ammonia.
	SIGTTO Recommendations for Liquefied Gas Carrier Manifolds		
	SIGTTO Liquefied Gas Handling Principles on Ships and Terminals (LGHP4)		
	SIGTTO, CDI, ICS, OCIMF: Ship to Ship Transfer Guide for Petroleum, Chemicals and Liquefied Gases	– Could be modified or used to develop recommendations for ammonia bunkering.	No updates noted related to ammonia.

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Subject	Rule/Guidance	Comment on Code/Standard – Gaps (2022)	Updates (2023)
	SGMF Bunkering Area Safety information LNG	– Not applicable to ammonia. SGMF could expand these tools and guidelines, or develop new ones, to cover ammonia as fuel.	No updates noted related to ammonia.
	SGMF FP05-01 Ver1.0 Gas as a marine fuel: Recommendation of Controlled Zones during LNG bunkering; May 2018		
	SGMF FP07-01 Ver3.0 LNG as a marine fuel: Safety and Operational Guidelines - Bunkering; December 2021		
	SGMF FP-08-01 Ver1.0 Gas as a marine fuel: Simultaneous Operations (SIMOPs) during LNG bunkering; May 2018		
	SGMF FP05-01 Ver1.0 Gas a marine fuel: Contractual guidelines; September 2015		
	SGMF TGN06-04 Ver1.0 Gas as a marine fuel: manifold arrangements for gas-fuelled vessels; May 2019		
	SGMF TGN06-06 Ver1.0 Gas as a marine fuel: LNG bunkering with hose bunker systems: considerations and recommendations; February 2020		
	SGMF TGN06-07 Ver1.0 Gas as a marine fuel: Bunker station location: Considerations and Recommendations: January 2021		
	EMSA *Guidance on LNG Bunkering to Port Authorities and Administrations*; January 2018	– Not applicable to ammonia. EMSA could expand or use this tool to develop ammonia guidance.	No updates noted related to ammonia.
Use & Consumption	IMO IGF Code	– IGF Code Part A-1 prescriptive provisions are specifically for natural gas (methane). Alternative Design process enables approval of other gases and low-flashpoint fuels, but it could be revised to include specific provisions for ammonia in the longer term. Development of interim guidelines is now added to the CCC workplan, commencing CCC 8 in September 2022.	– CCC 9 held in September 2023, decision made that the prepared draft interim guidelines to be further developed.
	IMO MARPOL Annex VI and NOx Technical Code	– Could include specific provisions for using and consuming anhydrous ammonia onboard ships. – Air emissions limits for NH_3 and N_2O from marine engines, and associated measurement and calculation procedures, are missing from Annex VI and the NTC. To consider in service monitoring of NH_3 emissions. – Regulation 18 of Annex VI would benefit from clarification on BDN and fuel-sampling obligations for ammonia as fuel. – No limits or guidelines exist for environmental impacts of potential NH_3 emissions to water in normal or emergency operations from exhaust- cleaning or fuel-system cleaning systems. Precedent exists for water quality limits for SOx EGCS under Annex VI but unclear which is appropriate instrument to regulate NH_3 discharges to water.	No updates noted related to ammonia.
	ISM Code	– Development of operational requirements under IGF Code, or Interim Guidelines, would facilitate operators undertaking obligations under ISM Code.	No updates noted related to ammonia.
	IMO STCW Convention	– Regulation for training of crew for IGF Code ships exists under STCW Convention. Question mark remains on application of ammonia under IGF Code, but development of training courses by flag Administrations is still required to enable crew certification for ammonia as fuel under STCW.	No updates noted related to ammonia.

Subject	Rule/Guidance	Comment on Code/Standard – Gaps (2022)	Updates (2023)
	SIGTTO ESD Systems - Recommendations for Emergency Shutdown and Related Safety Systems	– SIGTTO publications cover gas carriers and carriage of anhydrous ammonia but would benefit from specific consideration for ammonia gas cargo or fuel.	No updates noted related to ammonia.
	SIGTTO Recommendations for Relief Valves on Gas Carriers		No updates noted related to ammonia.
	SIGTTO Guidelines for the Alleviation of Excessive Surge Pressures on ESD for Liquified Gas Transfer Systems		No updates noted related to ammonia.
	SGMF FP00-01-06 Ver4.0 LNG as a marine fuel: An Introductory Guide; June 2021	– Not applicable to ammonia. SGMF could expand, or develop new, publications for ammonia as fuel.	– ABS acknowledged initiation of a workgroup by SGMF to develop a publication for ammonia as fuel.
	SGMF FP10-01 Ver1.0 Gas as a marine fuel: Work practices for maintenance, repair and dry-dock operations; May 2020		
	SGMF FP14-01 Ver1.0 Gas as a marine fuel: Operations of ships with Liquefied Natural Gas (LNG) competency and assessment guidelines; May 2021		
	SGMF TGN06-05 Ver1.0 Gas as a marine fuel: recommendations for linked emergency shutdown (ESD) arrangements for LNG bunkering; May 2019		
	IACS Unified Requirement M57 *Use of ammonia as a refrigerant*; 1993	– No significant gaps for supporting the application of ammonia as a refrigerant, however this publication has not been updated since original publication in 1993 and would benefit from updating.	
	IMO draft *Interim Guidelines for the Safety of Ships using Fuel Cell Power Installations*	– No significant gaps for supporting the application of marine fuel cells, however these guidelines do not cover fuel storage and distribution and therefore application is limited by lack of those IMO requirements.	
	IACS UR M78 *Safety of Internal Combustion Engines Supplied with Low Pressure Gas*	– Does not cover high pressure and cross-head (2-stroke slow speed) engines burning methane. – Does not cover other low-flashpoint fuels. – Could be updated to include all engine types and fuels in a more general way.	
	IACS Recommendation No.146 *Risk assessment as required by the IGF Code*.	– Could be updated to include specific requirements for ammonia.	
	IACS Recommendation No. 142 *LNG bunkering guidelines*	– Could be updated to cover bunkering guidelines for all liquefied gases or new publication could be developed.	
	IACS Recommendation Nos.26, 27 and 30; recommended spare parts for IC main and auxiliary engines and essential auxiliary machinery	– Could be updated to cover spare parts for DF engines and fuel supply systems.	
	IACS Recommendation No.138 Recommendation for the FMEA process for diesel engine control systems	– Could be updated to cover DF engines and fuel supply systems.	
	IACS Classification Societies Rules	– Harmonisation of class society rules or guidelines, through the development of URs, would facilitate harmonised application of ammonia as fuel.	– CCC 9/INF.16 submitted by IACS to the Group to provide information on gap analysis between ammonia as fuel and the IGF Code for LNG, taking into account the different properties, behaviours and hazards/risks.

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