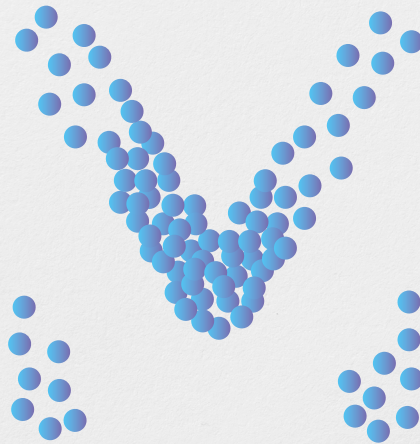




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A M M O N I A

AN INTRODUCTION TO AMMONIA
ACCIDENTAL RELEASE PREPAREDNESS AND RESPONSE

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SGMF is a collaborative, inclusive, membership-based non-governmental organisation (NGO).

We support the adoption of low and zero carbon marine fuels by developing and sharing industry best practice and fact-based knowledge. Our organisation advocates the use of these fuels only when done safely, responsibly and sustainably.

SGMF's mission is to facilitate the maritime sector's transition towards decarbonisation. For us, the future is clear.

More information on our organisation is available at: <https://www.sgmf.info>

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Yara Clean Ammonia



ABOUT THIS PUBLICATION

This publication serves as a comprehensive overview of the objectives and approach to preparedness and response in case of accidental ammonia release and mitigation of consequences (see figure 1 and Appendix A1 **A1 - Bowtie models**).

While the following is important in determining any preparedness and response, this document is agnostic about:

- whether or not the release is during normal operations, such as bunkering, fuel handling and preparation, and maintenance
- where the release is located on board the vessel, such as manifold, tanks, fuel preparation spaces and machinery spaces
- where the vessel is located, i.e. at sea, or in port and anchor

An Introduction to Ammonia Accidental Release Preparedness and Response offers a high-level overview of the topic. Its primary objective is to provide key knowledge that will aid the maritime industry in its development and adoption of ammonia as an alternative marine fuel.

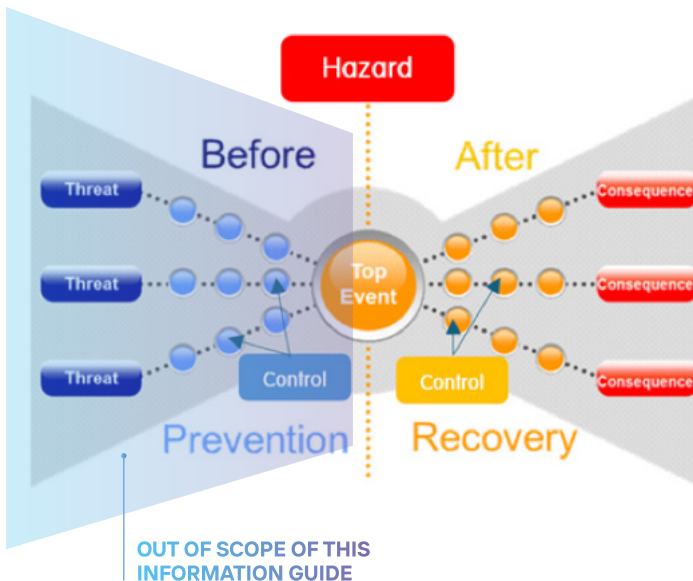


Figure 1 - Scope of this Introductory Guide

CONTENTS



Disclaimer	2
Acknowledgements	2
About this publication	3

INTRODUCTION TO AMMONIA

Introduction	5
Overview	5
What is Ammonia?	6
Ammonia properties	7
Ammonia Release Types and Behaviour	9
Ammonia vapour suppression by water spray	9
Ammonia recondensing	11
Release consequences	11

SAFTEY

Release preparedness and response	14
Key stakeholders	14
Hazard and safety zones	15
Release response objectives	18
Objective 1 - Minimising the amount released	19
Objective 2 – Contain any released liquid	22
Objective 3 – Minimise further vapour generation	23
Objective 4 – Reduce people's exposure to toxic vapour	24
Other Considerations	28
Fire and explosion	28
First aid	28
Decontamination	29
Communications	29
Competency and training	29
Appendices	30
A1 - Bowtie models	30
A2 - Hierarchy of controls	32
A3 - Application of the hierarchy of controls on board ammonia-fuelled vessels	35
A4 – AEGL (acute exposure guideline limits)	37

INTRODUCTION



OVERVIEW

Ammonia serves as a valuable resource in various industries and is frequently transported in bulk at sea. However, its successful adoption and sustainable use as a maritime fuel depend on the ability to demonstrate that it can be safely handled and used in critical locations like ports, harbours and on board vessels, all while safeguarding both human health and the environment.

Unlike conventional fuels where flammability is generally the key hazard, ammonia is toxic by inhalation, with limited flammability. This distinction necessitates a shift in safety management perspective away from fire and explosion hazards to a focus on toxicity.

In practical terms, safety management for ammonia aims to eliminate or reduce hazards and risks by implementing the hierarchy of controls (see Appendix A2 - Hierarchy of controls, including:

- The application of design and engineering practices: Employing sound design and engineering principles, such as the International Maritime Organization (IMO) International Code of Safety for Ships Using Gases or Other Low-flashpoint Fuels (IGF Code) gas-safe concept, to mitigate risks.
- The introduction of effective inspection and maintenance regimes: Establishing robust inspection and maintenance procedures to ensure the ongoing integrity of machinery and systems, emphasising process safety.
- Effective leakage detection and isolation: Implementing reliable systems for detecting and promptly isolating ammonia leaks to minimise the leak inventory/volume.
- Effective containment of liquid and minimising vapour generation to reduce personnel exposure.
- Establishing comprehensive emergency procedures: Developing well-defined emergency protocols that include prioritised objectives, including safe evacuation routes, and designated safe haven(s)/refuge(s), to manage any potential incidents.

This publication does not directly address the causes and prevention of ammonia releases. The information provided is based on the best practice of the ammonia production industry and the experience gained from the initial ammonia bunkering trials in Singapore, to help the reader decide what they need to consider when preparing for, and responding to, any ammonia release.

WHAT IS AMMONIA?

NH_3

Ammonia (NH_3) is a chemical compound composed of nitrogen and hydrogen atoms. In ammonia, each nitrogen atom forms bonds with three hydrogen atoms. This molecular structure makes ammonia an efficient hydrogen carrier, with approximately 10.7 kilograms of hydrogen contained in 100 litres of liquid ammonia.

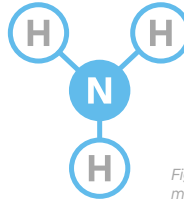


Figure 2 - Ammonia molecular structure

Ammonia is a naturally occurring compound that plays a crucial role in the environment, serving as a vital source of nitrogen for both plants and animals. In agriculture, ammonia is instrumental as a precursor for nitrogen-based fertilisers, supporting the growth of approximately 45% of the world's food crops.

Beyond agriculture, ammonia finds extensive industrial applications, such as serving as a refrigerant in various industrial processes, as well as in cleaning agents and as a key starting point in the production of pharmaceutical products.

AMMONIA PROPERTIES

The physical and chemical properties of ammonia are crucial factors to consider when reviewing the preparedness and response to an ammonia release.

Physical state: At normal ambient temperatures, ammonia exists as a colourless gas with a distinctive, pungent odour - which is caused by its chemical properties and not the result of any 'stenching agent'. It can readily condense into a liquid state under moderate pressure and ambient temperature (approximately 7.5 bar(g) at 20°C) or when cooled to around -33°C at atmospheric pressure.

The energy required to turn it from liquid to gas (heat of vaporisation) is relatively high. 1369kJ of energy is required to turn 1kg (approximately 1.5 litres) of liquid ammonia to 1.3m³ gas, as its expansion ratio is 1/850. By comparison, only 551kJ of energy is required to turn 1kg (approximately 2.2 litres) of liquefied natural gas (LNG) into 1.3 m³ gas at its expansion ratio of 1/600.

This, combined with its low boiling point, makes ammonia a good refrigerant. However, these properties also make it difficult for it to sustain combustion. Turning enough liquid into gas to achieve and maintain the low flammability limit requires a continuous and substantial energy source.

Solubility: Anhydrous ammonia, or ammonia gas, has significant solubility in water, which decreases as temperature increases. Approximately 700g of ammonia can be dissolved in 1kg of water at 10°C. With water at 30°C, it drops to 400g of ammonia.

Chemical reaction in water: When ammonia dissolves in water, it forms ammonium hydroxide (NH_4OH), also known as ammonia solution or aqueous ammonia. This solution is alkaline (a base) rather than acidic and potentially toxic to aquatic life and humans. This dissolution process is exothermic, releasing a significant amount of heat. It should be noted that this is an easily reversible reaction, and ammonia will easily evaporate from ammonium hydroxide.

Ammonia toxicity: Ammonia is a compound that can be toxic to humans and animals in certain concentrations. Toxicity classification is typically defined by regulatory agencies and organisations as a function of concentration (particles per million (ppm)) and exposure duration (time). One of the definitions used for ammonia is the one available from the United States Occupational Safety and Health Administration (OSHA), which classifies the toxicity of ammonia as follows:

Acute toxicity: Ammonia is toxic through inhalation and high concentrations of ammonia vapour can cause immediate irritation of the eyes, nose, throat and respiratory tract. Exposure to high concentrations can result in severe respiratory distress, lung damage and even death (see Appendix A4 – AEGL (acute exposure guideline limits)).

Chronic toxicity: Prolonged or repeated exposure to ammonia can lead to chronic health effects. These can include respiratory issues such as bronchitis and long-term damage to the respiratory system. Threshold limit value (TLV) is a level of occupational exposure to a hazardous substance at or below which it is believed that nearly all healthy workers can repeatedly experience exposure to the substance without adverse effects.

The American Conference of Governmental Industrial Hygienists (ACGIH) has set the TLV during 8 hours of exposure to ammonia to 25ppm.

Ammonia flammability: The US National Fire Protection Association (NFPA) classifies ammonia as flammable. However, to initiate ignition:

- First, the lower flammable limit (LFL) must be reached, which at 16% is approximately three times higher than for methane. This may only be achieved through release in a confined space, or in an open space with enough heat input to increase the vaporisation rate, and
- Second, a sufficiently high source of ignition is required (approximately 1,000 times higher than that of methane and roughly 10,000 times higher than hydrogen).

In an open space, the likelihood of igniting an ammonia gas cloud is low. If the vaporisation rate from a potential liquid pool is not sustained at a high enough level, by either an external heat source or very large surface area, for a vapour cloud to sustain LFL, then the vaporisation reduces, the LFL is no longer obtained, and combustion ceases naturally.

As it is exceptionally challenging to ignite, the International Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk (IGC Code) does not require flammable gas detection for ammonia carriage. (However, it must be acknowledged that explosions have been reported, primarily in confined spaces, when a substantial leak has led to the presence of at least 16% ammonia in the air (the LFL) along with a strong enough ignition source.)

In addition, the flame front speed being extremely low, the potential for blast wave generation is significantly reduced. So, in comparison to methane, ammonia does present a lower, yet still evident, risk of explosion.

AMMONIA RELEASE TYPES AND BEHAVIOUR



There are three different types of ammonia releases: liquid, aerosol (two-phase), and vapour.

LIQUID RELEASE

Only with ammonia at -33°C or colder The mass flow (kg/s) of a liquid release is determined by:

- Pressure
- Static head
- Density
- Hole diameter and shape
- Viscosity

The velocity of the liquid release also determines its form:

- Low velocity = will remain liquid, will fall to ground.
- High velocity = high mechanical break-up leading to a spray or two-phase/aerosol release (a mixture of vapour and liquid).

AEROSOL RELEASE

There are two mechanisms that can lead to a two-phase/aerosol release:

- A leak of warm ammonia liquid (warmer than -33°C) flashing off
- Cold ammonia -33°C or less at high velocity resulting in high mechanical break-up

VAPOUR RELEASE

The mass flow (kg/s) is determined by:

- Pressure
- Temperature
- Molecular weight
- Hole diameter and shape
- Surface area (pool)

AMMONIA VAPOUR SUPPRESSION BY WATER SPRAY

The use of water as a response tactic for an ammonia leak must be assessed and carefully considered to determine the most positive outcome for personal safety, environmental impact, and property damage. The automatic application of water during an ammonia release may worsen the incident by causing increased vaporisation or increased contamination. A release may dissipate into the atmosphere, limiting exposure but, by adding water to suppress vapours, will result in ammonium hydroxide production which will contaminate ground or water surfaces, causing greater impact to personnel and the environment.

Incident managers and responders should familiarise themselves with the three different types of ammonia releases, liquid, aerosol, and vapour, and understand what effects there will be when applying water.

If a decision is made to use water during an ammonia release incident, responders must understand that water applied directly to liquid ammonia should be avoided. Liquid ammonia reacts violently with water and will cause increased and aggressive off-gassing (the process of release of vapour to atmosphere).

Inside a confined or enclosed space, this may lead to vapour production moving into flammable ranges and increase the chances of ignition.

Outdoors, while it is unlikely that ammonia will reach the flammable range and ignition will be unlikely, the result of applying water will be an increase in concentration of the vapour cloud, which may also contribute to the intensity of any associated fire.

Aerosol releases, directly contacted with water, are not likely to be as aggressive a reaction but will still increase vaporisation, leading to results comparable to water being applied to a liquid pool.

Water applied to gas leaks will absorb the ammonia vapour but, depending on the release rate and amount of water supplied for suppression efforts, large amounts of vapour may pass through the water curtain/water wall, exposing downwind personnel and locations to ammonia. Responders must also be aware that the water used to suppress the vapours will be contaminated. The water will now be a corrosive liquid (aqueous ammonia/ammonium hydroxide) which will continue to off-gas ammonia, and if not confined to an appropriate area, the solution can contaminate a large area and expose personnel to ammonia gas. This contaminated water must also not be allowed to flow back to the source of the leak and contact any liquid ammonia.

Pre-designed water curtains or pre-assembled water walls do not require intervention from responders and can protect them from potential exposure. They can also save time if remotely operated. However, water applied using portable fog nozzles does not protect responders as it may expose them to contact with the corrosive liquid. These tactics should be thoroughly trained so that responders can make proper assessments on wind direction and direction of attack to prevent chemical burn injuries.

AMMONIA RECONDENSING

Ammonia recondensing occurs when there is a pressurised liquid release of warm ammonia (temperature $>-33^{\circ}\text{C}$), and the flash condition forces a rapid conversion of liquid to gas and driving the temperature locally below the equilibrium (less than -33°C). When that equilibrium displacement is confined in a funnel or a cover then the recondensation can occur.

For a liquid leak of cold ammonia (temperature -33°C or lower), it is different. Once the surrounding area of the pool is cooled to -33°C , the action of the funnel or cover is not to recondense but just to limit heat exchange between the liquid surface and the moving 'hot' air, thereby reducing the vaporisation of liquid to gas.

RELEASE CONSEQUENCES

The pungent smell and low odour threshold of ammonia, which allows it to be detected at concentrations well below hazardous levels, is often seen as a benefit, as it serves as an early warning signal during a leak incident and acts as a barrier to prevent further exposure. However, it is crucial to recognise that this low smell threshold can have limitations. In the case of regular exposure to levels of ammonia detectable by smell during specific operations or maintenance activities, the effectiveness of this early warning may diminish ('nose blind'), making it unreliable as the sole control measure. This can be mitigated by having ammonia detection and alarms set at levels similar to that at which it can be detected by smell, i.e. at 25ppm (see Objective 1 - Minimising the amount released).

Working in areas with ammonia vapour, especially in warm, humid environments, can be uncomfortable, prompting personnel to leave the area before serious toxic effects occur. Experience has also shown that toxicity-related fatalities in the vicinity of an ammonia leak primarily occur during large and sudden releases of the gas. In such situations, the duration of exposure becomes a critical factor in determining the severity of injuries. Appropriate personal protective equipment (PPE) and means of escape are key mitigations in these scenarios (see Objective 4 – Reduce people's exposure to toxic vapour).

Furthermore, there is a risk of permanent injuries, such as scarring, if a person is near a leak source and is exposed to either liquid or aerosol spray. These injuries result from chemical burns, caused by the alkaline (caustic) properties of ammonia, coupled with the extremely low temperatures associated with some types of leaks, which can be as low as -70°C . Appropriate PPE and means of escape are key mitigations in these scenarios (see Objective 4 – Reduce people's exposure to toxic vapour).

Ammonia only becomes dangerous if inhaled at relatively high concentrations over a relatively long duration. In most leak scenarios, the ability to escape and/or shelter in place is critical for emergency response strategies (see Objective 4).

For these options (escape and sheltering in place) to be effective, decontamination and the use of PPE need to be integrated into the designs of vessels, bunkering infrastructure, ports and terminals, and later reinforced by regular training in good practices. There must also be effective leadership supervision of the training or of operational activities.

When considering the consequences of an ammonia leak, it is necessary to consider its state, i.e. whether it is liquid, vapour or aerosol (two-phase), as the consequences will vary.

Liquid release

- Cold (-33°C)
- Personal injury, cold burns and frostbite
- Damage to assets (embrittlement)
- Caustic (between pH 11 and 12)
- Personal injury, chemical burns

Vapour release

- Toxicity
- Personal injury, potential fatality
- Flammability
- Fire and explosion in confined spaces

Aerosol release (two-phase)

In this case the situation may become dynamic, and the behaviour and consequences will be even more dynamic because of the combination of both liquid and vapour.

Note: Warm ammonia liquid pressurised and at a temperature above -33°C when released will immediately flash and become a two-phase aerosol release.

SAFETY



RELEASE PREPAREDNESS AND RESPONSE



KEY STAKEHOLDERS

The effectiveness of preparedness and response to an ammonia release will rely on the close coordination of all stakeholders (see Table 1). From early on in the initial design phase, a well-coordinated approach to design and operations, with clear communication and defined actions, is crucial for minimising the consequences of any such release.

KEY STAKEHOLDER	GENERAL DESCRIPTION AND INTRODUCTION
Ammonia receiver	The owner and/or operator of an ammonia-fuelled vessel.
Ammonia supplier	The fuel owner or organisations mandated by them in the operation or development of a bunkering activity.
Designer	Anyone involved in the design of a vessel, bunkering facility, equipment involved in bunkering, or terminal or port where a vessel may operate.
Regulator	Typically, a national or local body with jurisdiction over a bunkering location, terminal or port where a vessel may operate.
Competent authority	The owner/operator of the port, where the bunkering operation will take place, or of the terminal or port where a vessel may operate. (This may be the same as the competent authority.)
Competent port authority	The fuel owner or organisations mandated by them in the operation or development of a bunkering activity.
Terminal operator	Operator of a terminal where bunkering takes place.
Emergency services	First responders, firefighters, medical personnel, police officers, etc.
Port users	Users operating within the boundaries of a terminal or port on both land and water.
Neighbouring facilities and the public	Stakeholders typically located outside the boundaries of a port.

Table 1 - Key stakeholders in release preparedness and response

HAZARD AND SAFETY ZONES

A key safety control is to define zones where there is the potential for risks to personnel, infrastructure/equipment and/or the environment. The purpose of the operational zoning is to minimise harm to people and damage to equipment by identifying controls to mitigate release consequences such as:

- Controlling access to exclude non-essential people (to avoid additional injuries or deaths in the event of an accident)
- Protecting essential staff by ensuring that PPE is used (to minimise the likelihood of injury or death in the event of an accident)
- Raising those people for the potential risk exposure

Hazardous zone (toxic or flammable)

The hazardous zone is a three-dimensional space in which a flammable or toxic atmosphere can be expected to be present frequently enough to require special precautions for the control of potential ignition sources (flammability) and/or personnel access (toxicity). Hazardous zones are always present but addressed via appropriate design techniques and safety practices.

Hazardous zones for flammability are defined in regulations such as the IGF Code, and relevant local regulations. Currently there is no regulatory definition of a hazard zone for toxicity, but SGMF's Ammonia Bunkering Guidelines do provide a definition using the US Environmental Protection Agency (EPA) acute exposure guideline limits (AEGL) (see figure 3 and Appendix A4).

Safety zone (toxic or flammable)

The safety zone can be defined as the three-dimensional envelope of distances inside which most leak events are expected to occur and where, in exceptional circumstances, there is a recognised potential for a leak of ammonia liquid or vapour to harm life or damage equipment/infrastructure.

Determination and size of zones

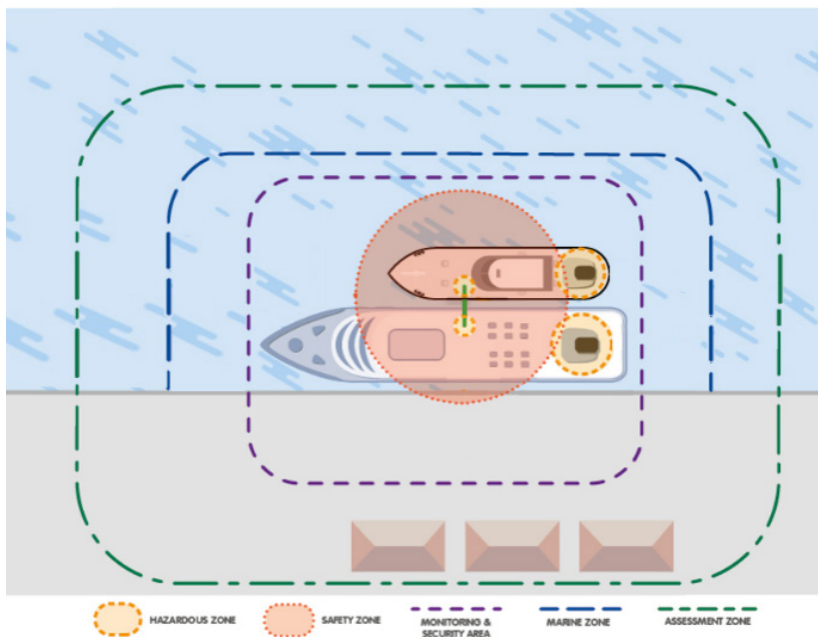
In the design of vessel, infrastructure and planning of operations:

- **AEGL contours** of a dispersion model can be used to define the operational toxic hazardous zone, and
- **AEGL and LFL** contours of a dispersion model can be used to define toxic and flammable safety zones.

These dispersion models show the expected behaviour of a credible, but theoretical, leak scenario using documented assumptions including:

- The design of the ammonia-fuelled vessel
- The design of the ammonia bunkering infrastructure
- The configuration of the ammonia transfer system
- Transfer flow rate
- System pressure
- Ammonia storage condition, i.E. Cold atmosphere or warm pressurised
- The time to detect and isolate the leak
- The amount of ammonia static inventory involved
- Wind speed and direction, atmospheric stability, humidity and sea temperature
- Day or night
- Physical layout and obstructions

***Note:** It should be highlighted that these assumptions help determine **the expected behaviour** of any leak, enabling toxic hazard and toxic safety zones to be established and controls to be put in place for operations to commence.*



	10 mins	30 mins	60 mins	4 hours	8 hours
AEGL-1	30ppm	30ppm	30ppm	30ppm	30ppm
AEGL-2	220ppm	220ppm	160ppm	110ppm	110ppm
AEGL-3	2,700ppm	1,600ppm	1,100ppm	550ppm	390ppm

Figure 3 - Application of AEGLs to toxic zoning as per SGMF Ammonia Bunkering Guidelines

In practice, in a release situation, the **actual** level of exposure (dose) needs to be determined using the **actual conditions at the time of the release**, i.e.:

- The inventory released
- The ammonia temperature and pressure
- The form of release (liquid, vapour, two-phase)
- The release source (leak, vent, etc.)
- The release location (in port, at anchor etc.)
- Local conditions such as air temperature, humidity, wind direction, sea temperature
- Whether it is day or night
- The operations under way and people potentially at risk

The reliability and accuracy of this data will have a big impact on the effectiveness of any response and on people, the environment and property.

In the event of a leak, the measurement of the release will be needed to define the actual hazard and safety zones for an effective response to the actual release conditions, so it is important that this measurement is always available and effective. Remote live monitoring using Fourier Transform Infrared (FTIR) cameras is in use in some locations to achieve this.

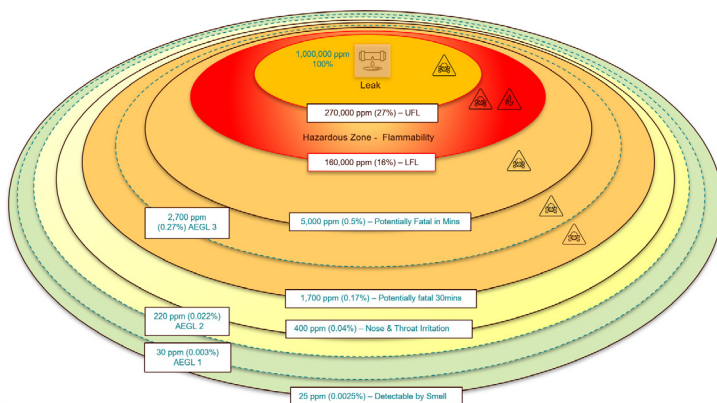


Figure 4 - Relationship of concentration levels

RELEASE RESPONSE OBJECTIVES

The ammonia production industry has many years of experience in ammonia release preparedness and response. The prioritised objectives aimed at reducing people's exposure are contained in operational release preparedness and response plans have been set as follows:

1. **Minimise the amount released**, liquid and vapour
2. **Contain** any released liquid
3. **Minimise** further vapour generation from any liquid released
4. Further **reduce** people's exposure to the release

When considering these objectives, coordination between all the key stakeholders will improve the effectiveness of the release preparedness and response. To develop solutions to achieve the four objectives, all key stakeholders in ammonia release preparedness and response must also consider the hierarchy of controls (see Appendix **A2 - Hierarchy of controls**). This hierarchy aligns well with the design process, since substitution and engineering are more practicable earlier in the design process. If decisions to mitigate by design are not taken early, then there is the potential to rely on less effective administrative controls and PPE.

It is essential that these controls are **effective, independent, and auditable**. This is critical when they require input or action from multiple stakeholders (see Table 1).

For example, if a port or terminal needs to be notified of a release to evacuate staff, then relying only on the vessel's radio communication may take longer than alternative methods, such as visual and audible alarms or use of a bunker safety link/linked emergency shutdown (ESD) system to communicate the release, which may also be more effective. The notification by the vessel may be directly affected by the release or there may be other immediate priorities, such as stopping the release or helping injured people, before alerting the port or terminal.

OBJECTIVE 1 - MINIMISING THE AMOUNT RELEASED

Once a release has occurred, minimising the quantity released will depend on several factors, including the:

- Initial design of the vessel and systems to reduce the potential release inventory
- Process parameters, temperature, pressure, flow rate, etc.
- Effective detection of the release
- Speed of isolation of the release source

INITIAL VESSEL AND SYSTEM DESIGN

While not the subject of this publication, the initial design of the vessel provides the best opportunity to limit the inventory of ammonia that may be released by considering the following:

- Equipment sizing – minimising trapped volumes
- Equipment location – minimising piping between parts of the system
- Isolation and sectioning – correct location and number
- Process conditions

The design decisions taken will have a significant impact on the preparedness and response required in the case of any ammonia release.

STORAGE/TRANSFER/PROCESS CONDITIONS

As previously discussed, the nature of an ammonia release is influenced by various factors such as pressure, temperature, velocity, and flow rate. A critical factor is the saturation temperature and pressure of the ammonia at the release source. Specifically, if the ammonia temperature is higher than -33°C (warm ammonia), the liquid will immediately vaporise with a volume expansion of approximately 850 times from liquid to vapour. This will result in an aerosol release, drastically increasing the quantity of airborne ammonia.

This factor can also be optimised during the design phase by minimising the warm ammonia quantity handled in the entire process.

RELEASE DETECTION

To be able to respond to a release, it must first be identified, and there are various ways in which this can be achieved, most commonly through; single point detection, one-dimensional detection and two-dimensional detection.

Single point detection

Single point detection instruments measure concentrations of gas, or changes in temperature at a specific location. They are generally fixed but can be portable.

- The instrument response times depend on the technology and vary between 1 second up to 90 seconds.
- Detection relies on having them in sufficient numbers and locations for any release to activate them.
- Technologies include
 - Electrochemical
 - Infrared (non-dispersive infrared sensor (NDIR))
 - Chemisorption
 - Charge carrier
 - Catalytic bead
 - Photoionisation detector
 - Photo-acoustic infrared (pair)
 - Polymer thin-film capacitive/capacitance sensor
 - Resistance temperature detector (RTD)
 - Chemical tube – ‘short-term’ tubes



One-dimensional detection

These instruments can detect ammonia along a path, thereby increasing the area being monitored.

- Paths can range from as low as a few metres up to 50km.
- Response times between 3 seconds to 1000 seconds.
- Technologies include:
 - Open path laser spectroscopy
 - Open path ultraviolet (UV) spectroscopy
 - Optical fibre as distributed temperature sensor



Two-dimensional detection

Two-dimensional detection devices identify a release within an area so have a greater coverage per device.

- Response times can be fast but variable.
- Technologies used are:
 - Ultrasonic leak detector
 - Ultrasonic leak imaging
 - Optical – visual/infrared field
 - FTIR spectroscopy active monitoring



EMERGENCY SHUTDOWN

Emergency shutdowns are required by the design standards for gas-fuelled vessels (IGF Code). They cover both releases on board such as in machinery spaces but also operations such as bunkering.

In the event of a release being detected, the activation of an emergency shutdown will isolate the potential release source. This emergency shutdown can be fully automatic or fully manual. The IMO regulations define the levels at which a shutdown should be triggered but not the time it should take.

For example, in a bunkering scenario, considering the time it takes to stop a transfer, from leak detection to full ESD isolation, SGMF defines four ESD types:

1. **A fast-acting fully automated ESD system** (requiring no human interaction) which acts in **10 seconds**.
2. **A fully automated ESD system** (requiring no human interaction) which acts in **30 seconds**.
3. **A semi-automatic ESD system** which requires some level of human interaction and acts in **2 minutes**.
4. **A fully manual ESD system** which requires multiple human actions, and acts in **10 minutes**.

When bunkering, the shutdown systems are linked between the supplier and receiver so that an incident on either side of the transfer will activate the ESD.

Consideration needs to be given to notifying third parties who are not directly involved in ammonia vessel operations, such as other port users, as they may be impacted by any release.

More information on bunkering shutdown systems can be found in the SGMF publication *Recommendations for Linked Emergency Shutdown (ESD) Arrangements for LNG Bunkering – TGN06-05*.

OBJECTIVE 2 – CONTAIN ANY RELEASED LIQUID

The facts that ammonia is toxic by inhalation and its liquid to gas (L/G) ratio is very high (1/850) mean that, in the event of a liquid ammonia release, collecting and draining it in a safe and controlled location must be the next objective. Collecting and containing the liquid also enables it to be controlled and isolated from heat sources (see design, adopting the hierarchy of controls, and that it does not rely only on human intervention in using PPE.

Objective 3 – Minimise further vapour generation).

DRAIN SYSTEMS

As far as possible, when a liquid leak source is identified, design consideration should be given to collecting and routing the liquid to a closed drain system in a safe location such as a knock-out (KO) drum or sump.

SPRAY SHIELDS

Spray shields are available to cover potential release sources such as valves, flanges and flexible hoses. These can come with built-in drain devices that can collect liquid ammonia.



Flange Shield fitted with PTFE Drain



PIPE-IN-PIPE/DOUBLE-WALLED PIPES

Pipe-in-pipe and double walled pipes, or pipes in a trunking, also provide an opportunity to contain and drain any leak to a safe location. This benefit is lost if these double-walled pipes and trunks are continually ventilated, as this potentially introduces a heat source which will generate vapour that is then discharged to atmosphere or generates effluent in a treatment system.

ENCLOSED SPACES

If the release is in an enclosed space, it may help to contain the liquid, but again any benefit may be lost if the space is continuously ventilated or if it is fitted with an automatic water spray system. Absorbed ammonia vapour will rain out as ammonia hydroxide and create potential hazards elsewhere if not effectively managed.

LIQUID MANAGEMENT

Once the leaked liquid is collected and drained, it is essential that safe management and disposal are included in the initial design, adopting the hierarchy of controls, and that it does not rely only on human intervention in using PPE.

OBJECTIVE 3 – MINIMISE FURTHER VAPOUR GENERATION

When 100% of the liquid leak cannot be collected and drained, the next objective must be to prevent further vapour generation and maintain the released ammonia as far as possible in its safer liquid state.

VAPOUR GENERATION

As described in the physical properties of ammonia, the heat of vaporisation is high, meaning that it is relatively easy to keep ammonia as a boiling liquid as long as it can be isolated from any external heat source.

Once the leaked ammonia has cooled down the material that it comes into contact with (forming a pool), the remaining heat sources to control will be sunlight, ambient air movement or the possible ingress of a contaminant such as water.

In many situations, a pressurised vapour release can be recondensed by shielding its jet using tarpaulins, covers, containment pipes and hose. It should then be led to a safer location such as a covered pool, tank, etc. (or the drain system mentioned in Objective 2).

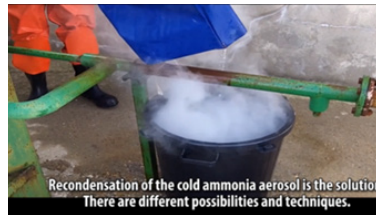


Figure 5 - Recondensation of ammonia vapour



Figure 6 - Recondensing and collecting of ammonia (Image: Yara Clean Ammonia)

As can be seen in Objective 4, water can be useful in reducing the consequences of a vapour release. However, if used incorrectly, particularly if it comes into contact with ammonia liquid, water has the potential to worsen the situation. Ammonia absorption into water generates a huge amount of heat, and this heat input will then violently vaporise more ammonia from the liquid pool.

Radiant heat from sunlight is another heat source that can increase the vaporisation of ammonia liquid. In shore-based release response, covers are used to prevent this.

While increased ventilation may be used to dilute gas to safer concentrations, to contain a gaseous release or to direct vapour to a favourable location, it should be noted that ventilation/airflow over liquid ammonia can also introduce heat and subsequently vaporise the liquid ammonia, producing more vapour. The use of ventilation should therefore be carefully considered and should include a good understanding of the state of the leaking ammonia (i.e. liquid, aerosol or only gas), the amount of vapour involved, and where the release is being discharged to, so that it does not introduce hazards to 'safe' locations.

OBJECTIVE 4 – REDUCE PEOPLE'S EXPOSURE TO TOXIC VAPOUR

While reducing people's exposure will start as soon as a release is detected, and people will be notified (see Communications), addressing the first three objectives will have a significant impact on reducing people's exposure to toxic vapour.

ESCAPE

The ability to escape any vapour cloud can be as simple as moving upwind or across wind from the release. For a vessel at sea, this could be achieved by altering the course of the vessel to ensure that the vapour cloud moves away from people. For a vessel moored alongside, unable to manoeuvre or at anchor, this may not be possible, in which case it may require shelter in place.

The following will impact people's ability to escape:

- Poorly designed tank connection spaces, fuel preparation spaces, machinery spaces and bunker stations
- Alarms and indicators that are not clearly understood
- Poorly identified or complex escape route
- Lack of exercises and training

SHELTER IN PLACE

Where the ability to escape is limited, the option to shelter in place becomes essential.

Shelter in place is a location that can be isolated from any potential vapour cloud, e.g. offices or purpose-built shelters. In the case of a vessel, this may include the accommodation, control rooms and lifeboats. In the case of other stakeholders such as those on vessels (non-ammonia) that are anchored or moored nearby, or shore personnel, crane operators or other third parties nearby, consideration will need to be given as to how this may be achieved. A key factor here will be determining the vapour's actual behaviour and location.

VAPOUR DISPERSION

As well as reducing exposure to the ammonia release by isolating the people from the hazard source (escaping and sheltering in place), how to reduce the hazard source should also be considered. This is done either by dilution/dispersion or absorption.

There are various ways of dispersing vapour to protect people. It can be ventilated out, if in an enclosed space, but knowing where the vapour will go is essential to avoid creating a hazard elsewhere.

In the open air, 'leaf blowers' and fans have been successfully deployed to disperse vapour so that personnel can access valves for isolation or to aid casualties.

Water can be used on vapour, but great care is required if there is the potential for any liquid or aerosol, as this may lead to the generation of more vapour.

When water is used, it absorbs the vapour, creating ammonia hydroxide which is a liquid that will drop out of the air and behave in the same way as any other liquid, forming pools and running to any low points. The absorption of the ammonia is a reversible reaction so care needs to be taken, as the ammonia hydroxide may off-gas and create a hazardous situation elsewhere.

There have been incidents where water sprays have been used to try and direct or disperse ammonia vapour, and this has resulted in ammonia hydroxide raining down on people, causing harm and damaging equipment.

PPE

Although it is the last line of defence, personal protective equipment must play a key role in isolating people from hazard sources. However, as PPE is the least effective control (see Appendix A2 - **Hierarchy of controls**), it should not be relied on as the only barrier.

The following types of PPE are common:

Operators and other personnel in an area where ammonia is likely to be present but with a low risk of exposure (not handling ammonia equipment directly, not in a high-risk zone during specific high-risk activities such as transfer, maintenance, etc.) and who may need to be able to escape rapidly to a place of safety in the event of an ammonia leak.

For this purpose, in addition to standard PPE (hard hat, face shield/goggles and gloves) they should carry cartridge-type gas masks. These provide a means of respiratory protection and escape in case of emergency and can provide a minimum of 15 minutes of non-contaminated air (see Figure 7).



Figure 7 - Minimum PPE used when inside toxic hazardous or safety zones

Operators. People responsible for tasks such as connecting the bunkering system or undertaking maintenance, who may have a higher risk of encountering ammonia leaks and splashes. For this level of exposure, a lighter chemical suit should be enough to shield against ammonia-related hazards (see figure 8). Operators should also be equipped with a full-face mask with an ammonia removal cartridge. This combination will enable them to quickly escape to a safe area, within seconds if required.



Figure 8 - PPE used where there is a risk of ammonia vapour or liquid splashes

Emergency responders. These people are tasked with accessing contaminated areas to render the system safe, a process that may take a long time, e.g. to close valves. For this level of exposure, a gas-tight suit is essential (see figure 9). This suit should provide full coverage for the entire body, be impermeable to ammonia and offer some protection in cold environments. In addition to the suit, the use of self-contained breathing apparatus (SCBA) is highly likely to be necessary.



Figure 9 - PPE used by emergency responders

**LOW RISK OF
VAPOUR/NO RISK
OF LIQUID SPLASH**

This level of PPE is enough to escape the area. It must not be used for protection against liquid projection, inside aerosol, or dense gas releases, or areas where the concentration of ammonia is greater than 25ppm.

Can be used by all personnel present in a location where ammonia is handled, but only if their activity does not involve direct ammonia handling.

**HIGH RISK OF
VAPOUR/LOW RISK
OF LIQUID SPLASH**

Suitable for maintenance or connection/disconnection, e.g. where the presence of vapour or liquid cannot be determined.

Only suitable for limited liquid exposure enabling escape.

**HIGH RISK OF VAPOUR
+ AEROSOL/DENSE
CLOUD OR HIGH RISK
OF LIQUID SPLASH**

For exposure in emergency response or similar situations.

Suitable for long-term liquid exposure and dense gas to enable response.

Table 2 - Use of PPE based on risk

OTHER CONSIDERATIONS



FIRE AND EXPLOSION

Experience from the ammonia production industry is that neither self-sustained ammonia fires nor ammonia jet fires have occurred in open spaces. There have been situations in which a non-ammonia fire has been intensified by the release of ammonia, but in this case, the ammonia released is consumed by the fire and so the toxicity hazard of the release is removed.

When extinguishing a fire that could be fed by an ammonia leak, be aware that this may result in a toxic gas cloud instead.

In the event of fire, current protocol is to treat the fire and, once it has been suppressed, immediately retreat to reassess and potentially adjust strategy before responding to the ammonia release.

A release in an enclosed space can reach the LFL, and if the ammonia finds an ignition source such as equipment not suitable for hazardous locations, then fire/deflagration is a possibility.

FIRST AID

Because of its toxic and caustic properties, in all cases of ammonia exposure, whether in vapour or liquid form, immediate first aid is crucial. The affected area should be flushed with water at low pressure and, depending on the duration of respiratory exposure, oxygen should be given to the casualty.

Sometimes it may be difficult to evaluate the degree of the casualty's exposure and experience has shown that someone can be relatively fine after some oxygen, but their breathing can deteriorate rapidly after a short while. Whatever their exposure to ammonia, it is essential that they receive medical attention or, at a minimum, surveillance for some hours after the exposure. Obtaining specialist medical attention promptly is of the utmost importance.

Access to means of providing decontamination from ammonia such as emergency showers should be available:

- Close to potential release sources but without being affected by the release
- Close to places of refuge or evacuation routes

Before providing first aid to a casualty, the responder's own safety should be considered, as contamination and off-gassing may result in them also becoming casualties.

DECONTAMINATION

Decontamination of any casualty should take place before they are placed in an enclosed space such as an ambulance or lifeboat. There are cases where off-gassing of ammonia from a casualty in an enclosed space has made it impossible to provide first aid. However, it is unlikely that the levels will be life threatening.

Centre for Disease Control (CDC) and other similar organisations recommend that where clothing or PPE has been contaminated with cold liquid then it should not be removed without ensuring that it is not attached to the skin by drenching with water.

While decontamination of chemical suits can be achieved by using water, the wash water needs to be managed as this will contain ammonia hydroxide, which can be carried on boots and shoes or may flow to other locations and off-gas ammonia.

The use of fans and blowers has been successful in decontaminating chemical suits.

COMMUNICATIONS

While ammonia-fuelled vessels, bunker vessels and bunker locations will have means of communication, including alarms, in accordance with regulations such as the IGF Code and related guidelines, or in line with industry standards such as those detailed in SGMF's publication Ammonia as Fuel Safety and Operational Guidelines – Bunkering, Revision 1, 2024 – FP23-O1, these may not apply to other stakeholders.

Alerting all stakeholders to any ammonia release is essential and will need consideration to provide an effective response to any release.

COMPETENCY AND TRAINING

It is imperative to provide comprehensive training for first responders, to equip them with the knowledge and skills necessary to effectively control ammonia leaks, so that both the quantity of released gas and the potential for gas dispersion can be reduced.

APPENDICES



A1 - BOWTIE MODELS

A potential release of ammonia can be assessed using a bowtie model which enables the stakeholder to identify the threats and consequences of the event, and the controls that should therefore be put in place.

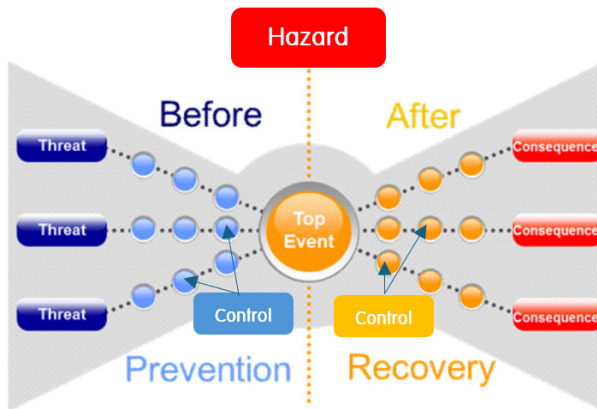


Figure 10 - Bowtie diagram

Top event: The release of the hazard. Sometimes called the first event in a chain of consequences.

Hazard: Something with the potential for harm in terms of human injury or ill health, damage to property, damage to the environment, or a combination of these.

Threat: A situation or condition that can lead to a loss of containment (top event) of the hazard that leads to harm (consequence).

Consequence: The ultimate harm that may occur after loss of containment, e.g. fire, explosion, fatality, pollution.

Control: Measure put in place to decrease the likelihood or consequences from an unwanted event. These can:

- Prevent the unwanted event occurring
- Reduce the loss of control of the hazard (e.g. reduce or contain energy release)
- Reduce the effects (e.g. provide a shield from the hazard)
- Reduce the severity and duration of consequences (e.g. emergency response and medical treatment)

For a control to be valid, it must be:

- **Effective:** The control prevents the top event or consequence when it is activated, i.e. it must be big enough, fast enough and strong enough, and must function as intended, when intended.
- **Independent:** The control needs to be independent of the initiating event (threat) as well as of the components of any other control already used to prevent the top event or its consequence. Controls cannot be considered if they have a common cause of failure.
- **Auditable:** The control should be evaluated to check that it will operate when it is called on (e.g. through inspection, testing and record keeping).

The effectiveness of a control also needs to be maintained through activities such as inspection, maintenance, exercising and training.

As for any project, the integration of safety concepts in the early phases is key to implementing highly efficient risk control measures.

It is during the development stage (concept selection, basic and detailed engineering) that hazards and their associated unwanted events can be identified so that choices can be made to control them effectively, or even sometimes eliminate them completely. This is where the hierarchy of controls methodology can work well to minimise risk levels.

A2 - HIERARCHY OF CONTROLS

The hierarchy of controls (shown in Figure 11) is a universally adopted system that has been championed by numerous safety organisations. This structured approach offers the means of deciding which are the most effective actions to manage and mitigate exposures to hazards. It frequently serves as a guiding principle in shaping regulatory frameworks.

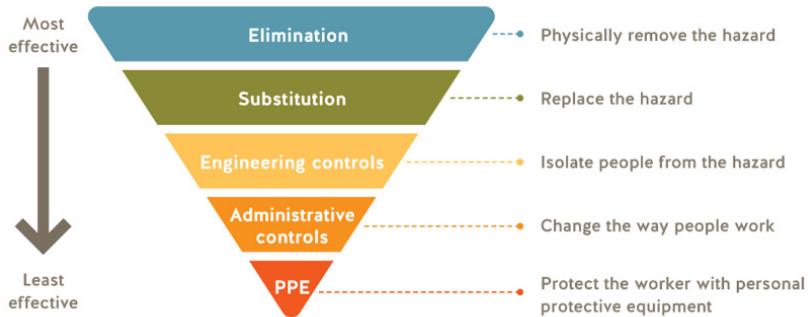


Figure 11 - Hierarchy of hazard controls

The hierarchy of controls provides five distinct levels of measures arranged from the most to the least effective: elimination, substitution, engineering controls, administrative controls and finally personal protective equipment (PPE).

1. **Elimination** makes sure the hazard **no longer exists**. Even if it is the most effective solution to protecting workers, this level is the most difficult to implement as, by nature, **hazards are inherently linked to a material or an activity**. This means that eliminating a hazard might only be achieved by physically removing the associated material or not performing the required activity. In some cases, it is just not possible, so the next level of control measure must be considered.

As an example, when inspecting equipment located 15m above ground, the height hazard cannot be eliminated unless the inspection activity is cancelled. In this situation, safer access for the workers can be planned using the next level of control, i.e. changing the way (or the process by which) the activity is performed, e.g. using a temporary working platform (purpose-built with scaffolding) instead of relying on PPE such as a safety harness.

2. **Substitution** means changing out a **material** or **process** to reduce the hazard. When considering substitution, it is important to compare the hazard introduced by the substitute. Effective substitutes **reduce the potential for harmful effects** and do not create new risks.
3. **Engineering controls** reduce exposure by **preventing hazards from coming into contact with workers**. For hazardous substances, it translates primarily into ensuring that the hazards are kept confined (Keep it in the pipe!) and when that is no longer the case, that they are kept away from workers.

The most effective engineering controls:

- Are part of the original equipment design
- Remove or block the hazard at the source before it comes into contact with the worker
- Prevent users from modifying or interfering with the control
- Require minimal human/user interface for control and operation
- Operate correctly without interfering with the work process or making the work process more difficult

Engineering controls can cost more upfront than administrative controls or PPE. However, long-term operating costs tend to be lower, especially when protecting multiple workers. In addition, as accidents are extremely damaging, the high effectiveness of engineering controls in drastically reducing their occurrence is very valuable.

4. **Administrative controls establish work practices**. They normalise the way work is done through **procedures** or give workers more information through **training**. Used together with higher level controls, they aim to reduce the duration, frequency or intensity of exposure to hazards.

Procedures are rooted in the findings of a sound risk assessment which serves as the foundation for safe work practices. When coordinated with training and competency requirements, they guarantee that workers are adequately prepared and skilled to carry out the procedures effectively and consistently.

5. **PPE** is equipment worn to **minimise exposure to hazards** and plays a crucial role in safeguarding workers. However, it is important to emphasise that PPE represents the lowest level of control in the hierarchy: its effectiveness hinges on its proper selection and use.

Employers should not rely on PPE alone to control hazards when other effective control options are available. When selecting PPE, factors such as what the equipment is intended to protect the user from and the required training and competency should be taken into consideration.

By the time this ultimate step of the control system is reached, unwanted events must be thoroughly understood, and the potential exposure type, duration and frequency must be defined. In addition, the context in which these exposures may occur (confined/congested/open areas, weather conditions, normal operation or emergency response, etc.) must be integrated into the control.

The selected PPE will then require a dedicated training and competency programme to be developed to ensure that workers will be able to use it effectively.

The importance of leadership

It is crucial to recognise that, just as with all risk management strategies, the maturity of safety culture is driven by exemplary safety leadership. The commitment of all stakeholders is paramount to ensure that the hierarchy of controls outlined above will be applied effectively.

A3 - APPLICATION OF THE HIERARCHY OF CONTROLS ON BOARD AMMONIA-FUELLED VESSELS

The hierarchy of controls methodology presented in the previous Appendix should guide the emerging ammonia-fuelled ship industry as regards introducing ammonia as a marine fuel. Its early adoption and application are key to ensuring the safe use and acceptance of ammonia.

Because systems such as bunkering stations, onboard storage, fuel preparation rooms and machinery spaces are still in the design phase, this is a unique opportunity to integrate risk control measures higher up in the hierarchy.

1. **Elimination:** Since the proposed exercise is to use ammonia as a marine fuel to benefit from its carbon-free properties, this initial hazard control level cannot be implemented, and the next level must be considered.
2. **Substitution:** This control involves substituting fully-pressurised or semi-refrigerated ammonia for fully-refrigerated ammonia.

The long experience acquired in the fertiliser industry has demonstrated that the potential for harmful effects from a volume of stored liquid ammonia can be significantly reduced if the process conditions are kept fully refrigerated and close to atmospheric pressure. In this state, as opposed to fully pressurised at ambient temperature, the vapour dispersion in the same leak scenario will be minimised and the toxic cloud footprint at ground level considerably reduced.

Opting to adopt these **safer process conditions** in an early phase of the project provides efficient and significant risk control measures. In the case of ammonia, using its physical properties is the only option at this control level, while the next options relate to equipment design at the detailed engineering stage.

3. **Engineering controls:** Preventing ammonia from coming into contact with workers first requires potential release sources or leakage scenarios to be identified.

The identification of potential release sources should cover normal operations such as:

- Inerting/purging during bunkering operations
- Equipment opening for preventive/corrective maintenance and inspection activities
- Ammonia slip from the operation of main and auxiliary engines, fuel cells, boilers or other combustion units

Leakage scenarios should also cover abnormal situations such as:

- Equipment failure (corrosion, stress, fatigue, etc.)
- Operating failure (process deviation, human error, etc.)
- External events (mechanical impact, weather conditions, etc.)

Once those have been comprehensively identified and minimised, it should be considered whether workers can be physically isolated from the release or leak sources, and finally robust mitigation must be implemented for any remaining workers' exposure.

Wherever feasible, design solutions should be engineered to eliminate the potential release or leak sources or minimise the likelihood of their occurrence. The following approaches may be applicable to the marine industry:

- Inerting and purging systems could be designed so that the ammonia is collected and routed to an ammonia recovery system.
- The frequency of equipment opening could be minimised by designing it with less requirement for maintenance or external inspection.
- The exhaust treatment unit could be designed to deal with possible pollutant or ammonia slip.
- Interlocks could capture any process parameter deviation and shut off the operation automatically to bring it back to a safe state (covering onboard ammonia equipment and bunkering operations).
- Critical operations could be automated to reduce the need for human interaction.

Engineering controls should ensure that a single failure cannot result in the release of ammonia coming into contact with workers.

This is where the **gas safe concept** should be introduced, so that whenever possible, the hazard can be isolated through secondary confinement such as pipe-in-pipe or double-wall systems. This is particularly relevant for spaces such as the engine room, where the presence of workers cannot be avoided during normal operation.

Nevertheless, by design, solutions should be evaluated to reduce the need for workers to be present in such hazardous areas.

Finally, the following engineering controls should complete the possible measures:

- The segregation of hazardous and non-hazardous areas to ensure that any remaining potentially hazardous events could only occur in their defined spaces.
- Early leak detection and automatic isolation of the main inventories to minimise the quantity of ammonia released.
- Drip trays and water mist systems to reduce the size and dispersion of a gas cloud, and to minimise the area exposed to hazardous concentration levels.

4. **Administrative controls:** The vast majority of administrative controls can only be finalised once the detailed engineering of the ship and its associated equipment have been frozen for a final risk assessment exercise. A comprehensive set of procedures can then be drawn up to safely address normal operations, preventive maintenance, routine inspection, anticipated abnormal situations or repairs, and emergency conditions, followed by the associated training and competence development programme.

Even when properly designed, some engineering controls selected at the previous level will need some user input to work as intended, and that means training and competency requirements should also be incorporated. This is essential to ensure that anyone interacting with these controls possesses the necessary skills and knowledge to operate them effectively and consistently.

In the maritime context, it is important to note that the development of administrative controls will require collaborative efforts.

The bunkering procedures and associated emergency response plans will for example require close coordination with ports, harbours, terminals, bunker suppliers and other stakeholders or interested parties.

The ship operation will require close coordination with the providers of integrated systems such as ammonia engine manufacturers, tank and boil-off gas (BOG) equipment suppliers.

A4 – AEGL (ACUTE EXPOSURE GUIDELINE LIMITS)

As set by the US Environmental Protection Agency (EPA), AEGLs estimate the concentrations at which most people—including sensitive individuals such as old, sick, or very young people—will begin to experience health effects if they are exposed to a hazardous chemical for a specific length of time (duration). For a given exposure duration, a chemical may have up to three AEGL values, each of which corresponds to a specific tier of health effects.

The three AEGL tiers are defined as follows:

- **AEGL-3** is the airborne concentration, expressed as parts per million (ppm) or milligrams per cubic metre (mg/m³), of a substance, above which it is predicted that the general population, including susceptible individuals, could experience life-threatening health effects or death.
- **AEGL-2** is the airborne concentration (expressed as ppm or mg/m³) of a substance above which it is predicted that the general population, including susceptible individuals, could experience irreversible or other serious, long-lasting adverse health effects or an impaired ability to escape.
- **AEGL-1** is the airborne concentration (expressed as ppm or mg/m³) of a substance above which it is predicted that the general population, including susceptible individuals, could experience notable discomfort, irritation, or certain asymptomatic non-sensory effects. However, the effects are not disabling and are transient and reversible on cessation of exposure.

All three tiers (AEGL-1, AEGL-2, and AEGL-3) are developed for five exposure periods: 10 minutes, 30 minutes, 60 minutes, 4 hours, and 8 hours. (see table 3) shows how the ammonia AEGL values vary with exposure duration.

	10 mins	30 mins	60 mins	4 hours	8 hours
AEGL-1	30ppm	30ppm	30ppm	30ppm	30ppm
AEGL-2	220ppm	220ppm	160ppm	110ppm	110ppm
AEGL-3	2,700ppm	1,600ppm	1,100ppm	550ppm	390ppm

Table 3 – AEGL exposure times

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