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International Institute of Ammonia Refrigeration
1110 North Glebe Road
Suite 250
Arlington, VA 22201

+ 1-703-312-4200 (voice)
+ 1-703-312-0065 (fax)
www.iiar.org

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Technical Paper #8

Probability in Ammonia Refrigeration Risk Assessment

Anders Lindborg
Ammonia Partnership AB, Nyponv.
24, 260 40 Viken, Sweden
Tel. +46 42 238 155
anders@ammoniapartnership.se

Abstract

Designers and users of ammonia in refrigeration and heat pumps consider it a safe and economical refrigerant. The number of injuries and lethal accidents are extraordinarily rare compared to other risks in society. This is not generally known and myths which depict ammonia as very dangerous continue to influence regulators and society at large. This paper demonstrates that ammonia's dangers have been greatly exaggerated.

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Introduction

The incidence of accidents and fatalities involving ammonia refrigeration is extraordinarily rare compared to other risks in society. There is a general unawareness of this, with society pronouncing ammonia, with its heavy, pungent smell, as both dangerous and frightening. This paper explains why ammonia doesn't deserve its reputation. When designers and users of ammonia for refrigeration, heat pumps and ORC[1] processes consider all safety codes, standards and legal regulations they conclude that ammonia is a safe and cost-effective refrigerant.

Information about risk includes probability and consequence. Consequence is used in describing accidents while probability for an accident is rarely or never used. The reason is that information about number of accidents related to a nation and time is missing. Probability must always be included in risk assessment. Probability is presented in respect of a number of European countries, Australia and the USA, as these are familiar to the author and can be verified. Other countries are also under investigation and other means of comparison may well exist.

Risk

Managing risk requires that the hazards of ammonia are well understood so that the risks associated with ammonia can be prevented, prepared for and mitigated.

Hazard

- means peril associated with chemical and physical characteristics
- is associated with type of release and circumstances for an emergency event

[1] Organic Rankine Cycle, reversed refrigeration process to generate energy.

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Risk means

- experiencing an activity
- observing its potential hazards
- recognizing the hazards
- being exposed to the danger that constitutes the risk
- making a risk assessment
- implementing risk management

Risk assessment in ammonia refrigeration includes

- probability or frequency, which seldom or never is referred to because information is missing
- consequence, often referred to in negative scenarios or even fantasies by less informed persons
- lack of expertise and knowledge

Ammonia

The ammonia discussed here is anhydrous ammonia (NH_3), used only as a refrigerant and not in other applications such as fertilizer, or in farming or the chemical industry. Ammonia is unsurpassed as a refrigerant, having excellent thermodynamic qualities that involve environmental advantages. All life is dependent on the recirculation of nitrogen, in which the breaking down of natural substances to ammonia is an essential part. Use of ammonia as a refrigerant will continue in the future since society cannot afford not to use it.

There is a belief that ammonia is both poisonous and explosive, which is not entirely true if one examines the definitions of *poisonous* and *explosive*. This belief has often been a hindrance to profitability in the refrigeration industry. Most people have experienced, to a greater or lesser extent, the smell of ammonia, while only a few people have actually been injured by it. Furthermore, although flammable, ammonia

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does not explode: it *flash burns* as confined smoke does in a burning building. Burning ammonia has low flame propagation, <8 cm/s [5].

This presentation does not describe ammonia's thermodynamic properties or how a refrigeration system that uses ammonia is designed, constructed and operated, but instead addresses the general issue of safety. Ammonia systems designed during the past 20–30 years in compliance with pressure vessel legislation are very high quality, with excellent standards of safety. Older systems can be unsafe and should be analysed for risks by experts (not least in connection with corrosion). Service staff and personnel with operational responsibility can cause spillage, so the provision of training and information are worthwhile, low-cost, preventive measures.

The Smell—An Important Advantage

Ammonia is the only refrigerant that has a strong, characteristic smell. When ammonia is mentioned, there is often a negative reaction, with the opinion being expressed that it is dangerous, toxic and explosive and has a terrible smell. The smell is in fact an advantage since the smallest leaks are discovered immediately and then corrected. Most other gases have no smell and represent greater potential hazards.

Comparison With Some Other Modern Refrigerants

The vaporization heat transfer capabilities of ammonia are high and the liquid fluid flow rate is low because of ammonia's high latent heat. This is the reason why the technology used differs from that used with other refrigerants. This low liquid flow has limited the use of ammonia for smaller refrigerating capacities. With new technology, however, it can in the future also be an alternative for extremely small systems with charges of some hundred grams.

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All the properties of a refrigerant listed prior to the Montreal Protocol have since then been added, with arguments relating to the environmental ODP and GWP[2], zeotropic and azeotropic blends and for CO_2 the supercritical process. All these characteristics and categories have to be taken into consideration in order to get the correct picture of a refrigerant. For example, HFC refrigerants are not recommended for industrial systems because leaks are more difficult to prevent and the price of replacing the charge is too high—a double penalty on top of the environmental challenges created by their release. Furthermore there is no such thing as an ideal refrigerant and it is not likely, within the foreseeable future, that there will be a new refrigerant with properties that match or are better than those we have today [1, 2 and 3].

Ammonia Accidents, Information and Statistics

Number of systems and number of releases

Literature on ammonia refrigeration systems dates back more than 100 years, but there is much ground that has not yet been covered. There are experts with long experience, but they have little or no influence on the policy process because they do not interact frequently with governmental safety experts, code authorities, insurance companies, etc. Often, they speak a different language from the regulators because few ammonia refrigeration experts are trained in industrial hygiene and regulatory affairs. Moreover, there is a clear need for extensive documentation on the subject of ammonia as a refrigerant in order to increase understanding and to improve accessibility and confidence in the operation of ammonia refrigeration systems.

It would be desirable to have definite information spanning many years as to the number of ammonia systems and the releases that have occurred. Case histories

[2] Ozone Depletion Potential and Global Warming Potential

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indicate that the probability of releases causing property damage or personal injury is very small. It has, however, proved difficult or impossible to collect significant amounts of this kind of information.

There are several lists of ammonia releases and accidents in the chemical industry, as a fertilizer in agriculture and in refrigeration. They all describe the consequences, but the descriptions are often by people who do not understand ammonia and are made without any relation to probability in risk assessment. This results in anecdotal descriptions of limited value. The interpretation is made by the public who have no experience of ammonia.

Number of fatal accidents with ammonia

Incidents involving ammonia leaks are few in relation to the large number of systems in existence. Fatal accidents in a number of countries are presented in Table 1. These figures have been checked regarding source and background in different ways but there may be some minor errors. The figures only refer to fatal accidents related to ammonia refrigeration, not other applications involving ammonia. These data give an Annual Death Rate (ADR) of < 2 per 109 populations per year. As a benchmark, the ADR for lightning accidents in the USA is 32 per 109 and year, traffic accidents in Sweden is 5 per 105 per year. To put these values into context, these and other data are presented in Figure 1, where an indication of social attitudes to such risks is also included.

In a report by Prof. Berghmans 1994 [4], investigation is made into accidents involving ammonia. According to information available from Japan from 1951 to 1990, the figure is 2.5 persons per 109 inhabitants per year. Since then, over the past 20 years, the quality of industrial refrigeration should have improved.

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Who is injured or killed by ammonia?

Accidents involving ammonia have occurred and studies of them show that nobody outside the vicinity of the system has been injured. People who have been injured or have died as a result have been located at the point of the leakage, (Figure 2), and have usually been actually working on the system. The operational and service staffs are those who are in the danger zone of a few metres. Injuries can be avoided by using PPE—personal protection equipment—such as overalls (no bare arms or legs in summer), gloves and protective full-face filter mask.

Fatal accidents and accidents requiring medical treatment usually occur within just a few metres of the release (Figure 2). At a distance of 200 metres the characteristic smell is obvious. A distance of 1,500 metres is the safety distance in respect of large, industrial releases involving many tons, e.g., storage tanks and railcars. The impact of releases depends greatly on weather conditions such as temperature, wind speed and climate inversion.

Categories of reaction and injury to human beings

A study by Bird and Germain (1996) identified a ratio hierarchy that relates the different levels of impact to individuals following a release, (Figure 3). Statistical comparison in the US gives 640 opportunities to learn from accidents and prevent, mitigate and prepare for one big accident, almost same as the 600 in the Figure 3.

The levels of impact are identified as follows

Unaffected – persons are not aware of an accident or release. No smell.

Awareness – the smell is obvious and can be identified as ammonia. May call for help (911 or 112) but not go to hospital.

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Inconvenience – depending on people's experience of ammonia. Those with experience will walk away while others may even panic. Some may ask for a medical check or even treatment. No damage or injury.

Medical treatment is needed and the victim can recover.

Acute medical treatment of more severe conditions. Cure is not possible e.g. total eye damage.

Fatal. In most accidents a single person is involved.

Summary

Lack of Knowledge

Lack of knowledge by the general public results in a negative attitude towards ammonia. This lack of awareness is even found in the refrigeration industry because more than 95% of the people in the refrigeration industry work with refrigerants and technical solutions other than ammonia. It is easy to question situations one does not completely understand, especially if the situation seems hazardous. Many authorities and planners have not acquainted themselves with the regulations for ammonia and consider it hazardous. Ammonia, however, is a natural substance and compliance with the European Pressure Equipment Directive and Machinery Directive and corresponding Codes in other countries and modern safety standards will result in safe ammonia systems.

Persons lacking expertise and experience of ammonia have no right forbid its use.

Toxicity

Ammonia is sometimes described as being poisonous but what is a poison? Philippus Theophrastus Bombastus von Hohenheim or Paracelsus, Swiss doctor, chemist and philosopher (1493–1541), is quoted as having said, *the dose makes the poison*. The amount of a substance a person is exposed to is as important as the nature of the substance. A modern definition is that a poison is a substance that, even in very small quantities, has a dangerous or deadly effect on living organisms. It is not possible to conceal ammonia, which is the only refrigerant that gives a warning long before the concentration can be considered dangerous.

The level of concentration that a trained individual cannot put up with is far from dangerous, (Table 2). Ammonia may be noticed by human beings in concentrations of less than 4–20 ppm and it starts to become life threatening at concentrations exceeding approximately 700–1000 ppm, depending on the time of exposure. There are different opinions in different nations what level is IDLH (300 ppm) which is a definition of Immediate Danger to Life and Health. There is no universal or international standard.

Flammability

The word *explosive* is used in relation to rapid fire behaviour, with a flame propagation of many meters per second (m/s) and detonation in kilometres per second (km/s). Since ammonia burns with low energy—about half that of hydrocarbons—the flame propagation is low, about 8 centimetres per second (cm/s) according to ISO 817 [5]. Ammonia can self-ignite if the temperature is above 651°C and, as a refrigerant, is classified in group B2 (low flammability) in accordance with ISO 817 and ASHRAE 34. Ammonia's flammability range is from 15% to 28% or 33% depending on the test method and reference. Ammonia can only burn in enclosed spaces, not outdoors in the open without a supporting flame, and it is therefore not classified as flammable in connection with outdoor use.

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In order to ignite ammonia, an ignition source with minimum energy is needed and this energy, compared to other flammable substances, is considerable. Ammonia requires minimum ignition energy of 680 mJ, while methane, ethane and propene require 0.21–0.26 mJ and hydrogen gas requires 0.02 mJ [6]. Hence electrical equipment for ammonia systems is encapsulated well tight or placed outside the machinery room to eliminate ignition sources.

Open flames or boilers are not allowed in ammonia machinery rooms under any safety standards. Similarly, naked electric bulbs are a possible ignition source, so lighting must have a spray-proof cover such as a plastic hood. Fluorescent lighting must also be covered although such light fittings do not heat up during use.

Fire progress is short-lived and depends on the volume of the room. After just a few seconds of fire, a certain amount of the oxygen in the room has been used up and the ammonia/atmospheric oxygen balance is no longer flammable. The fire dies if other material is not ignited.

Safety codes and standards

Present day refrigeration systems using ammonia are very safe, because ammonia has been used for more than 150 years and a body of knowledge regarding safe practices has been developed. As early as 1918, the first safety directives for refrigeration systems were drawn up in the USA. These were followed by VBG 20 in Germany in 1933, and the predecessor of the Swedish Refrigeration Code in 1942. There are now standards in most European countries. Europe has EN 378:2008 Parts 1–4 [7], the USA has ASHRAE 15 and ANSI/IIAR 2. Europe has legislation in the Machinery Directive, the Pressure Equipment Directive and the ATEX Directive when applicable. In addition, technology, material and design have all improved. The systems of today have come a long way over the years, and are now extremely safe.

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The refrigeration industry

The refrigeration industry has not been effective in arguing the safety case for ammonia. It needs to deliver the message that this refrigerant is not difficult to handle and is safe provided existing safety codes and legislation are respected. The latter are crystal clear and do not require extra interpretation.

The greatest costs resulting from an emission of ammonia are in connection with cleaning up, community relations, and resuming production. The best way to deal with this is prevent all minor incidents! The smell of an ammonia leak cannot be concealed and the media will cause it to spread much further than any neighbours would notice. The distance for sensing the smell during worst special weather conditions in cold climate is some kilometre for a major emission and threshold 5 ppm. The media will spread information about the smell worldwide in just a few hours.

Future of ammonia

Ammonia's future is assured since it has superior properties as a refrigerant and will therefore survive. Ammonia has always been the refrigerant used in large, industrial contexts. Carbon dioxide is a good or, in some applications, better alternative, and promoting its use can be less complicated than for ammonia with regard to safety. For air conditioning applications, water is an interesting refrigerant if ammonia is not used.

With good quality systems and reasonable amounts of charge, many new ammonia applications will be developed. The political pressure on HFCs will increase and this will result in new technical solutions with natural refrigerants such as ammonia. Used correctly, ammonia not only has a good level of safety but also is efficient, economical and environmentally friendly.

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Probability of a release and risk assessment

Statistics regarding fatal accidents resulting from ammonia releases can be used to estimate the number of harmless releases in a country/state. These statistics should be used in risk assessment for ammonia refrigeration. To refer only to consequences is an expensive misjudgement.

Use ammonia with respect as it is environmentally friendly, offers better efficiency than most refrigerants and it is cost-effective for its user.

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Table 1. Reported fatal accidents from ammonia refrigeration in some countries

Country	No. of years incl. 2008	No. of Deaths
Sweden	68	0
Norway	63	1
Denmark	63	0
Finland	63	0
Iceland	30	0
Germany	22	2
USA	15	8
Australia	30	0
New Zealand	30	0
The Netherlands	29	1
Chile	30	1
Italy	30	0

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Table 2. Physiological effects[1] of ammonia on humans

Gas ppm	Effect on unprotected person	Human reaction	Exposure time and regulated exposure limits
5[2]	Threshold value for discovering ammonia, temperature dependent, easier in a low temperature and dry atmosphere		
20	Most people notice the smell	Not dangerous. Characteristic smell = warning!	Unlimited, in most countries.
25	Characteristic smell	Not dangerous. Warning!	MAC (Maximum Allowable Concentration) in most countries. TLV-TWA in US. (Threshold Limit Value-Time Weighted Average) OEL (Occup. Exp. Limit)
35	Characteristic smell	Not dangerous. Warning!	TLV-STEL in US. (Time Weighted Average-Short Term Average)
50	The smell is obvious. Unaccustomed person wants to leave the area.	Not dangerous. Warning!	ATEL (Acute Toxicity Exposure Limit), 8 hour working day permitted in many countries. MAC = 50 ppm in some countries

[1] In case of exposure, it is rare that a person has measuring equipment. Experience is based on reconstruction after the event. The concentration is not quantified.

[2] 2–5 ppm is possible to detect by smell and depends on the individual, air temperature and humidity. The advantage of a low sensory threshold for detecting ammonia is that the gas gives an early warning, so that the hazardous area can be evacuated. Even people without a sense of smell are warned of an ammonia presence since the gas affects mucous membranes and damp skin with pain.

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Gas ppm	Effect on unprotected person	Human reaction	Exposure time and regulated exposure limits
100	No harmful effect on healthy individuals. Unpleasant, can cause panic for people who are unaccustomed.	Not dangerous.	Do not wait longer than necessary.
200	Strong smell	Not dangerous	Toxic end point defined by US EPA RMP (Risk Management Program)
300	People with experience of ammonia will leave the area.	Not dangerous, not accepted by experienced person.	IDLH (US, Immediately Dangerous to Life and Health), filter masks are not accepted beyond this limit in US.[3]
400 –700	Immediate irritation in eyes and respiratory system. Even an accustomed person cannot remain.		In normal conditions, there will be no injury even if exposure time is up to 30 minutes.
1,700	Coughing, cramp of vocal cords, serious irritation in nose, eyes and respiratory system.		30 minutes' exposure results in injury and need for acute medical care.
2,000 –5,000	Coughing, cramp of vocal cords, serious irritation in nose, eyes and respiratory system.		30 minutes or less can result in death.
7,000	Unconsciousness, respiratory distress		Lethal within minutes.

[3] Practical use of filter masks with new K-filter show that they can be used in concentrations 10,000 to 15,000 ppm for some minutes.

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Figure 1. Probability of deaths in society, Prof. Jan Berghmans, Leuven, Belgium

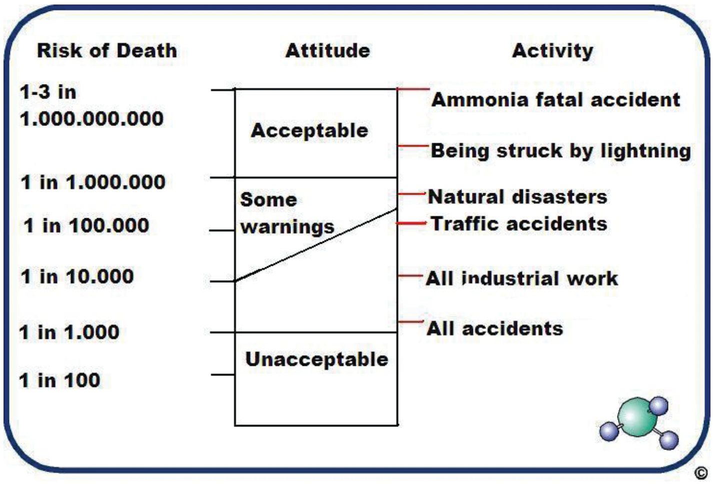


Figure 2. Influence at accidents: Fatal accidents occur close to the release

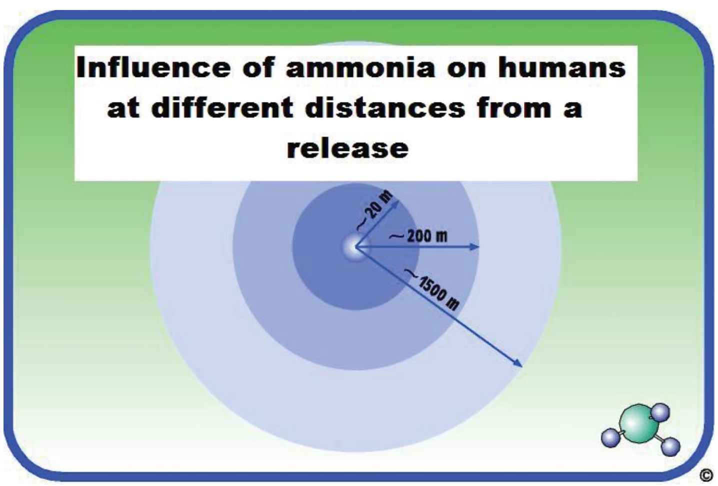
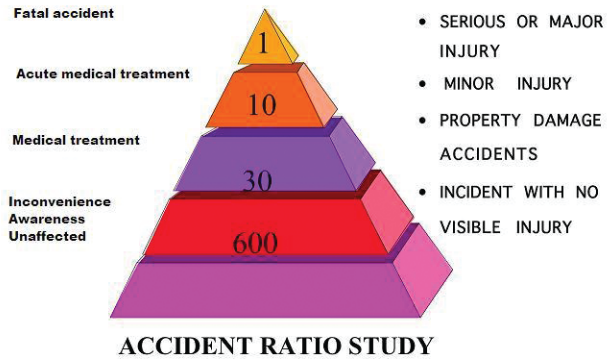


Figure 3. Accident Ratio Study, (Bird and Germain, 1996)



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