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ASHRAE Position Document on

AMMONIA AS A REFRIGERANT

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EXECUTIVE SUMMARY

Globally, there is a growing interest in ammonia as a refrigerant. Restrictions on chlorine and fluorine containing refrigerants have focused attention on ammonia to emerge as one of the widely used refrigerants that, when released to the atmosphere, do not contribute to ozone depletion and global warming.

Ammonia is an efficient refrigerant used in food processing and preservation, as well as many other refrigeration and air-conditioning processes. Ammonia has desirable characteristics as a refrigerant, which have been well known for over a century. It is corrosive and hazardous when released in large quantities. Because of its irritating odor, persons will not voluntarily stay near concentrations that are health threatening. Although ammonia will burn in a narrow range of high concentrations, it is difficult to ignite and will not support combustion after the ignition source is withdrawn.

ASHRAE considers that the continued use of ammonia is necessary for food preservation and air conditioning. ASHRAE promotes a variety of programs to preserve the economic benefits of ammonia refrigeration while providing for the management of risks.

ASHRAE will:

- Promote authoritative information on ammonia by seminars and publications.
- Continue research on ammonia topics such as handling, application, operation, control of emissions and new technology.
- Maintain and develop standards and guidelines for practical and safe application of ammonia in refrigeration systems.
- Provide programs and publication of innovative designs and application of ammonia refrigeration.
- Advise governments and code officials with information regarding ammonia.

AMMONIA AS A REFRIGERANT POSITION DOCUMENT

1.0 BACKGROUND/HISTORY OF USE

Ammonia (chemical symbol NH_3, United Nations Chemical I.D. #1005) is produced both naturally and as a byproduct of numerous man-made reactive processes. Large amounts of naturally occurring ammonia gas come from livestock animals, soil surfaces and even the human body. Manmade processes that emit ammonia to the atmosphere include fuel combustion processes and sewage treatment plants.

The nitrogen component of ammonia was first recognized as an important fertilizer around 1840, and ammonia was first used as a refrigerant around 1850. Ammonia was first commercially produced in the United States about 1880 as a distillation by-product of the processing of coal to produce coke and coal gas.

The first direct synthesis commercial process was developed in Germany by Fritz Haber and Carl Bosch in 1913. The wide variety of uses for ammonia throughout agriculture and industry, combined with varied and highly efficient manufacturing processes, has kept the costs of commercially manufacturing ammonia low.

2.0 CURRENT USES OF AMMONIA

Ammonia is an alkaline, colorless chemical compound that is well recognized as the basis for household cleaning products, and also has many agricultural, industrial and commercial uses. It is available in four generally recognized grades—fertilizer, refrigerant, federal and metallurgical—depending on its level of purity.

Refrigeration grade ammonia is 99.98 percent pure and is relatively free of water and other impurities (maximum: 150 ppm water, 3 ppm oil, 0.2 ml/g non-condensibles). It is readily available inexpensive, operates at pressures comparable with other refrigerants and is capable of absorbing large amounts of heat when it evaporates.

Of the estimated 100 million metric tons of ammonia produced commercially throughout the world each year (14-16 million metric tons in the United States), over 80 percent is used for agricultural purposes. Some of the agricultural uses of commercial ammonia include:

- Direct injection into soil as a fertilizer (amount can be as much as 150 pounds annually per acre).
- Production of urea (colorless crystalline material that is a highly concentrated form of nitrogen fertilizer and a source of protein in livestock feeds).
- Pre-harvest cotton defoliant.
- Anti-fungal agent on certain fruits.

The remaining 20 percent of commercially manufactured ammonia is used for numerous industrial applications, such as:

- Direct injection in selective catalytic reduction control of nitrogen oxides for stack emissions.
- Direct injection of ammonium hydroxide for stack emissions to neutralize sulfur oxides from sulfur-containing fuels.
- Nitrogen component for the manufacture of explosives such as TNT and nitroglycerin.
- Closed-loop refrigerant in many industrial refrigeration systems.
- Neutralizing agent for acid constituents in sewage treatment plants.

Less than 2 percent of all the ammonia commercially produced in the world is used as a refrigerant.

3.0 REFRIGERATION USES OF AMMONIA

With increased regulation being placed upon the use of chlorofluorocarbon (CFC), hydrochlorofluorocarbon (HCFC) and hydrofluorocarbon (HFC) based refrigerants, and the pending phase-out of CFCs and HCFCs altogether, alternative refrigerants for use in existing refrigeration systems are actively being investigated. These alternative refrigerants must have thermodynamic characteristics similar to those of Halocarbons and be safe for humans and the environment.

Ammonia is one alternative refrigerant for new and existing refrigerating and air-conditioning systems. Ammonia has a low boiling point (-28°F @ 0 psig), an ozone depletion potential (ODP) of 0.00 when released to atmosphere and a high latent heat of vaporization (nine times greater than R-12). In addition, ammonia in the atmosphere does not directly contribute to global warming. These characteristics result in a highly energy-efficient refrigerant with minimal environmental problems.

From a purely economic analysis, without unnecessary regulatory burdens, ammonia should find broader applications as a refrigerant than it currently enjoys.

Ammonia's use in the HVAC&R industry should be expanded as regulatory and code officials become informed of its relative safety. Applications for ammonia-based refrigeration systems include thermal storage systems, HVAC chillers, process cooling and air conditioning, district cooling systems, supermarkets, convenience stores, air conditioning for the International Space Station and Biosphere II and increasing output efficiencies for power generation facilities.

4.0 HEALTH AND SAFETY

Ammonia is hazardous at high concentration levels. The National Institute for Occupational Safety and Health (NIOSH), in its 2007 Pocket Guide[1], has set the immediately dangerous to life and health (IDLH) level, the level at which an individual could be exposed for 30 minutes without a respirator and not experience any lasting health effects, at 300 parts per million. Ammonia's sharp, irritating, pungent odor actually helps reduce exposure to potentially dangerous concentrations. The average odor threshold is 5 ppm[2], well below concentrations that may cause harmful effects to the human anatomy.

The chart below, which is based on data from ATSDR 2004[3], shows the effects of various concentrations of ammonia.

Body Part	Concentration	Effect
Eyes	500 ppm and below	No permanent eye damage to even chronic exposure (see Ref 4)
Eyes	100-200 ppm	Eyes irritated (see Ref 4)
Skin	5000 ppm and above (vapor) Pure liquid	Full body chemical suit required (see Ref 2) Second degree burns with blisters (see Ref 2)
Lungs	400 ppm 1700 ppm 2400 ppm	Immediate throat irritation (see Ref 2) Cough (see Ref 2) Threat to life after 30 minutes (see Ref 2)

The self-alarming property of ammonia is recognized by virtually all engineers, designers, technicians and mechanics that deal with and work on ammonia systems regularly. Thus, small leaks are repaired quickly and not neglected or dismissed as insignificant.

The threshold limit value (TLV) consists of two components—the time-weighted average (TWA) concentration and the short-term exposure limit (STEL). The TWA is the time-weighted average concentration for a normal eight-hour work day and a 40-hour work week. The STEL is a 15-minute time weighted average exposure that should not be exceeded at any time during the work day, even if the eight-hour TWA is within the TLV. The TWA of ammonia is 25 ppm[1]. The STEL for ammonia is 35 ppm[1].

Modern ammonia systems are fully contained closed-loop systems with fully integrated controls, which regulate pressures throughout the system. Also, every refrigeration system is required by codes, which are effective, mature and constantly updated and revised, to have safety relief valves to protect the system and its pressure vessels from over-pressurization and possible failure. The most common and preferred method of release is by venting of the vapor from the relief valves to the atmosphere. Ammonia is lighter than air (molecular weight of ammonia is 17, molecular weight of air is 28).

5.0 ENVIRONMENTAL ASPECTS

Ammonia is not a contributor to ozone depletion, greenhouse effect or global warming.[5] Thus, it is an environmentally friendly refrigerant. Ammonia has no cumulative effects on the environment and a very limited (a few days[6]) atmospheric lifetime. Because of the short lifetime of ammonia in the atmosphere, it is considered to be biodegradable. It is even used to reduce harmful stack gas emissions by injection into boiler and gas turbine exhaust streams. [2]

Ammonia may be released to the atmosphere by sources such as decaying organic matter, animal excreta, fertilization of soil, burning of coal, wood, etc. and by volcanic eruptions. Ammonia may be released into water as effluent from sewage treatment and/or industrial processes and as run-off from fertilized fields or areas of livestock concentrations. Ammonia may be released into soils from natural or synthetic fertilizer applications, livestock excrement, the decay of organic material from dead plants and animals or from the natural fixation of atmospheric nitrogen.

6.0 CONSIDERATIONS OF AMMONIA AS A REFRIGERANT

While the benefits of ammonia as a refrigerant are well known (high energy efficiency, zero ODP, zero GWP, low TEWI, self-alarming pungent odor), barriers to expanding its use into HVAC&R applications must be addressed. These barriers, both real and perceived, generally relate to human health and environmental safety, and to ammonia refrigeration system installation cost.

6.1 Human Health and Environmental Safety

Anhydrous ammonia (Chemical Abstracts Service, CAS #7664-41-7) is currently classified by the U.S. Environmental Protection Agency (EPA) as an extremely hazardous substance (SARA7 Title III, Sec. 302). It is included on the following SARA Title III lists:

- Reportable Quantity List (Section 304) -Chemicals on this SARA Title III list require notification to EPA and state and local agencies of releases in excess of the reportable quantity (currently 100 pounds).
- Extremely Hazardous Substance List (Section 302) -Chemicals on this SARA Title III list, at facilities with quantities in excess of the Threshold Planning Quantity (TPQ), are subject to SARA Title III requirements, which mandates numerous reporting and planning provisions. The TPQ of ammonia is 10,000 pounds.
- Section 313 - Chemicals on this SARA Title III list are subject to the Emergency Planning and

Community Right-to-Know Act of 1986 annual toxic release inventory reporting (Form R).

While the EPA addresses ammonia from the environmental perspective, the U.S. Occupational Health and Safety Administration (OSHA) addresses ammonia from the perspective of worker safety. OSHA defines ammonia as a hazardous material and, depending on its use, imposes certain regulations on its use, storage, handling and occupational exposure.

EPA and OSHA classify all CFCs and HCFCs as hazardous substances, and thus the use of these refrigerants requires specific reporting and management practices comparable to ammonia.

6.2 Risk Assessment

All refrigerating systems require risk assessment; ammonia systems are not exceptions. OSHA's Process Safety Management (PSM), 29CFR1910.119, provides guidelines for a comprehensive program developed by employees and management at facilities to ensure that proper safety, maintenance and operating procedures are followed, and thereby minimize potential hazards. This PSM incorporates ANSI/ASHRAE Standard 15, Safety Standard for Refrigeration Systems[8]. Although it only affects plants with large refrigerant charges, its requirement for what-if or hazop analyses are directed towards reducing risks and promoting plant safety, so this PSM could be a good program for smaller plants also.

Facilities affected by OSHA's PSM are also affected by EPA's Risk Management Program (RMP), which is intended to prevent, detect and respond to accidental releases of hazardous chemicals and to inform local communities of the risks.

With an appropriate application of PSM and RMP programs to ammonia refrigeration systems, safety to individuals, communities and the environment is enhanced. However, the application of PSM and RMP programs must be refined and tailored to avoid imposing unreasonable and overly burdensome barriers on new and existing ammonia refrigeration systems.

7.0 ASHRAE ACTIVITIES

ASHRAE has a long history of involvement with the use of ammonia as a refrigerant, dating back to the earliest applications for refrigeration. ASHRAE has a significant role to play in encouraging the proper and safe use of ammonia in the following areas: policy; research, standards, codes and guidelines and technology exchange and education.

7.1 Policy

ASHRAE's Ammonia as a Refrigerant Position Document emphasizes the important role that ammonia can play as an alternative to CFC, HCFC and HFC refrigerants. It also identifies ASHRAE's concerns about the use of ammonia and establishes what the Society will do to encourage and support its proper and safe use as a refrigerant.

Ammonia has been identified by the EPA[9] as a viable alternative to currently used refrigerants because it does not deplete the ozone layer or contribute to global warming.

The United Nations Environmental Programme (UNEP) has identified ammonia as an excellent refrigerant for replacement of many current CFC and HCFC applications [2006 Technical Options Report] as part of the reassessment of the Montreal Protocol. Other countries, notably Germany, have established policies to encourage and promote the use of ammonia, including the replacement of such HCFC refrigerants as R-22 for applications such as water chillers and commercial refrigeration systems for supermarkets.

Other international organizations have issued positions or statements of support for the use of ammonia as a refrigerant. These include the Australian Institute of Refrigeration, Air-Conditioning and

Heating[10], the International Institute of Refrigeration[11], the German Institute of Refrigeration[12], etc.

7.2 Research

ASHRAE is unique among technical engineering societies because it sponsors an extensive member-supported research program. In 2009-2010, the funding for ASHRAE research projects was over $3 million. A significant portion of current projects relate to alternative refrigerants, including ammonia. In past years, ASHRAE has promoted several research projects related to various aspects of ammonia refrigeration. The most recent ASHRAE research plan includes a goal eight to facilitate the use of natural and low global warming potential (GWP) synthetic refrigerants and seek methods to reduce their charge. ASHRAE has had recent and/or current research projects that involve ammonia, including:

- Condensation-Induced Hydraulic Shock Laboratory Study, $81,800 project managed by TC 10.3 at Georgia Institute of Technology (970-RP).
- Evaporation of Ammonia Outside Smooth and Enhanced Tubes with Miscible and Immiscible Oils, $115,675 project managed by TC 1.3 at Texas Tech University (977-RP).
- In-Tube Condensation of Ammonia in Smooth and Enhanced Tubes With and Without Miscible Oil, $147,000 project managed by TC 1.3 at University of Illinois (1207-RP).

ASHRAE actively encourages the submission of proposals for new research projects related to refrigeration and other applications that relate to ammonia. Several future ammonia projects are included in the most recent research plan.

A number of other refrigeration-related organizations are interested in use of ammonia as a refrigerant. A general list of ammonia-related potential research projects has been developed.

7.3 Standards, Codes and Guidelines

ASHRAE plays a major role in development of voluntary standards and guidelines governing the application and use of refrigerants, including ammonia. In addition, other organizations adopt the technical requirements developed by ASHRAE into various codes and regulations.

The most important ASHRAE standards dealing with ammonia are ANSI/ASHRAE Standard 34-2007, *Designation and Safety Classification of Refrigerants*, and ANSI/ASHRAE Standard 15- 2007, *Safety Standard for Refrigeration Systems*. Standard 34 classifies ammonia as a Group B2 refrigerant, because of toxicity and flammability concerns. Standard 15 establishes the requirements for safely applying ammonia in refrigerating systems. In general, ammonia can be used in unlimited quantities in direct systems for industrial occupancies. However it must be used in indirect (secondary) systems for commercial and public occupancies, while its general use in small absorption equipment is unrestricted.

In addition, ASHRAE has issued recommendations on the recycling, recovery and reuse of refrigerants, including ammonia [ASHRAE Standard 147-2002].[14] Standard 147 encourages the consideration of ammonia as an alternative to CFC and HCFC refrigerants, and contains information on the ozone depletion potential and global warming potential of ammonia and other commonly used refrigerants.

Other technical organizations have issued standards/ guidelines addressing the proper application of ammonia as a refrigerant. These standards/guidelines cover the design and installation of ammonia refrigeration systems [ANSI/ IIAR 2-2008].[15] International standards also address safety and application of ammonia [ISO 5149, Refrigeration Safety[16]; ISO 1662, Refrigerating Plants - Safety Requirements[17]; CEN EN 378, Refrigerating Systems Safety and Environmental Requirements[18]].

The proper application of ammonia as a refrigerant is governed by state and local building, mechanical and electrical codes. In the U.S., these codes are issued by various model code organizations such as International Code Council (ICC) and National Fire Protection Association (NFPA). Because of its classification as a hazardous chemical, ammonia is often specifically covered by various requirements in fire codes. The Code Interaction Subcommittee of ASHRAE's Standards Committee will review proposed fire and mechanical codes that could affect refrigeration applications. ASHRAE has established a policy to encourage adoption of ASHRAE standards in model codes.

Electrical codes, especially the National Electric Code[19], are relevant to ammonia because ammonia in high concentrations can form flammable mixtures with air. Standard 15 establishes design procedures for applying ammonia, including proper ventilation levels, which are referenced in electrical codes to assure the safe application in buildings.

In some cases, very stringent local toxic gas ordinances have been applied to ammonia, even though they were intended to apply to highly toxic chemicals. These types of ordinances can be very restrictive.

7.4 Technology Transfer and Education

ASHRAE plays a very important role in providing technical information on the proper application of ammonia as a refrigerant. In this role, ASHRAE assists in transfer of technology and in education of the technical community. These important activities are carried out through a number of vehicles: ASHRAE Handbook, ASHRAE Journal and ASHRAE Transactions; special publications; and through a number of educational forums.

The major sources of technical information on ammonia is the ASHRAE Handbook. The 2009 *Fundamentals*[20] volume contains general information on Thermodynamics and Refrigeration Cycles. (Chapter F2) and on Refrigerants (Chapter F29), including the thermodynamic properties of ammonia. The other major resource for information on ammonia is the 2010 *ASHRAE Handbook—Refrigeration* volume[21], covering Liquid Overfeed Systems (Chapter R4), Ammonia Refrigeration Systems. (Chapter R2) and Refrigeration System Chemistry (Chapter R6). An additional resource is the ASHRAE publication Thermodynamic Properties of Refrigerants [1986].[22]

ASHRAE has published a number of technical papers, articles and special reports addressing the use of ammonia. These include notices and articles regarding ammonia refrigeration in ASHRAE Journal. Technical papers presented at ASHRAE meetings are published in ASHRAE Transactions, and in various special publications. A summary of more than 30 technical articles and references can be found on ASHRAE Online.

Key parts of ASHRAE's technology exchange and education functions are fulfilled by the Annual and Winter Conference technical programs, including seminars, forums, symposia and technical sessions. In addition, the Society offers a self-directed learning course on the Fundamentals of Refrigeration. Local ASHRAE chapters also sponsor refrigeration-related programs and speakers, which have recently shown a strong interest in ammonia.

Technical activities focusing on ammonia are addressed within ASHRAE by the Refrigeration Committee, which is now a standing committee. In addition to the Refrigeration Committee, the Chapter Technology Transfer Committee (CTTC) encourages grass roots regional and chapter activities, which focus on refrigeration. The Refrigeration Committee maintains a speakers list of speakers/topics that includes ammonia. Various technical committees (TCs 10.1, 10.3, 10.5, 1.3, 8.5 etc.) also focus on ammonia-related issues.

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