AMMONIA:
THE NATURAL REFRIGERANT OF CHOICE

(AN IIAR GREEN PAPER)

CONTENTS

EXECUTIVE SUMMARY

Ammonia is perhaps most well recognized as a household cleaner. However, ammonia makes another important contribution to daily life as an industrial refrigerant. It is responsible for the year-round availability, volume and variety of food and beverages served daily on breakfast, lunch and dinner tables around the world. Ammonia refrigeration is among the most significant developments of modern times and a primary contributor to our modern lifestyle.

The development of mechanical refrigeration dates back to the Industrial Revolution. Today, ammonia remains the most commonly used refrigerant in large systems to process and preserve food and beverages. Ammonia has been at the forefront of advances in refrigeration technology, making it essential to the food processing, storage and delivery infrastructure of our economy. More recently, ammonia refrigeration systems have been used for air conditioning in publicly accessed buildings and increasing output efficiencies for power generation facilities.

From an operational perspective, ammonia is generally accepted as the most efficient and cost effective industrial refrigerant available, an important benefit to consumers because lower operating costs contribute to lower food prices. It has found applications in enhancing the efficiency of power generation facilities. Beyond its economic advantages, ammonia is a natural refrigerant that is environmentally benign in the atmosphere.

With heightened attention given to global warming and the extraordinary international efforts made over the past decade to reduce the use of refrigerants harmful to the environment, ammonia is well positioned to be the refrigerant of the 21st Century. Policies that encourage the expanded use of ammonia as a refrigerant would be compatible with current and emerging environmental protection and energy-efficiency goals.

The advantages of ammonia in refrigeration are well known. Ammonia does not destroy atmospheric ozone and does not contribute to the greenhouse effect linked to global warming. In fact, ammonia, one of the most common compounds found in nature, is essential to earth's nitrogen cycle and its release in the atmosphere is immediately recycled. The use of ammonia as a refrigerant is consistent with international agreements on reducing global warming and ozone depletion. Because of ammonia's proven applicability as a safe and efficient refrigerant for over 150 years, it is immediately available for wider usage and new applications. From a purely economic analysis, without unnecessary regulatory burdens, ammonia should find broader applications as a refrigerant than it currently enjoys.

I. INTRODUCTION TO AMMONIA REFRIGERATION

Mechanical refrigeration was developed in the 19th century based on the principle of vapor compression.[1] The first practical refrigerating machine using vapor compression was developed in 1834 and by the late 1800s refrigeration systems were being used in breweries and cold storage warehouses.[2] The basic design of the vapor compressor refrigeration system, using one of many available refrigerants in a closed cycle of evaporation, compression, condensation, and expansion, has changed very little since the 1870s. Present day systems are more efficient, include engineered safety features, are available in smaller sizes, and require comparatively smaller capital outlays.

Early refrigerants included ammonia, sulfuric ether, carbon dioxide, sulfur dioxide, methyl chloride, and some hydrocarbons.[3] Of these, only ammonia has secured a lasting role as a refrigerant.

Ammonia was first synthesized in 1823 by reacting air and hydrogen and the first commercial production of synthetic ammonia began in 1913.[4] Presently, there are an estimated two billion metric tons of ammonia present in the world. Of this amount, approximately five percent is man-made. Approximately 18 million metric tons of ammonia are produced annually in North America alone, and of this amount, less than two percent is used for refrigeration.[5] Since ammonia is a common, naturally occurring compound in the environment and can be naturally broken down into harmless hydrogen and nitrogen molecules (the atmosphere consists of nearly 80% nitrogen), it is often referred to as a "natural refrigerant".[6]

Ammonia was first used as a refrigerant in the 1850s in France and was applied in the United States in the 1860s for artificial ice production.[7] The first patents for ammonia refrigeration machines were filed in the 1870s.[8] By the 1900s, ammonia refrigeration machines were being commercially installed in block ice, food processing, and chemical production facilities.[9] From 1875 onwards, ammonia refrigeration was being applied to ice rinks, first as a brine chiller and later as a direct refrigerant[10]

During the 1930s, air conditioning markets began to develop, first for industrial applications and then for human comfort.[11] The use of smaller units for domestic refrigerators increased substantially between 1920 and 1930. By the 1930s, halocarbons such as chlorofluorocarbons (CFCs) had been developed to replace the use of poisonous refrigerants such as sulfur dioxide and methyl chloride. Halocarbons were believed to be the perfect refrigerants because they had no odor, were nontoxic, were comparable in power requirements and price with the other refrigerants, and were suitable for equipment available at that time.

Over the seven-decade period from the 1930s through the 1990s, nearly all state and local building codes, air-conditioning equipment standards, design standards for air-conditioning systems, and installation guidelines were developed for equipment and systems utilizing one of the many halocarbon refrigerants. In the United States, most engineering standards applicable to air conditioning systems and equipment were developed by the American Society of Heating, Refrigerating and Air-conditioning Engineers. In addition, major equipment suppliers developed products to comply with these codes that permitted only halocarbon refrigerants. Architects, consulting engineers, and contractors applied these halocarbon systems in their air-conditioning project designs and installations.

During the same seven decades, the amount of halocarbon refrigerants lost to the atmosphere through leaks due to system design and maintenance is estimated to have exceeded many times the amount actually required by refrigeration plants, thereby increasing the demand for halocarbons and securing the refrigerants' commercial success.[12] Consequently, halocarbons became the refrigerant of choice for residential and commercial air conditioning applications, while ammonia remained the refrigerant of choice for the industrial refrigeration industry. This growth in the use of halocarbons, promoted as safe refrigerants under trade names such as "Freon", took place before their damaging impact on the environment was known.

Today, ammonia refrigeration is used significantly in the food processing and preservation industries and to a certain extent in the chemical industries.[13] Ammonia refrigeration is the backbone of the food industry for freezing and storage of both frozen and unfrozen foods.[14] It is the workhorse for the post-harvest cooling of fruits and vegetables, the cooling of meat, poultry, and fish, refrigeration in the beverage industry, particularly for beer and wine, refrigeration of milk and cheese, and the freezing of ice cream.[15] Practically all fruits, vegetables, produce and meats, as well as many beverages and juices, pass through at least one facility that uses an ammonia refrigeration system before reaching our homes.

More recently, air conditioning provided by ammonia refrigeration systems have found limited applications on college campuses and office parks, small scale buildings such as convenience stores, and larger office buildings.[16] These applications have been achieved by using water chillers, ice thermal storage units, and district cooling systems. In Europe, where regulatory regimes have encouraged new applications, ammonia refrigeration systems have been used safely for air conditioning in hospitals, public buildings, airports, and hotels.[17] Ammonia refrigeration has also been used to provide air conditioning for the International Space Station and Biosphere II.[18] Installation at power generation facilities represents an emerging application of ammonia refrigeration. Unfortunately, a broader application of ammonia as a refrigerant is hampered by restrictive regulations at all levels in the U.S.

II. ADVANTAGES OF AMMONIA AS A REFRIGERANT

Ammonia is a naturally-occurring compound, made up of one atom of nitrogen and three atoms of hydrogen, with the chemical formula NH_3. Ammonia is a key intermediary in the nitrogen cycle, and under normal conditions, is essential for many biological processes.[19] Most of the ammonia in the environment comes from the natural breakdown of manure and dead plants and animals.[20] Ammonia can be found in water, soil, and air, and is a source of much-needed nitrogen for plants and animals.[21] In fact, ammonia is among the most abundant gasses in the environment.[22]

Refrigerant-grade ammonia is 99.98% pure – free of water and other impurities. It is readily available, inexpensive, and capable of absorbing large amounts of heat when it evaporates. The operating pressures of ammonia are comparable with other refrigerants. Ammonia's ability to absorb larger amounts of heat per volume makes it possible to use smaller pipes and smaller components compared to other refrigeration systems while delivering the same amount of refrigeration.[23]

As a refrigerant, ammonia offers three distinct advantages over other commonly used refrigerants. First, ammonia is an environmentally compatible refrigerant because it has an ozone depletion potential (ODP) of zero and a global warming potential (GWP) of zero.[24] Second, because of its superior thermodynamic properties, ammonia as a refrigerant requires less energy than other refrigerants when used in large industrial systems. Third, ammonia refrigeration has a proven safety record, in part because of the physical properties of ammonia, not the least of which is ammonia's well-recognizable and easily-detectable odor, compliance with voluntary industry standards, and an industry of well-trained operators.

Ammonia is an environmentally compatible refrigerant.

Ammonia does not harm atmospheric ozone. It is now well recognized that halocarbons released into the atmosphere will eventually reach the stratosphere and the ozone layer.[25] Halocarbons are extremely chemically stable, with estimated life cycles of two to three centuries. When released into the atmosphere, this stability allows halocarbons to migrate through the troposphere and into the stratosphere.[26] At this altitude, the intense ultraviolet rays of the sun break down halocarbon molecules, often releasing chlorine ions, which in turn act as catalysts to break down ozone molecules.[27] This process reduces the ozone layer's effectiveness as a filter against ultraviolet radiation, resulting in higher amounts of ultraviolet radiation reaching the surface of the earth with harmful biological consequences.[28] Increased radiation causes increased health risks in humans and damages the flora and fauna of the ecosystem.

The 1987 Montreal Protocol on Substances that Deplete the Ozone Layer, under the auspices of the United Nations Environmental Program went into force on January 1, 1989 and has since been revised and strengthened.[29] The United States, Canada, Japan and the European Economic Community, major producers and users of CFCs, were among the signatories.[30] The Protocol ensured that production of CFCs ceased at the end of 1996 and has led to the implementation of their gradual reduction in developing countries.[31] Amendments adopted in 1992 and 1995 covered hydrochlorofluorocarbons (HCFCs), which have a much lower ozone-depleting potential than CFCs and had been relied upon to speed up CFC reduction.[32] Under the Protocol, HCFCs will be gradually phased out by 2030. Certain countries have set earlier target dates for phase-out of HCFCs.[33]

Just as it does not damage atmospheric ozone, ammonia, with a life cycle in the atmosphere of less than one week, does not contribute to the greenhouse effect responsible for global warming. Global warming results from the short wave, near infra-red radiation that reaches the earth from the sun.[34] About fifty percent of the sun's radiation reaches the earth.[35] This is absorbed by the earth's surface which re-emits the radiation in longer, far infra-red wavelengths. This re-emitted radiation is partially absorbed by gasses known as greenhouse gasses.[36] Greenhouse gasses are either natural (CO_2, water vapor, etc.) or man-made (CO_2, N_2O, CH_4, CFC, HCFC, HFC, etc.).[37]

The 1997 Kyoto Protocol to the United Nations Framework Convention on Climate Change controls emissions of greenhouse gasses.[38] The Protocol defines six gasses or family of gasses: carbon dioxide (CO_2); methane (CH_4); nitrous oxide (N_2O); hydrofluorocarbons (HFCs); perfluorocarbons (PFCs); and sulfur hexafluoride (SF_6).[39] HFCs were developed in order to enable CFC and HCFC phase-out.[40] Within the framework of the Protocol, developing countries will reduce emissions of these gasses by at least five percent with respect to 1990 levels during the 2008 and 2012 period.[41] CFCs and HCFCs, which are governed by the Montreal Protocol, are not included in the Kyoto Protocol.[42]

Under each protocol, each signatory nation establishes its own rules and procedures to meet the phase-out goals.[43] The Clean Air Act Amendments of 1990 gave statutory recognition to the Montreal Protocol's phase-outs in the United States and established a comprehensive set of regulatory requirements for recovery, recycling, and disposal of CFCs when equipment containing them is serviced or discarded.[44] The Amendments also directed the U.S. EPA to establish a program for the control or phase-out of substances harmful to the stratospheric ozone layer. Through the Significant New Alternatives Policy (SNAP) Program, the agency has identified ammonia as an acceptable substitute to ozone depleting substances in the major industrial sectors, including refrigeration and air conditioning.[45]

Ammonia has superior thermodynamic properties and as a refrigerant results in lower CO_2 emissions and requires less energy.

Generally speaking, ammonia refrigeration systems cost 10-20% less to install than systems using alternative industrial refrigerants. Thermodynamically, ammonia is 3-10% more efficient than other refrigerants; as a result ammonia systems use less electricity than systems with alternative refrigerants. The cost of ammonia itself is significantly less than other industrial refrigerants and less ammonia is also generally required to do the job as compared to other industrial refrigerants. All of this adds up to lower operating costs for food processors and cold storage facility operators, and that means lower grocery bills for the average household.

Ammonia and its alternatives function as refrigerants in various types of systems that consume electricity or other types of energy during operation. Due to its highly favorable thermodynamic properties, ammonia used as a refrigerant requires less primary energy to produce a certain refrigeration effect compared to other commonly used refrigerants. Therefore, its indirect global warming effect due to CO_2 emissions from electric power plants can be considered one of the lowest of all refrigerants.[46]

Proper environmental impact assessment of refrigerants and their systems requires consideration of both their direct and the indirect contribution to global warming. Refrigeration systems *directly* contribute to global warming through the greenhouse gas effect of their fugitive refrigerant emissions. They *indirectly* add to global warming through carbon dioxide emissions resulting from the conversion of fossil fuels to energy required to operate the systems.

The Total Equivalent Warming Impact (TEWI), is defined as the sum of these direct and indirect contributions. It is a concept developed in the early 1990's to help system design engineers assess refrigerants and their systems using a single number rating system. More recently, the concept of Life Cycle Climate Performance indicators (LCCP) was introduced to further refine the TEWI concept. The LCCP program was designed to include the two main elements of the TEWI calculation as well as the assessment of the environmental impact of refrigeration production, distribution and end-of-life disposal.

The TEWI and the LCCP concepts illustrate how important energy efficiency and low global warming potential (GWP) of refrigerant emissions are to refrigeration and air conditioning systems.

The Alternative Fluorocarbons Environmental Acceptability Study (AFEAS) and the U.S. Department of Energy (DOE) funded TEWI studies using a *systems approach* to determine the overall contribution of refrigerants to global warming. The studies focused on:

- Technical options that could be implemented by the year 2000
- Energy and global warming impacts of next generation fluorocarbons as well as not-in-kind (NIK)/non-fluorocarbon technologies that could be developed or improved to replace CFCs and HCFCs
- Refrigeration and air conditioning technologies that can be commercialized during the phase-out of HCFCs

The studies demonstrate the importance of assessing both the direct and indirect contributions of all refrigeration alternatives when selecting the best environmental option. The studies conclude that energy efficiency is a powerful tool to mitigate future potential climate change.[47]

Ammonia refrigeration is inherently safe.

In any mechanical refrigeration system, leaks will occur. This fact is exacerbated when the leaks involve odorless refrigerants as evidenced by the abundant supply of CFCs in the atmosphere today. The inherent safety of ammonia refrigeration is explained in part by ammonia's characteristic odor, which signals even the smallest leak, at concentrations far lower than any dangerous level.[48] Ammonia's safety record as a refrigerant is also explained by other physical characteristics such as its density and limited range of flammability, engineering advances for refrigeration systems, and the solid record of well-trained ammonia refrigeration systems operators.

Ammonia's self-alarming quality is due to its well recognizable and easily detectable odor. Even the slightest traces of ammonia in the air can be detected. This allows for the safe and immediate repair of system leaks or sources of leaks. Contrasted to the penetrating odor of ammonia, other commonly used refrigerants like the halocarbons are odorless and their escape difficult to detect without mechanical systems. The pungent odor of ammonia will encourage individuals to leave the immediate area of release before harmful concentrations will exist.

The safety record of ammonia refrigeration is also due to the fact that ammonia is 1.7 times lighter than air and thus easily vented by mechanical means into the atmosphere.[49] If a leak occurs in a refrigeration system under pressure, only the pressurized gas and, absent additional heat, a smaller amount of the liquid in that space will be released.[50]

Releases of liquid ammonia are rare. Because ammonia vapor is lighter than air, it will rise and quickly become diluted in the atmosphere.[51] In the presence of moisture, a visible water vapor cloud will form.[52] In contrast, halocarbons are heavier than air and will collect at ground level, displacing oxygen and posing a risk of suffocation.

Ammonia is difficult to ignite and exhibits a narrow range of flammability.[53] Ammonia is flammable only at high concentrations and under extremely limited conditions. Because ammonia will not sustain a flame on its own, ignition of ammonia vapor requires an uninterrupted external flame source. Ammonia's burning velocity, at a maximum of 8cm/s, is substantially lower than other flammable refrigerants, and is not high enough to create an explosion. For these reasons, ammonia explosions are rare. Properly designed ammonia refrigeration systems that are well ventilated and free of open flames or ignition sources mitigate against potential explosion.[54]

Also significant to ammonia's safety record is the fact that individuals who work with ammonia refrigeration systems have specific training available to them. A wide range of education and hands-on instruction is currently provided by industry associates, contractors, and community colleges. Additionally, industry codes and standards along with applicable federal regulations, provide further operational and system design safeguards.

III. SAFE USE OF REFRIGERANTS

A well-designed and properly maintained refrigeration system requires its owner and operator to be familiar with the operation of the equipment and the characteristics of the refrigerant. Prevention is key to ensuring a safe work environment associated with any refrigeration system.[55] Workers must be knowledgeable of emergency procedures and applicable standards.[56] In addition, regulations require regular inspection of safety equipment and ongoing training to prepare workers in the event of an emergency.[57]

The risks associated with any refrigeration system that must be addressed through appropriate control mechanisms include accidental releases, releases occurring during operations and maintenance, and engineering flaws. Modern plants have state of the art detection and ventilation systems. These systems provide immediate warning once the presence of a refrigerant reaches a pre-selected level and immediately remove the released refrigerant from the confined space.[58] Ammonia refrigeration safety features address minimizing the refrigerant charge, suitable ventilation, ammonia absorbing systems, restricting the use of ammonia in public locations, and promoting indirect cooling systems.[59]

In the event of a leak of any refrigerant, evacuation and ventilation are important mechanisms for minimizing exposure. The true danger of any refrigerant occurs when an individual is unable to leave a confined space with a high concentration of a refrigerant or when liquid refrigerant comes in direct contact with the body, particularly the eyes.[60] Under normal circumstances, individuals will always seek relief from ammonia before its presence becomes a serious health hazard. Air containing amounts of ammonia in which a person is willing to remain is generally not dangerous; however, as with any irritating atmosphere, care should be taken to prevent prolonged exposure.

IV. REGULATORY REGIMES FOR REFRIGERATION SYSTEMS

Industry codes and standards have been developed and revised over the years to address risks associated with refrigeration systems, and they incorporate appropriate systems requirements and personnel training. These industry-driven codes and standards, which have done the most to achieve acceptable levels of safety associated with ammonia refrigeration systems, include certain system engineering and design standards and operating codes developed by the International Institute of Ammonia Refrigeration (IIAR), American Society of Heating, Refrigerating and Air Conditioning Engineers (ASHRAE) and the American National Standard Institute (ANSI): the 1999 American National Standard for Equipment, Design and Installation of Ammonia Mechanical Refrigeration Systems (ANSI/IIAR 2-1999); and the 1994 American National Standard: Safety Code for Mechanical Refrigeration (ANSI/ASHRAE 15-1994).

Three categories of federal regulations have application to activities involving ammonia.[61] The Occupational Safety and Health Administration (OSHA) within the Department of Labor administers most workplace safety requirements and has promulgated standards addressing workplace hazards associated with ammonia and applicable to ammonia refrigeration systems. The Environmental Protection Agency (USEPA) administers most federal environmental requirements, including numerous reporting and risk management requirements applicable to ammonia refrigeration systems. The Department of Transportation (USDOT) administers most requirements applicable to the transportation of ammonia. In addition, multiple state and local codes are also applicable to ammonia refrigeration systems.

While these federal, state and local regulatory regimes attempt to address environmental and workplace safety issues, a more tailored application, reflecting an appropriate understanding of ammonia refrigeration, would reduce certain regulatory barriers that prevent the expanded use of ammonia as a refrigerant. A more tailored application of regulations would at the same time enhance the intended environmental and safety goals by channeling resources to the most critical aspects of systems operations and integrity.

Facilities in many countries that store or handle hazardous chemicals have established Process Safety Management (PSM) programs. PSM is a comprehensive program developed by employees and management at facilities to ensure that proper safety, maintenance, and standard operating procedures are followed. A PSM program is intended to examine and minimize potential hazards.[62] Facilities have also developed Risk Management Programs (RMP) to prevent, detect and respond to accidental releases of hazardous chemicals and to inform local communities of the risks.[63] The PSM and RMP programs were developed to address highly hazardous materials and grew out of the Bhopal incident and others at petrochemical refineries. In the U.S., both are applicable to ammonia refrigeration only because of the hazards incident to the transportation of ammonia and ammonia's widespread use.

As currently applied under U.S. law, PSM and RMP requirements create regulatory burdens for ammonia refrigeration applications. Paperwork and document retention are particularly burdensome. Significant resources are required by facility operators to engage the regulatory compliance system. These regulations as presently constituted divert resources from more effective preventive measures and inhibit the expanded use of ammonia refrigeration systems. With an appropriate application of PSM and RMP programs to ammonia refrigeration systems, safety to individuals, communities, and the environment would be enhanced.

V. A NEW VISION FOR AMMONIA REFRIGERATION

Ammonia offers many advantages as a refrigerant. It has no ill effects on atmospheric ozone, does not contribute to the greenhouse effect, and its LCCP is highly favorable. Because ammonia also has favorable thermodynamic properties, ammonia refrigeration systems are more efficient than most traditional and newer refrigerants. Finally, ammonia refrigeration has a strong safety record, one that is comparable to other refrigeration systems in use today.

Certainly the growing environmental concerns relating to halocarbon refrigerants has sparked a renewed interest in ammonia refrigeration. However, demand has been most notable in the Northern European market where regulations are more accommodating.[64]

Ammonia has found its greatest application as a refrigerant in industrial settings, primarily in the food processing and food distribution sectors. It is also used in the petrochemical and pharmaceutical sectors. Ammonia refrigeration has been the refrigeration of choice for dairy-related products, ice making, and cold storage.[65]

Ammonia air conditioning applications are found in government office buildings, museums, airports, colleges and hospitals. Enhancing the efficiency of power generation facilities represents a new application for ammonia refrigeration. With regulations properly tailored to ammonia refrigeration systems, the application of ammonia refrigeration systems will become more widespread.

To realize ammonia's full potential as a refrigerant, certain regulations will require a more tailored application to ammonia refrigeration systems. In particular, application of the PSM and RMP regimes must be refined and tailored to avoid the burdens and barriers imposed on existing and new ammonia refrigeration systems. Local regulations can also achieve their health and safety goals with more informed applications that do not restrict the broader use of ammonia refrigeration systems.

NOTES

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[57] Ibid., 45.
[58] Ibid., 27-29.
[59] Paul de Larminat: Expanding the Use of Ammonia (ASHRAE Journal, March 2000), 36.
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[62] Ammonia Refrigeration, 45.
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[64] Paul de Larminat: Expanding the Use of Ammonia (ASHRAE Journal, March 2000), 40.
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