



## FOCUS ARTICLE

## The Good, the Bad, and the Ugly of Using Anhydrous Ammonia Refrigerant in the Process Industries

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Ammonia (R-717) was among the early refrigerants, first used in 1850 in France<sup>(2)</sup>. It was introduced in the US in the 1860s for artificial ice production, after which the first ammonia refrigeration machines were patented in the 1870s. Ammonia is one of the early chemicals to secure a lasting role as a refrigerant. It is still used today in large, commercial cooling applications.

### Ammonia Production:

Ammonia, chemical formula  $\text{NH}_3$ , is a common naturally occurring compound and one of the most abundant alkaline gasses in the environment. It was first synthesized in 1823 by reacting air with hydrogen<sup>(2)</sup>. Before the start of World War I, most ammonia was obtained by the dry distillation of nitrogenous vegetable and animal products; by the reduction of nitrous acid and nitrites with hydrogen; and also by the decomposition of ammonium salts by alkaline hydroxides or by quicklime. Today, most ammonia is produced on a large scale by the Haber-Bosch process<sup>(3)</sup> in units with capacities of up to 3.300 metric tons per day. Of the 18 million metric tons of ammonia produced in North America annually, approximately 2% is used for refrigeration.

### The Good About Ammonia as a Refrigerant:

Ammonia offers three distinct advantages over other commonly used industrial refrigerants. First, ammonia is naturally occurring and therefore environmentally compatible<sup>(2)</sup>. Second, ammonia has superior thermodynamic qualities to other refrigerants. As a result ammonia refrigeration systems use smaller pipe sizes and require less heat transfer area<sup>(6)</sup> and hence use less electricity – ammonia is approximately 15-20% more efficient than its hydrochlorofluorocarbon (HCFC) alternatives<sup>(4)</sup>. Third, ammonia's recognizable strong pungent odor is its greatest safety asset. Unlike most other industrial refrigerants that have no odor, ammonia's odor makes leaks more easily detectable. Besides the three distinct advantages above, ammonia is also cheap and not as flammable as other chemicals that are used as refrigerants, such as propane and butane<sup>(5)</sup>.

## The Bad About Ammonia as a Refrigerant:

The major disadvantage of ammonia as a refrigerant is its toxicity. Due to ammonia's hygroscopic nature, it migrates to moist areas of the body, including the eyes, nose, throat and moist skin. Skin and respiratory-related diseases are aggravated by exposure<sup>(6)</sup> and even possible fatality at higher concentrations. The vapors may cause severe burn injuries. Liquid ammonia will cause frostbite because its temperature at atmospheric pressure is -28°F<sup>(7)</sup>.

A number of organizations have established employee exposure limits for ammonia.

For occupational exposures, the Occupational Safety and Health Administration's (OSHA) Permissible Exposure Level (PEL) is an 8-hour time weighted average of 50 parts per million (ppm). The American Conference of Governmental Industrial Hygienists recommends an 8-hour average exposure of no more than 25 ppm.

For emergency response, the National Institute of Occupational Safety and Health (NIOSH) has established the Immediately Dangerous to Life and Health IDLH concentration at 300 ppm<sup>(1)</sup>. Concentrations of 5000 ppm can be lethal<sup>(8)</sup>. The American Industrial Hygiene Association (AIHA) has developed Emergency Response Planning Guidelines (ERPGs) for toxic substances to assist in planning for catastrophic releases to the community. The ERGP-2 represents the concentration which individuals could be exposed to for one hour without irreversible or serious health effects and was set at 200 ppm for ammonia.

Ammonia vapors are a fire and explosion hazard at concentrations between 16% and 25% in air. Mixtures involving ammonia contaminated with lubricating oil from the system, however, may have a much broader explosive range. A study conducted to determine the influence of oil on the flammability limits of ammonia found that oil reduced the lower flammability limit as low as 8%, depending on the type and concentration of oil<sup>(7)</sup>.

## The Ugly About Ammonia as a Refrigerant:

A number of accidental releases of ammonia have occurred from refrigeration facilities in the past. Releases result from a number of failures that include plant upsets leading to over pressure conditions and lifting of pressure relief valves; seal leaks from rotating shafts and valve stems; refrigerant piping failures due to loss of mechanical integrity from corrosion; physical damage of system components from equipment collisions; hydraulic shock; and hose failures that occur during ammonia deliveries. Some of these incidents have led to injury and on-site fatalities as well as causing adverse off-site consequences. In addition to risks of personal injury, ammonia releases have the potential of causing significant monetary losses including: product loss due to ammonia contamination, interruption of refrigeration capacity, product loss due to refrigeration interruption, and potential for equipment and property damage resulting from the incident. The Factory Mutual Loss Prevention Data Bulletin 12-61 describes several incidents with property damage ranging from \$100,000 to \$1,000,000 per incident<sup>(7)</sup>. The damage to a company's reputation in the community in which they operate, and in some cases nationally or globally, can be immense.

### The following describes several recent incidents in more detail:

1. An ammonia release in Alabama resulted from hydraulic shock in an ammonia refrigeration system. 32 people were hospitalized, including 4 being admitted to an Intensive Care Unit.<sup>(12)</sup>
2. A liquid ammonia leak from a failed fan motor which then struck a pipe in the refrigeration unit at a cold storage facility in Shanghai killed 15 people and injured 26 others<sup>(9)</sup>. A proper inspection and vibratory analysis program included in the general maintenance and mechanical integrity program could have prevented this event.
3. An accidental anhydrous ammonia release occurred onboard a tender boat docked in Sitka Alaska, when a person trying to drain the oil from the ship's ammonia tank opened the valve too quickly. 50 lbs. of ammonia were drained into the engine room. This caused numerous people to seek medical care for symptoms related to the exposure. The person who opened the valve later died from exposure<sup>(10)</sup>. Having the appropriate safety control mechanisms, including a self-closing emergency shutoff installed in the pipeline and also wearing appropriate personal protective equipment (PPE), including respirators or self-contained breathing apparatus (SCBAs) could have limited the exposure in this case.

4. In a 1992 incident at a meat packing plant, a forklift struck and ruptured a pipe carrying ammonia for refrigeration. Workers were evacuated when the leak was detected. A short time later, an explosion occurred that caused extensive damage, including large holes in two sides of the building. The forklift was believed to be the source of ignition. Physical barriers would have provided mechanical protection against puncture and have prevented the initial release <sup>(7)</sup>.
5. Motors utilized in ammonia refrigeration system compressors are the open drive type and not hermetic due to ammonia's incompatibility with copper. Also, hot gas bypasses are not typically utilized in ammonia compressor systems as they would shut the compressor down due to high oil temperatures on screw compressors or blackened heads on reciprocating compressors.
6. Excess water and air are typically removed from ammonia refrigeration systems with the use of batch remediators and foul gas Purgers respectively.

### Ammonia Refrigeration Process:

Ammonia Refrigeration shares many similarities to standard vapor compression refrigeration, including:

1. Compressor - mechanical device that increases the pressure of a gas by decreasing its volume and the heart of the system,
2. Condenser - condenses ammonia gas to liquid by removing heat,
3. Expansion device - regulates the refrigerant in the evaporator,
4. Evaporator - changes liquid ammonia to gas by taking up latent heat.

But in ammonia refrigeration, that is where the similarities stop.

The differences in ammonia refrigeration include <sup>(11)</sup>:

1. Although it is easier to keep oil in the compressor, as the oil is heavier and it does not mix with ammonia, the typically paraffinic type oil is also a good collector of welding slag and dirt and therefore must be changed on a routine basis.
2. Ammonia is corrosive to copper, so copper, brass and bronze cannot be used in ammonia refrigeration systems, your metal choices are typically mild steels, stainless steels, and nickel.
3. Unlike normal cooling compression refrigeration systems, the ammonia systems utilized in refrigeration and cold storage facilities cannot tolerate time delays for cooling to start, therefore ammonia systems require pressurized storage vessels to store liquid ammonia and also allow for separation of vapor and liquid.
4. Unlike typical refrigerants which dislike water and hence require liquid desiccant dryers to remove moisture, ammonia has an affinity for water and water increases ammonia's evaporation temperature while also decreasing its freezing point, however too much water will cause the oil to turn to sludge, therefore maintaining a water content of  $\leq 0.4\%$  is acceptable.

### Ammonia Detection:

Ammonia's strong pungent odor makes it easily detectible by smell. Ammonia can also be detected visibly by a white vapor cloud or by fixed or portable ammonia gas detectors.

### Ammonia System Safety:

Ammonia can be safely used as a refrigerant provided the system is properly designed, constructed, operated, and maintained. Ammonia refrigeration facilities should be aware of the potential hazards of ammonia releases and be prepared to respond appropriately to releases should they occur. Hazard awareness can be enhanced by:

- > Ensuring that all the applicable process safety information is complete and up to date including:
  - Safety Datasheets (SDS) with all critical data/information.
  - Process technology including block/process flow diagrams (PFDs & BFDs), process chemistry and operations, chemical inventories, and operating limits with ranges and what steps to take if a deviation from normal operating limits occurs.
  - Equipment and specification including materials of construction, Process and Instrumentation Diagrams (P&IDs), Hazardous (electrical) area classifications, emergency relief system design, design codes and standards, safety systems including detection, interlocks, and suppression systems, and recognized and generally accepted good engineering practices (RAGAGEP).
- > Conducting a proper **Process Hazard Analysis (PHA)** using an experienced leader and appropriate methodology.
- > Setting up an effective **Process Safety Management Program**, including training and an adequate emergency response plan should an incident occur.

The following are some of the basic measures recommended by Chemical Accident Prevention Group of EPA's Region III for ammonia refrigeration facilities that are not covered under OSHA's Process Safety Management (PSM) standard 29 CFR 1910.119 to prevent releases or reduce the severity of releases that do occur <sup>(7)</sup>:

- > Establish training programs to ensure that the ammonia refrigeration system is operated and maintained by trained and knowledgeable personnel.
- > Consider using a spring-loaded ball valve (dead-man valve) in conjunction with the oil drain valve on all oil out pots (used to collect oil that migrates into system components) as an emergency stop valve.
- > Develop and require refrigeration maintenance personnel to follow written, standard procedures for maintaining the system including such routine procedures as oil draining. Consider developing in-house checklists to guide maintenance personnel while they execute these procedures.
- > Never remove oil directly from the refrigeration system without pumping down and properly isolating that component.
- > Provide barriers to protect refrigeration equipment, i.e., lines, valves, and refrigeration coils, from impact in areas where forklifts are used.
- > Develop and maintain a written preventive maintenance program and schedule based on the manufacturers recommendations for all of the refrigeration equipment.
- > Perform regular vibration testing on compressors. Document and analyze results for trends.
- > Investigate all reports of an ammonia odor and repair all leaks immediately. Leak test all piping, valves, seals, flanges, etc., at least four times a year.
- > Consider installing ammonia detectors in areas where a substantial leak could occur or if the facility is not manned 24 hours/day.
- > Replace pressure relief valves (PRVs) on a regular schedule (consult ANSI/IIAR Standard 2- Equipment, Design, and Installation of Ammonia Mechanical Refrigerating Systems); document replacement dates by stamping the replacement date onto each unit's tag.
- > Ensure that the ammonia refrigeration system is routinely monitored. In designing new systems or retrofitting existing systems, consider the use of computer controls to monitor the process parameters.
- > Keep an accurate record of the amount of ammonia that is purchased for the initial charge to the refrigeration system(s) and the amount that is replaced. Consider keeping a record of the amount of lubricating oil added to the system and removed from the system.
- > Ensure that good housekeeping procedures are followed in the compressor/recycle rooms. Ensure that refrigeration system lines and valves are adequately identified (e.g., by color coding or labeling) by using an in-house system.
- > Properly post ammonia placards (i.e. NFPA 704 NH3 diamond) and warning signs in areas where ammonia is being used as a refrigerant or being stored (for example, compressor room doors). Properly identify the chemicals within the piping system(s); label all process piping, i.e. piping containing ammonia, as "AMMONIA." Label must use black letters with yellow background. (This requirement is not the same as the in-house color-coding system.)
- > Periodically inspect all ammonia refrigeration piping for failed insulation/vapor barrier, rust, and corrosion. Inspect any ammonia refrigeration piping underneath any failed insulation systems for rust and corrosion. Protect all uninsulated refrigeration piping from rust and/or corrosion by cleaning, priming, and painting with an appropriate coating.
- > Carry out regular inspections of emergency equipment and keep respirators, including air-purifying and self-contained breathing apparatus (SCBA), and other equipment in good shape; ensure that personnel are trained in proper use of this equipment.
- > Consider using the compressor room ammonia detector to control the ventilation fans.
- > Identify the king valve and other emergency isolation valves with a large placard so that they can easily be identified by emergency responders, in case of an emergency. These valves should be clearly indicated on the piping and instrumentation diagrams (P&IDs) and/or process flow diagrams.
- > Establish emergency shutdown procedures and instructions on what to do during and after a power failure.
- > Establish written emergency procedures and instructions on what to do in the event of an ammonia release.
- > Regularly conduct emergency response drills
- > Stage a realistic response spill exercise with the local fire department
- > Mount a compressor room manual switch outside of the compressor room and identify it with a placard for use in an emergency.

- > Mount windsocks in appropriate places and incorporate their use into the facility emergency response plan.
- > Keep piping and instrumentation diagrams (P&IDs), process flow diagrams, ladder diagrams, or single lines up-to-date and incorporate them into training programs for operators.

## Conclusion:

With all ammonia's environmental and energy efficient advantages, anhydrous ammonia is dangerous, and things can go wrong in the handling, storage and processing of ammonia if appropriate systems, procedures, and safeguards are not setup and followed. While there are inherently safer refrigerants available, selection of a refrigerant is made based on a number of variables. There have been numerous hazardous releases of anhydrous ammonia over the years from refrigeration systems due to inadequate maintenance, debris getting into the compressor cylinders causing failure, overheating due to lack of lubrication, accidental impacts, and inadequate inspections. Any company utilizing ammonia refrigerant systems should implement a proper Process Safety Management (PSM) program and conduct Process Hazard Analysis (PHAs) led by qualified subject matter experts, considering all hazardous data – flammability, toxicity, etc. These steps will ensure that the handling, processing, and storage systems are adequate and appropriate safety management programs, including inspection, monitoring and protection systems are in place and conducted and reviewed on a routine basis.

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## DEKRA Process Safety

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### Process Safety Management (PSM) Programs

- > Design and creation of relevant PSM programs
- > Support the implementation, monitoring, and sustainability of PSM programs
- > Audit existing PSM programs, comparing with best practices around the world
- > Correct and improve deficient programs

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- > Flammability/combustibility properties of dusts, gases, vapors, mists, and hybrid atmospheres
- > Chemical reaction hazards and chemical process optimization (reaction and adiabatic calorimetry RC1, ARC, VSP, Dewar)
- > Thermal instability (DSC, DTA, and powder specific tests)
- > Energetic materials, explosives, propellants, pyrotechnics to DOT, UN, etc. protocols
- > Regulatory testing: REACH, UN, CLP, ADR, OSHA, DOT
- > Electrostatic testing for powders, liquids, process equipment, liners, shoes, FIBCs

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- > Dust, gas, and vapor flash fire and explosion hazards
- > Electrostatic hazards, problems, and applications
- > Reactive chemical, self-heating, and thermal instability hazards
- > Hazardous area classification
- > Mechanical equipment ignition risk assessment
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