# Dealing with an Ammonia Spill

GLOBAL COLD CHAIN ALLIANCE®

Supply Chain Committee

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## Introduction

An ammonia release can present a dangerous and costly peril to the cold storage industry. Proper planning and effective management, however, can make the difference between an emergency that can injure employees or take lives and cost millions of dollars and one that produces only temporary inconvenience.

Anhydrous ammonia is one of the most widely used chemicals in the world. Ammonia's thermodynamic properties make it an excellent industrial refrigerant. As a result, it is estimated that the chemical is used in as many as 95 percent of the world's industrial refrigeration systems. In particular, the one property that makes ammonia such a great refrigerant is its high "Latent Heat of Vaporization," or enthalpy. Latent heat is the amount of energy in the form of heat released or absorbed by a substance during a change of phase (i.e. solid, liquid, or gas). Ammonia is uniquely capable of absorbing high amounts of heat in the cold storage facility and thus bringing down or maintaining the low temperatures needed for the preservation of perishable products.

While ammonia has been successfully and generally safely used as an industrial refrigerant for well over 100 years, like most other chemicals it must be handled properly in order to prevent unwanted consequences in the event of a release. In such cases, it is essential to have basic knowledge about ammonia and specific knowledge about what actions are to be taken. Over many years, considerable information about ammonia refrigeration systems and methods used to deal with ammonia releases have been developed and/or gathered by the Global Cold Chain Alliance (GCCA) and the Global Cold Chain Foundation (GCCF). This white paper is designed to summarize portions of that body of information.

## Properties of Ammonia

Anhydrous ammonia is a colorless gas with a pungent odor. This odor enables most people to detect the presence of ammonia at around five (5) parts per million (ppm). Ammonia in high concentration is extremely corrosive to skin, eyes, the respiratory tract, and mucous membranes. Anyone working on an ammonia refrigeration system must be knowledgeable about the system, take proper precautions, utilize suitable Personal Protective Equipment (PPE), and understand the emergency action plan or response plan for the specific facility.

The U.S. National Institute of Occupational Safety and Health (NIOSH) has established a Recommended Exposure Limit (REL) for ammonia of 25 ppm, with a Short Term Exposure Limit (STEL) of 35 ppm. The U.S. Occupational Safety and Health Administration (OSHA) have established the Permissible Exposure Limit (PEL) value for ammonia at 50 ppm. The Immediately Dangerous to Life and Health (IDLH) value for ammonia is 300 ppm. An IDLH level requires the use of self-contained breathing apparatus (SCBA) for respiratory protection.

Ammonia is a very basic, or alkaline, substance which boils at -28°F (-33°C) at normal atmospheric pressure and freezes at -108°F (-78°C). Liquid ammonia is lighter than water, weighing 5.15 lb. per gallon at 60°F (0.608 kg/L at 15°C). However, in the presence of moisture or in areas of relatively high humidity, the liquefied anhydrous ammonia gas forms vapors that are heavier than air. These vapors may spread along the ground or into low-lying areas with poor airflow where people may become exposed. Ammonia vapor burns in a mixture with air only when the ammonia concentration ranges between 16-25 percent (NIOSH lists 15-28 percent) by volume, although contamination with oil makes ammonia flammable at even lower concentrations. Note: 15-28 percent represents 150,000 to 280,000 ppm.

Ammonia can form a toxic, explosive gas when exposed to chlorine and corrode copper, brass, zinc, silver and many other alloys with which it may come in contact.

For detailed information about the properties of ammonia, please refer to Safety Data Sheets (SDS) or Material Safety Data Sheets (MSDS) for Anhydrous Ammonia.

## Emergency Management

Effectively dealing with an ammonia release requires multiple phases of attention—planning, reporting, responding cleanup, and business recovery.

### Planning

When developing or managing a plan, some baseline data should be considered and completed. This includes:

1. **Identify expected hazards. A h**azard assessment needs to be done by an individual who has appropriate technical knowledge and experience. This information forms the basis for selection of personal protective equipment (PPE) and development of emergency response procedures.
2. **Make sure all potential participants are involved in planning, whether the response involves only your employees or other employees/responders at the site or off site.**
3. **Determine how employees will be alerted such as siren, radios, alarms, etc.**
4. **Determine evacuation and/or shelter-in-place procedures, primary and alternate options.**
5. **Determine your employee-desired actions in a true emergency response event, such as notification only, defensive actions, offensive actions. This will help to determine training levels and equipment needed by your personnel.**
6. **Determine support needed for response such as medical support, equipment, hazmat team, etc., and their response times.**

## The Plan - Emergency Action Plan or Emergency Response Plan

Emergency response planning regulations are governed in the United States under OSHA and found in 29 CFR 1910.120(q). OSHA states that an emergency response plan shall be developed and implemented to handle anticipated emergencies prior to the commencement of emergency response operations. The plan has to be documented.

Employers who will only evacuate their employees from the danger area when an emergency occurs, and who do not permit any of their employees to assist in handling the emergency, are exempt from the requirements of part 120(q) if they provide an emergency action plan in accordance with 29 CFR 1910.38.

Basically, if an employer would only expect all employees to evacuate and notify in an emergency, then an action plan is acceptable. If an employer needs employees to take offensive or defensive actions in an emergency, then a full response plan is required.

There are several considerations when determining needed or desired actions by employees. This includes facility size, number of personnel, outside support from fire department, and/or HAZMAT response teams including their training level, equipment and response time.

## Elements of an emergency action plan (can refer to 29 CFR 1910.38)

An emergency action plan must include at a minimum:

- Procedures for reporting an ammonia release or other emergency
- Procedures for emergency evacuation, including type of evacuation and exit route assignments
- Procedures to be followed by employees who remain to operate critical plant operations before they evacuate
- Procedures to account for all employees after evacuation
- Procedures to be followed by employees performing rescue or medical duties (if applicable)
- The name or job title of every employee who may be contacted by employees who need more information about the plan or an explanation of their duties under the plan

## Elements of an emergency response plan (can refer to 29 CFR 1910.120(q)

The employer shall develop an emergency response plan for emergencies that shall address, as a minimum, the following areas:

- Pre-emergency planning and coordination with outside parties
- Personnel roles, lines of authority, training, and communication
- Emergency recognition and prevention
- Safe distances and places of refuge
- Site security and control
- Evacuation routes and procedures
- Decontamination
- Emergency medical treatment and first aid
- Emergency alerting and response procedures
- Critique of response and follow-up
- Personal Protective Equipment (PPE) and emergency equipment

It is essential that an Emergency Action Plan (EAP) or Emergency Response Plan (ERP) be developed and in place on the first day that a facility goes on line, and that the plan be revised and updated in conjunction with any changes in systems, plans, laws, regulations, or advances in emergency response methodology. The plan should provide crystal clear guidance for handling fire, ammonia releases, and any other kinds of emergency conditions that may arise. The plan should be in writing and consideration for posting key elements of the plan throughout the facility. Employees who are directly involved in carrying out the plan must be trained in the specific actions for which they are responsible in the event of

an emergency, as required in the U.S. under OSHA's 29 CFR 1910.38 Emergency Action Plans, 1910.39 Fire Prevention Plans, and 1910.120(q)

### Emergency Response Plans

Plant personnel who are not specifically responsible for carrying out elements of the plan should have a general understanding of the facility's emergency action plan and what they must do or where they must go in the event of an emergency. The overriding goals of every ammonia refrigeration facility must be the prevention of accidental ammonia releases and the protection of human life and health in the event of a release.

## Release Reporting

Prompt reporting of ammonia releases is critical both in summoning emergency responders and avoiding costly penalties. It is recommended that every facility publishes and distributes a "Four Call Card" and that all key personnel be instructed to carry and use the "4CC." Please note that in some locations facilities may be required to call state and local Environmental Protection Agencies (EPAs) along with any other agency requirements. The "Four Call Card" should also be saved to key personnel's cell phones, tablets, etc. as an added precaution.

**Red Hot Cold Storage** Alexandria, Virginia Four Call Card

1. Alexandria Fire Department – 703-123-1234 or 911
2. National Response Center – 800-424-8802
3. Virginia Emergency Response Commission – 804-123-1234
4. Local Emergency Response Committee – 703 -555-1234

**Call 1** – In the case of an ammonia release, the local fire department should be notified at the first possible moment, to enlist emergency responder assistance and/or to ensure that the fire department is on call should an easily managed release get out of control. This would be for releases beyond basic maintenance situations.

**Note:** Not all fire departments are experienced in handling ammonia emergencies and inadequately trained fire firefighters can turn a minor ammonia problem into a more serious problem as easily as anyone else. It is strongly recommended that you meet with local fire department officials before you ever need to rely on them; that you develop an ongoing relationship with the local fire department; that you understand the fire department's capabilities and weaknesses; and that you understand their role, your role, and the role of other emergency response personnel in the event of an ammonia release. Proper coordination and planning with the local fire department will surely help to prevent conflicts in the event of an emergency.

**Call 2** – In the U.S., an ammonia spill of 100 or more pounds (45.36 or more kg) within a 24-hour period must be immediately reported to the National Response Center at 800- 424-8802 (or 202-267-2675). The Reportable Quantity (RQ) amount for anhydrous ammonia is 100 pounds. The following information must be provided:

- The name of the chemical (ammonia)
- The fact that ammonia is on EPA's list of extremely hazardous substances
- Estimated size of release (using engineer's best estimate)
- Location, time and duration of the release
- Disposition of released ammonia (into the air, down the drain, etc.)
- Measures taken (medical response, evacuation, ventilation, neutralization, etc.)
- Contact information (names and phone numbers) for obtaining further information
- NOTE – the NRC will give you a 6-digit log number; record that number.

**Call 3** – In the U.S., the Emergency Planning and Community Right to Know Act of 1986 (EPCRA) requires each state governor to appoint a State Emergency Response Commission (SERC) to, among other things, receive reports and notifications of releases. To avoid serious financial penalties, the SERC must be contacted immediately after calling the National Response Center. Refer to applicable State websites if you do not know your SERC contact information.

**Call 4** – EPCRA also mandates the creation of Local Emergency Planning Committees (LEPC's) and requires facilities to send release notifications to the LEPC with jurisdiction over the facility. There are some 3000 LEPC's in the US. Refer to SERC contacts to obtain the appropriate LEPC contact information if not known. In some counties, a 911 call will meet this reporting requirement.

**Note:** The Fire Department or other responding companies may also make release notifications based on their own protocol. Even though the local fire department may have called the NRC, SERC and/or LEPC, their calls DO NOT meet the facility's responsibility. Facility must also make their OWN calls, even if duplicative.

**Note:** It is necessary to follow-up calls 3 and 4 with follow up written reports (SERC and LEPC).

**Note:** Calls 2, 3, and 4 must be made "immediately." While the term is not precisely defined in the rules, the courts have interpreted this to mean sixty minutes. (EPA has interpreted it to mean within as few as 15 minutes.) To avoid the unpleasantness of financial penalties on top of other tribulations associated with a release, these calls should be made within the designated window of the time that a release is detected. In addition, if a release is below the RQ, but has offsite impacts, that could also make a facility responsible to report. Some States have lower limits and require any amount unintentionally

released to be reported.

**Note:** EPA may show up months after a release and levy large fines for failure to make the above notifications on a timely basis. Be sure to keep a record of all your reporting calls, including the name of the person calling, the numbers called, the names of the agencies and persons answering the calls, the precise times and dates of each call, and brief comments made in the course of the calls.

Once the above calls are made, a PRW should immediately notify its insurance carrier, regardless of the amount of ammonia released. In many policies, this is required in order to prevent voiding of the coverage. The reverse side of the "4CC" provides a convenient place to keep these numbers handy.

**Red Hot Cold Storage**
Alexandria, Virginia
Four Call Card

GCCA Insurance Program – (816) 960-9946

Key Customer #1 – 123-456-7890

Key Customer # 2 – 123-456-7890

Key Customer # 3 – 123-456-7890

## Cleanup

When an ammonia spill occurs in an area where product is being held, that product may be injured. The degree of damage resulting from exposure to ammonia is influenced by many factors. The concentration of ammonia, length of exposure, temperature, type of product and manner in which the product is packaged all influence the extent of ammonia injury.

Monitoring and determining ammonia levels inside the facility and even outside areas may be important. Ammonia concentration levels can be obtained from fixed sensors at a facility or through handheld air sampling equipment. Equipment can vary and it is important to know the read range for any units being used to monitor a release. Handheld equipment could be from the facility's equipment inventory or being used by outside response personnel and teams.

Air sampling data should be obtained periodically over the incident's time line. Prior to any personnel entering an area impacted by a release, it would need to be deemed safe or at a level requiring respiratory personal protective equipment.

Monitoring the outside, and even verifying the negative (no ammonia present) can help with limiting potential liability claims.

Warehouse temperatures should also be measured and recorded periodically. This will ensure product quality assurance.

If a product is directly contaminated by liquid ammonia, that product is normally considered a total loss. The determination of contamination of food products further from the source of an ammonia leak or spill requires evaluation and testing. There are several tests for assessing ammonia damage in exposed products. These tests include:

- Visual evaluation of the product to detect negative aesthetic changes
- Sensory (taste) tests to detect negative flavor changes
- pH measurements to determine the magnitude of pH increase in the food tissue
- Ammoniacal nitrogen tests to measure the concentration of ammonia in the food tissue

**(NOTE**: Product tissue samples for evaluation should be taken from the outermost half-inch of each sample unit. Acceptable lots will have satisfactory sensory results; the pH of the tissue will not be more than 1.0 pH unit greater than the control samples, and the ammonia content will not be greater than 0.10 percent).

Examination of products involved in a large ammonia release reveals that products packaged in polymeric films are not likely to be significantly damaged by exposure to high ammonia concentrations, that products loosely packed in waxed paper or cardboard cases are quite likely subject to permanent damage, that ammonia apparently causes a decrease in viable microbial count, and that unpackaged, fresh produce held at refrigerated storage temperatures as well as frozen foods held in large tote bins are most vulnerable to being irreversibly damaged by ammonia vapor. An article on this event entitled "How to cope with product exposure to ammonia – assuring quality after ammonia leaks" is available from GCCF headquarters.

However, it is not axiomatic that foods exposed to ammonia vapor are irreversibly damaged or are rendered unmarketable, and, in fact, the USDA-FSIS has in certain cases authorized the use of ammonia vapor as a treatment to reduce the microbial population of product. See GCCF Research Summary #1987-03 for information regarding ammonia spills, their effects, recommended steps for dealing with them, and an extensive list of references to consult for further details.

There are several successful methods for removing ammonia both from the facility and from product stored in the facility.

a) Ventilation: While there is no single approved cleanup procedure, controlled ventilation is considered a primary option following an ammonia release. With ventilation, fans are used to push the ammonia-laden air inside the cold storage facility outside, lowering the concentration of ammonia to more tolerable levels. Ventilation of gaseous ammonia should be initiated as soon as possible using open doors to the outside of the building. Fans should be set up to increase air circulation and gaseous ammonia removal. Be aware of where the ventilation is going and ensure there are no downwind threats or concerns.

   Ventilation with outside air will, naturally, increase the temperature of the air space inside the cold store. While raising the air temperature increases the rate of ammonia dissipation, an upper tolerance limit for air temperature in the cold store space should be set; when the temperature limit is attained ventilation should be terminated and the outer doors closed. Air temperature increase in the cold store space, if of limited duration, does not have a significant effect on the

temperature of frozen product held in the space. The effect on refrigerated (non-frozen) products may be significant and ventilation duration should be shorter.

b) Absorption: Unfortunately, ventilation alone may not eliminate all ammonia, especially ammonia that may be trapped in crevices and corrugated case flutes after a spill. Additional efforts to eliminate ammonia vapor from the facility following ventilation usually involve absorption or neutralization. Although water absorbs ammonia to form ammonium hydroxide, a weak alkali similar to household ammonia, disposal is problematic when the temperature in the cold store is <32°F (0°C). In any case, it is important to properly dispose of the water/ammonia solution and not to discharge it to the storm drain or sewer drain. A little bit of ammonia can drastically change the pH of water.

c) Neutralization: Acids can be used to effectively neutralize ammonia. Strong acids, such as sulfuric acid and hydrochloric acid, are very good at neutralizing ammonia vapors but are extremely hazardous to handle and difficult to apply. Their usage for this purpose is not recommended. Weaker acids, such as acetic (found in vinegar) and carbonic are also effective in neutralizing ammonia vapor.

   Carbon dioxide is a non-toxic, acid-forming gas that can neutralize ammonia. In the presence of sufficient water vapor, carbon dioxide reacts with ammonia to form ammonium carbonate monohydrate. If carbon dioxide is released into a cold store atmosphere it will combine with water vapor to form carbonic acid, which in turn reacts with any ammonia present to neutralize it.

   Regardless of the quantity of ammonia released, after the initial ventilation step has been completed, the quantity of carbon dioxide released initially should not exceed 1 pound per 100 cubic feet of cold store air space. After this initial treatment, the amount of ammonia remaining in the space should be measured using an ammonia meter—then the space can be either re-ventilated or retreated with additional carbon dioxide (but never more than 1 pound per 100 cubic feet of air space).

   It is crucial to have sufficient water vapor present in order for neutralization to occur. Ventilation (especially with warm, humid air) usually raises the relative humidity in the cold store space enough to allow neutralization to occur. If insufficient water vapor is present, this problem can be addressed by introducing water- soaked burlap bags (containing some propylene glycol as an antifreeze) into the cold store space. Propylene glycol is an effective antifreeze and is Generally Recognized as Safe (GRAS) for food use under FDA CFR 21 Part 184.1666.

   Water evaporating from the cloth will increase the amount of water vapor in the space enabling the carbon dioxide to do its work. If the water vapor from the burlap bags is not sufficient, it is recommended that a "stream of steam" be used instead of spraying hot water in the room to raise the humidity. Depending upon the air volume in the cold store and the concentration of ammonia and water vapor, the quantity of carbon dioxide required to completely neutralize all ammonia could require more than one treatment. When the carbon dioxide is released, industrial fans must be used upward at a 30-60 degree angle, to circulate it among the product and keep it from settling. Ammonium carbonate is a powder like substance with possible large lumps settling out onto the racking, product, floors, etc. and can also be problematic to be cleaned up from the release area.

   Carbon dioxide in its solid form (dry ice) can also be used to neutralize ammonia fumes. Large amounts of dry ice are more difficult to acquire quickly, more costly, and slower acting than liquid or gaseous $CO_2$. There are, however, situations in which the use of dry ice may be advantageous. For instance, dry ice may be placed on pallets within an aisle of a cold room, allowing the use of

$CO_2$ while cleanup efforts continue. Large industrial fans should be placed behind the dry ice. Air circulation is imperative for dry ice to be effective. In this way, it may be possible to maintain tolerable working conditions within a room as product movement and continued operations stir up fresh ammonia fumes.

In addition, liquid $CO_2$ is also available in 50-pound (23-kg) and larger cylinders. The amount of $CO_2$ needed depends on the size of the room and the concentration of ammonia present. It takes 44 pounds (20kg) of $CO_2$ and 36 pounds (16.3kg) of $H_2O$ to neutralize 34 pounds (15.4kg) of ammonia.

One of the most difficult aspects of the cleanup entails removing the odor of ammonia from packaging materials once it has penetrated pallets of corrugated cases and seeped into the flutes of the corrugated board. This entrapped ammonia is difficult to neutralize with carbon dioxide because it takes substantial time for the $CO_2$ to come into contact with the ammonia in the flutes, especially for cases in the interior of pallets.

To neutralize the ammonia odor in the corrugated flutes, it is necessary to work with relatively small lots of product. Take several pallets of the problem cases into a smaller room. With the room temperature set at +10 to +15°F (-12.2 to –9.4°C) to allow for a greater amount of water vapor to be present in each cubic foot (28.3 L) of air in the room, discharge 20 to 30 pounds (9 to 14 kg) $CO_2$ into the room. (As noted above, several treatments of $CO_2$ may be required.) Assure that there is a high degree of air circulation in the room using industrial size fans. The fans should be aimed in an upward direction and toward the pallets to avoid having the carbon dioxide settle near the floor. Once the ammonia has been neutralized, Shut the room and lower its temperature so the product is returned to a 0°F (-18°C) environment.

Be patient. It may, on occasion, become necessary to break down tightly stacked pallets to allow the carbon dioxide to interact with cases removed from the center of pallets, but ultimately the ammonia in the case flutes will be neutralized. Important points to remember are that relative humidity is near the air saturation point, that fans are adequately circulating the $CO_2$, and that persistence will be rewarded.

Another possible method to neutralize ammonia involves passing the contaminated air through a tank filled with a mixture of water, citric acid, and propylene glycol, causing the ammonia to react with the citric acid and form ammonia citrate. Because this method entails considerable set-up and plumbing it is not generally recommended.

Ozone ($O_3$) is another powerful oxidizing agent for controlling ammonia odor. Studies conducted by GCCF demonstrated that packaging material (corrugated shipping case test strips) equilibrated with 2,000 ppm ammonia lost most of its ammonia odor when exposed to a moderate $O_3$ level (0.4 ppm) in a small sealed chamber (764 liter room) at ambient temperature for 18 hours. Unfortunately, ozone presents a number of serious problems, including explosion potential, toxic exposure to plants and animals, and oxidative rancidity of poorly packaged food products, which are high in lipid content. Furthermore, some major food manufacturing companies may not allow ozone to come in contact with their products. For example, high fat products such as butter and cheese can quickly become rancid when exposed to ozone. In 1987, a GCCF Ozone Committee recommended that ozone should only be considered for odor removal in warehouses devoid of people and food products.

**Note:** It is necessary when dealing with an ammonia release that the atmosphere be carefully monitored to determine exposure levels. It is recommended that each facility have a functional relative humidity meter

and a carbon dioxide meter in addition to a meter for measuring gaseous ammonia concentration. Constant air monitoring with appropriate skin and respiratory protection deserves priority attention. It is important to understand that all chemicals must be treated with respect and it is recommended that someone having a solid understanding of ammonia properties and interactions be present when dealing with a release.

## Conclusion

Needless to say, there is no one plan to resolve all issues when it comes to cleaning up after an ammonia release. Warehouse location, ambient conditions, and room size and configuration, along with the amount of the product, product type, and packaging, are all major factors. If a release occurs during the middle of winter in a northern climate, then ventilation, by itself, may be the way to go. In most cases that will not be sufficient, and introducing another chemical in an enclosed space in order to create a chemical reaction with ammonia requires that considerable precaution be taken.

Responding to emergencies is not typically part of an employee's regular job duties. It is important that personnel are not only trained, but that they maintain competency in case of an incident.

When developing or managing plans, one should consider other factors and issues that could be affected or could impact an emergency event. This could include security issues (both data and product), insurance issues, crisis and/or media communications, and business recovery. Consider all stakeholders who could include employees, emergency response employees, public sector personnel such as fire departments, HAZMAT teams, contractors, and the general public that surround your site.

Site considerations in developing a plan include your facility's size, number of employees, equipment and training levels. You should determine what outside support services are available and their response time. How long would it take for the first fire department engine company to respond? Are they a paid or volunteer department? What is their training level – awareness, operations? What is the response time for a HAZMAT team with technician level response personnel? Is this going to be a public sector HAZMAT team or do you need to pre-plan for contracted support? Are outside response personnel familiar with your facility and operation?

GCCA can provide assistance in dealing with various facets of a release once you have made all of the necessary emergency notifications. Please contact +1 703 373 4300 for assistance.