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Anhydrous Ammonia – Health and Safety Issues

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Salts of ammonia have been known from very early times; alchemists in the 13th century knew of it as sal-ammoniac, and dyers in the Middle Ages used it in the form of fermented urine to alter the color of vegetable dyes. Gaseous ammonia was first isolated by Joseph Priestly in 1774; by 1777 it was known to contain nitrogen, and by the mid 1880s its composition was ascertained.[i]

Anhydrous ammonia is used extensively throughout the world for the production of fertilizers, explosives and polymers, household cleaners, and for emissions control in power plants. We also find ammonia in agriculture, in the manufacture of synthetic fibers, plastics and in refrigeration plants. Approximately ninety percent of manufactured ammonia is used for agricultural purposes, either as a direct application of anhydrous ammonia (about 33% of the total), application of an ammonium solution (e.g. ammonium hydroxide or aqua ammonia), or as a dry fertilizer product; in the United States about three percent of production is used in refrigeration systems. Because of modern fertilizers, world food production has more than doubled since 1960, keeping pace with the population explosion.[ii]

Ammonia is a naturally occurring colorless gas that is an inhalation hazard with an extremely pungent odor; the odor threshold for ammonia vapor is between five and fifty parts per million (ppm). About 140 million metric tons are produced annually by commercial means, and this total is approximately equal to the amount produced naturally.[iii] The preponderance of naturally occurring ammonia is derived from decomposing animal excreta with the decay of organic materials (plants, dead animals, etc.) providing the balance.

Ammonia manufacture within the United States has been declining over the past decade, (but we are still the third largest fertilizer producer following China and India, and the second largest consumer in the world) while production internationally has been increasing. The two primary reasons for the U. S. decline are the cost of natural gas and labor. In agriculture ammonia is an efficient and widely used source of nitrogen with several advantages, including relative ease of application and ready availability; disadvantages include storage and handling under pressure requiring specially designed and well-maintained equipment as well as trained and properly equipped workers. Commercial use of anhydrous ammonia is normally in the liquid form, and the physical characteristics and properties have inherent dangers to users. Liquid ammonia is colorless and is normally stored under pressure between 60 and 160 psi in quantities of up to 50,000 gallons. The boiling point is -28º F (-33º C), and the freezing point is -108º F (-78º C); as a solid ammonia is white. Ammonia is extremely corrosive either as a liquid or vapor, and has a pH of 11.6.[iv] Ammonia terminal facilities also store their product in atmospheric tanks of up to 50,000 ton capacity; in this case the product is stored at less than one half pound of pressure and at -28º F.

Catastrophic releases are different for pressurized and atmospheric storage. A pressurized container that fails will provide a large, visible vapor cloud affecting the downwind zone with the size of the zone being dependent on the quantity of released product, prevailing wind conditions, amount of moisture in the air, temperature, and topography. The reason we can see this vapor cloud released under pressure is the affinity that ammonia has for water; the cold ammonia causes the water vapor in the air to condense and we see a white cloud which is a dense heavy vapor. During some uncontrolled releases these dense vapor clouds have been known to travel downwind for several miles and thus have a huge impact on the downwind zone. Failure of an atmospheric storage container will result in a large quantity of pooled liquid that will self-refrigerate with temperatures as low as -70º F and freeze the ground; there will be some vaporization of ammonia from the pool surface that will affect the downwind zone. Containment of any ammonia release is difficult since the vapors are lighter than air and generally dissipate before containment is possible. Covering small containers with a tarp or plastic sheet will contain escaping vapors and allow them to re-condense to a liquid, in addition to protecting the downwind zone.

Liquid or aerosol contact with the human body results in three types of injury: dehydration of body tissue caused by the absorption of moisture by the ammonia; caustic burning caused by the combination of ammonia and water creating a strong base; and freezing. The preferred decontamination media is the extensive use of water for a minimum of thirty minutes. At primary risk during an exposure are the areas of the body that are moist such as nasal passages, eyes, mouth and throat, around the neck, under the arms, and the groin. Ammonia that is released from storage under pressure as a liquid and aerosol has the potential for temperatures as low as -101º F because the vaporization of the ammonia requires energy; the ammonia gets this energy in the form of heat from the surrounding air, the equipment handling the liquid or the ammonia itself. The immediate concern for workers is the possibility of freezing the clothing to the skin and freezing the skin itself. Immersion of the exposed worker in a water source such as a tub or rapid soaking of clothing and skin is essential to defrost the clothing prior to removing it for further decontamination.

Vapor exposures up to 50 ppm are in a threshold range and not considered dangerous; however, you should be aware that the OSHA Permissible Exposure Level (PEL) is 50 ppm, the Short Term Exposure Level (STEL) is 35 ppm, and Immediately Dangerous to Life and Health (IDLH) is 300 ppm. From about 300 to 400 ppm the vapors are very unpleasant, but not yet deadly; typical reactions are hoarse coughing, heavy tearing of the eyes, and nose and throat irritation. Concentrations from 700 to 1,000 ppm will result in physical damage after a few minutes. Above 1,500 ppm there will be immediate injury and sudden asphyxiation. Concentrations between 5,000 and 10,000 are generally fatal in a few minutes.

Worker safety can be greatly improved through detailed training on the characteristics of ammonia and the use of appropriate personal protective equipment. In our terminal facility personnel wear coveralls to provide arm and leg protection from incidental splash and vapor effects. All personnel are required to wear chemical goggles during transfer operations when the likelihood of minor releases may be present; we have found that indirectly vented chemical goggles work best since they tend not to fog up like non-vented goggles.

In addition to the physical characteristics listed we find three other safety concerns in the use of ammonia. The first issue is that of pressure: in a closed container the vapor and liquid will be at equilibrium at -28º F and interior pressure will be zero. As the container starts to warm up we will find pressure rising to 114 psig at 70º F and to 250 psig at 115º F. For storage in fixed containers designed for ammonia this will not be a problem as there are pressure relief devices installed set to 265 psi in most parts of the U. S. (some States permit settings of 250 psi). Employees need to be cognizant of the fact the every piece of equipment that the ammonia comes in contact with is a potential pressure vessel, and this includes all plumbing, transfer hoses, compressors, pumps, valves, and safety relief devices. The potential for an exposure is greatest when opening and closing valves, and when making and breaking connections, and it is at these times the workers must be wearing the appropriate personal protective equipment.

The second safety concern is that of volume. The rule of thumb used in filling ammonia vessels is called the “85% Rule”; this means that a vessel is filled to the 85% level and no more; the reason for this is that the ammonia volume can increase by as much as 15% as the ammonia heats up. If we take 800 gallons of ammonia at 0º F and warm it up to 100º F we will end up with approximately 915 gallons which is about a 15% increase. This issue becomes serious when workers are filling tanks (either fixed or mobile), because as soon as the temperature starts to rise the potential increases for a pressure relief device to open releasing product to the atmosphere. Personnel working in facilities also need to be aware of these two safety concerns and insure that there are no places within the facility where ammonia can be captured between to dead ends, such as valves, without a pressure relieving device (hydrostatic relief valve) in place. An example of a system that did not have a safety device in place is shown below.

Exhibit 1. Ruptured Ammonia Hose. Maximum Working Pressure: 350 psi[v]
Stainless steel reinforced

Exhibit 2. Ruptured Ammonia Hose. 8" Crescent Wrench for Size Comparison[vi]

The final safety concern is that of fire and/or explosion. Anhydrous ammonia is classified by the U.S. Department of Transportation as a non-flammable gas for transportation and storage purposes. Shipping containers of over 1001 pounds gross weight are identified with a Class 2 non-flammable gas placard or a similar hazardous materials warning label for smaller containers. The reality is that at the right concentrations and in the right environment ammonia has the potential for ignition and deflagration. The flammable range is generally considered to be 16% to 25% by volume in air for clean anhydrous ammonia; this range can vary depending on the locations where it is used. In refrigeration systems for instance, the ammonia is constantly being re-compressed from a low-pressure to a high-pressure gas as it passes through the compressor; as a result it can pick up trace amounts of compressor oil which will then affect the flammability range. Studies conducted in Sweden showed that attempts to ignite ammonia outdoors were very difficult, but when water was sprayed on the ammonia ignition was easier. Ignition of the ammonia occurs because the bond binding the nitrogen and hydrogen atoms starts to break at approximately 850º F and ignition occurs at 1204º F. Likely ignition sources include welding systems in the shop or yard or electrical panels and circuits in a refrigeration plant engine room.

Other safety issues for those working with and around anhydrous ammonia include the potential for theft and terrorism. A current trend in the manufacture of illegal drugs is the use of anhydrous ammonia to speed up the production process for methamphetamine, a powerful central nervous system stimulant; this process, called the “Nazi Method” cuts production time considerably. The safety issue is that most people attempting to steal anhydrous ammonia have no knowledge of the systems they are breaking in to or the characteristics of ammonia; the potential result is a severely injured or dead thief. Frequently valves are left in the open position or hoses and valves are damaged beyond repair; the incident is discovered when the first facility worker shows up the next day or a neighbor smells ammonia and calls the police or sheriff. Thieves typically use small, makeshift containers to collect, store and transport the ammonia stolen from nurse tanks or applicator hoses. Buckets and coolers with duct taped lids, gasoline cans, and propane tanks have all been used for storage and transportation. Garden hoses or even bicycle tire inner tubes are used in the transfer process from tank to tank.

Terrorism is a concern for most Americans following 9/11. Terminal facilities with large volumes of anhydrous ammonia are frequently located at ports and are subject to stringent security programs under the guidance of the Department of Homeland Security and the oversight of the U.S. Coast Guard. Other facilities are located inland and come under the purview of agencies such as the U. S. Environmental Protection Agency and Department of Transportation. Regardless of the regulatory body providing guidance, it is imperative that facilities be aware of the potential and take appropriate security and safety steps for their employees.

In summary, while there have been very few serious injuries involving anhydrous ammonia, the potential for catastrophic incidents are present. Compliance with the requirements of Process Safety Management and Risk Management Programs are crucial in protecting employees and surrounding neighbors. Effective and frequent training, a solid respiratory protection program, and adherence to personal protective equipment policies and procedures should keep workers out of harms way.

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[v] CALAMCO Internal Files

[vi] CALAMCO Internal Files