Cooperative Research and Development Agreement (CRADA) between Chemical Security Analysis Center (CSAC) and Ammonia Safety and Training Institute (ASTI)

A Compendium of Empirical Data Supported by Technical Science Based Information About Anhydrous and Aqueous Ammonia

The Report is the first version of a living document that will change and update when new technical and science-based information compels an update.

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Ammonia Safety & Training Institute (ASTI)

www.ammonia-safety.com

ASTI's Recommendations Regarding Emergency Response Readiness for Anhydrous and Aqueous Ammonia Events, with Emphasis on Transportation and Water Proximate Emergency Events.

Volume 1: February 18, 2024

DISCLAIMER and Acknowledgement

This report is a work prepared under the Cooperative Research and Development Agreement (CRADA) between the Chemical Security Analysis Center (CSAC), a U.S. Department of Homeland Security (DHS) federal laboratory sponsored by the DHS Science and Technology Directorate (S&T), and the Ammonia Safety and Training Institute (ASTI). In no event shall either the U.S. Government, DHS, or the S&T CSAC have any responsibility or liability for any consequences of any use, misuse, inability to use, or reliance upon the information contained herein, nor does either party warrant or otherwise represent in any way the accuracy, adequacy, efficacy, or applicability of the contents hereof. The use of trade, firm, company, or corporation names including product descriptions does not constitute an official DHS endorsement of any service or product.

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ASTI is a non-profit organization that was incorporated as a non-profit 501(c)3 in 1992. Douglas Hill, President, and CEO for Hill Brothers Chemical based in Los Angeles, and Gary Smith Fire Chief for the City of Watsonville in California co-founded ASTI with a mission to make ammonia the safest managed hazardous material in the world. The ASTI team includes leaders from the ammonia industry, government, and public safety. The See www.ammonia-safety.com for more information about ASTI.

Ammonia historically provides many favorable health and environmental global benefits that need to be sustained. ASTI works with government, industry, and public safety (the Tripod) to make ammonia the safest managed hazardous material in the world. **There is no better chemical for addressing the betterment of food production, industrial processes such as steel manufacture, and ammonia's ability to supply bulk amounts of hydrogen as a fuel that decarbonizes the earth's atmosphere**.

Figure 0-1 CF Industries' Donaldsonville Complex is located on 1,400 acres along the west bank of the Mississippi River in southeastern Louisiana. It is the world's largest and most flexible ammonia production facility, serving customers on every continent.

The global production of ammonia has grown steadily over the last 100 years. In 2022 about 150 million metric tons was produced. The global concern to decarbonize the atmosphere has created a much higher demand for ammonia for its supply of hydrogen as a substitute for carbon based fuels has raised the new estimate for global production to 288 million metric tons by 2030.

ACKNOWLEGEMENTS

ASTI is a non-profit 501(c)3 organization comprised of an ASTI Board, staff, Associates, volunteers, and Tech Forum Members all of whom have contributed to the development of this report. Our collective interest is that the ASTI Mission will be achieved by making ammonia the safest managed pressurized, liquified, toxic Inhalation chemical in the world. ASTI expend extensive effort to strengthen the Tripod relationship between industry, government, and public safety to “Prevent ammonia emergencies or stop them small.” Visit the ASTI website (ammonia-safety.com) for more information about ASTI

CRADA Report Authors Note

This report is a compendium of empirical information that appropriately engages science and technical advisories to validate the assumptions gained from ASTI’s 35 years of training, emergency planning, and accident investigation of ammonia events.

The ASTI team applauds the leadership support provided by Dr. Sun McMasters and Jim Zarzycki for the entire CRADA team. We met our scheduled monthly meetings diligently and always shared information and insights that were very helpful for those of us who created reports and set up training exercises while employing a solid team approach.

Note to Readers: Please read pages **6 and 7** to understand “acronyms, terms, and definitions before reading the entire report. It is also wise to read pages **84-90** regarding “Debunking the Myths About Ammonia” and understand the historical insight about the safety and management of the hazards, risks, and threats of ammonia. This will facilitate a better understanding while reading the rest of the Report.

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ACRONYMS, TERMS, AND THEIR DEFINITIONS

AEGLs: Acute exposure guideline levels describe the human health effects from once-in-a-lifetime, or rare, exposure to airborne chemicals. Used by emergency responders when dealing with chemical spills or other catastrophic exposures, AEGLs are set through a collaborative effort of the public and private sectors worldwide.

Aerosol release: Ammonia will be stored under pressure within a tank. Any liquid ammonia released into the atmosphere will aerosolize producing a mixture of liquid and vapor at a temperature of –28ºf. The released ammonia rapidly absorbs moisture in the air and forms a dense, visible white cloud of ammonium hydroxide. www.epa.gov

Bowtie analysis provides a clear graphical representation of hazard scenarios to illustrate the threats that stimulate a hazardous event, the consequences of that event, and the barriers that mitigate its impact or prevent it from occurring altogether. www.aiche.org ›resources ›publications

Bunkering relates to the supply of fuel for use in ships. The term originates from the word 'bunker,' which refers to the storage containers where the fuel, called bunker fuel, is stored onboard. However, this basic definition barely scrapes the surface of the complexities within the bunkering process. https://bunkering101.com/bunkering/bunkering-meaning-unraveling-the-intricacies-of-marine-fuel-industry/

Cooperative Research and Development Agreement (CRADA) between the **Chemical Security Analysis Center (CSAC)**, a U.S. **Department of Homeland Security (DHS)** federal laboratory sponsored by the DHS **Science and Technology Directorate (S&T)**.

DOT Emergency Response Guidebook: https://www.phmsa.dot.gov/hazmat/erg/erg2020-english

EAP and ERP Emergency Action Plan that covers emergency operations outside of IDLH conditions and the Emergency Response Plan has response technicians that can enter IDLH conditions.

FEMA ChemResponder The Federal Emergency Management Agency CBRNResponder is a secure platform for chemical, biological, or radioactive/nuclear (CBRN) incident data sharing and multi-hazard event management. It serves as a hub and one-stop shop for all-hazards planning, preparedness, operational tools, and resources.

Four Stages of Response is based upon the One Plan framework developed and recommended for the creation of emergency plans for chemical users and public safety responders. The four stages (Discovery, Initial Response, Sustained Response, and Termination/Recovery) are summarized in the one-page 30-minute Plan produced by ASTI www.ammonia-safety.com

Hazard Zone (HZ) A HZ is a location within the plant that has high risk and threat that is co-located and interconnected within the zone. An HZ will have special emergency system controls and mitigations that are engaged during the four stages of emergency response.

IDLH (Immediately Dangerous to Life and Health): concentrations which upon exposure are likely to result in death or immediate or delayed permanent adverse health effects.

Initial Isolation Zone defines an area surrounding the incident in which persons may be exposed to dangerous concentrations of material and directs persons to move, in a crosswind direction, away from the spill to the distance specified in the Dept. of Transportation (DOT) Emergency Response Guidebook (ERG). https://www.epa.gov/emergency-response/safety-zones

Lagging indicators reflect historical performance by measuring outcomes or events that have already occurred. These are typically output-oriented, easy to measure, and hard to improve or influence. In many contexts, especially in safety and business performance, lagging indicators are used to assess past performance or results based on specific implemented actions or strategies. https://www.hseblog.com/leading-lagging-indicators/

Leading indicators are proactive and predictive measures used in various fields, especially in safety management, to identify and monitor potential risks before they result in negative outcomes. They provide insights into future health and safety performance and allow organizations to take preventive actions to mitigate potential issues.

MTPA (million tons per annum) is universally used as a metric tonne weight for ammonia production measurement value**. A metric tonne is 1,000 kilograms (2204.6 pounds).**

One Plan – Integrated Contingency Plan Guidance in the Federal Register (61 FR 28642). This guidance is intended to be used by facilities to prepare emergency response plans for responding to releases of oil and hazardous substances.

https://archive.epa.gov/emergencies/content/fss/web/pdf/tzallaspresent.pdf

Protective Action Zone defines an area DOWNWIND from the incident in which persons may become incapacitated and unable to take protective action and/or incur serious or irreversible health effects.

TLV-TWA (Threshold Limit Value-Time Weighted Average): the concentration for a normal 8-hour workday and a 40-hour workweek, to which nearly all workers may be repeatedly exposed, day after day, without adverse effect.

STEL (Short-Term Exposure Limit): the maximum concentration to which someone can safely be exposed for a period of up to 15 minutes -with a maximum of four periods per day.

UEL (Upper Explosion Limit): the highest concentration of a vapor or gas which will explode, ignite, or burn in the presence of an ignition source. Mixtures above this limit are too rich to burn.

LEL (Lower Explosion Limit): the lowest concentration of a vapor or gas which will explode, ignite, or burn in the presence of an ignition source. Mixtures below this limit are too rich to burn.

The U.S. Chemical Safety Board (CSB) is an independent, nonregulatory federal agency that investigates the root causes of major chemical incidents https://www.csb.gov/

EXECUTIVE SUMMARY AND PURPOSE OF THIS ASTI REPORT

The Ammonia Safety & Training Institute (ASTI) is a non-profit 501c(3) that has been working on making ammonia the safest managed hazmat in the world for 45 years. The ASTI mission is to prevent, mitigate, and prepare for ammonia emergencies so that a loss of hazard containment event can be prevented or stopped when the event is small. The ASTI team is dedicated to the mission and vision by affirming ammonia is a vital natural occurring chemical vital to the world's health, preservation of water and food safety, and a vital component in many industrial processes.

Ammonia is the most widely used compressed liquified gas in the U.S. Ammonia is a naturally formed (Nitrogen Cycle) chemical that supports plant growth and human wellness. In 1913 the Haber-Basch process made it possible to generate large volumes of ammonia that provided high volumes of fertilizer that saved about one-third of the world's population from starvation. Ammonia is the most efficient and effective industrial refrigerant that preserves foods and pharmaceuticals. It is also used for industrial processes such as making paint and producing steel and reducing the impact of nitrous oxide pollution and wastewater threats.

ASTI joined with the Chemical Security Analysis Center (CSAC) with a Cooperative Research and Development Agreement (CRADA) that included support for FEMA's ChemResponder system to support the evaluation of water-proximate ammonia plume models, and to revisit historical water proximate ammonia releases impacting shipping, off-loading, and bulk storage.

Purpose of the Report – Science and Conjecture: This report establishes a safety and emergency response concept of operations (CONOPS) addressing water-proximate releases of ammonia being shipped and transferred for onshore storage and dispensing. ASTI promotes a "Tripod" strategic approach whereby industry, government, and public safety work together to implement improvements in safety and emergency response readiness. This report explains how lagging indicators (science) are accepted as factual accounts of how ammonia events can be mitigated. Leading indicators are empirical conjectures learned from real events and live ammonia training experiences.

Figure Intro - 1

The focus of this report relates to ammonia released over water, into water, and underwater. The ASTI team explains how the use of water as a means of mitigating ammonia threats may in some cases not be the best option. **Chapter 5 Gaps Requiring Further Study** of this report summarizes unresolved green box concerns based upon the empirical conjecture that is explained in Parts 1 through 4.

This CRADA report, a living document is a compendium of information relating to safety concerns associated with loss of hazard containment of ammonia resulting in "events" that can be prevented using proven lagging indicators and mitigation measures (barriers) to stop a loss of hazard containment "Event" from becoming a "Top Event" (emergency event) requiring the use of leading indicators to decide a safe and effective incident action plan to contain and control the ammonia hazards. This report demonstrates the value of applying safe and effective operational capabilities by Tripod responders. ASTI team intends that this compendium will continue to grow in strength as we address the Chapter 5 green boxed concerns requiring more technical and science-based analysis. In the end it will be obviously discernible that ammonia is the safest managed hazmat in the world.

The status of safety and emergency response readiness for ammonia response benefits from a safety and emergency response collaboration between industry, government, and public safety. The ammonia refrigeration and the agricultural ammonia associations should join with the rapidly growing ammonia energy industry in producing hydrogen (supplied by green and blue ammonia). Global harmonization for safety and emergency response addresses the largest risk and threat concerns that hold ammonia back as the best option for safely the production and use of hydrogen.

History of Ammonia: The legend goes that ammonia was first discovered in ancient Egypt BC in the Siwa Oasis, where ammonium chloride salt from burning camel dung, was found close to the temple of Amun. Ammonia is formed easily when ammonium chloride salt is heated. Open the following link if you want to read a Brief History of Ammonia's existence on earth: www.linkedin.com/pulse/brief-history-ammonia-from-early-discovery-today's-david-schweinfurth

Charles Darwin's Discovery of Ammonia as a Must for Life to Exist: Darwin considered the origin of life and speculated that life began had occurred in a warm pond. He suggested that phosphoric and ammonia in the pre-biotic pond somehow had been changed chemically by, and electricity, leading to the synthesis of the needed to produce the first living. www.visionlearning.com library

To quote a letter written by Charles Darwin in 1871 to Francis Hooker, "…it is often said that all the conditions for the first production of a living organism are now present, which could ever have been present. But if (and oh what a big if) we could conceive in some warm little pond with all sorts of ammonia and phosphoric salts, light, heat, and electricity present, that a protein compound was chemically formed, ready to undergo still more complex changes, at the present day such matter would be instantly devoured, or absorbed, which would not have been the case before living creatures were formed."

The Evolution of Ammonia as the Most Popular Toxic Inhalation Gas in the World. Ammonia is associated with the Nitrogen Cyle, as a critical need within our environment and within our bodies. It's common knowledge that ammonia has high value for plants, animals, and human existence on earth.

https://americanhistory.si.edu/explore/stories/smithsonian-and-19th-century-guano-trade-poop-crap#:~:text=Any%20guano%20mined%20had%20to,and%20increase%20their%20crop%20yield.

Ammonia is considered by the U.S. Environmental Protection Agency and the Montreal Protocols as a natural refrigerant that is approved as a refrigerant of choice to replace carbon-based refrigerants because it does no harm to the Ozone, has very low impact on the global warming threat and is energy efficient, especially for industrial refrigeration operations that refrigerate large warehouses.

The following historical summary may help to inspire a better understanding of why ammonia as a chemical is of great value when the world-wide effort to decarbonize the earth's atmosphere. Ammonia is now being used to safely carry hydrogen to replace carbon-based fuels that generate electrical power and provide fuel for all forms of transportation.

The earliest European records note the use of guano as fertilizer date back to 1548.. See details: https://en.wikipedia.org/wiki/Guano#:~:text=The%20earliest%20European%20records%20noting,Europe%20until%20the%2019th%20century

Ammonia also evolved as a nitrate used for wartime munitions and was especially strategic for the manufacture of munitions during World War I. The demand for production of ammonia became a global need that required the best efforts of scientists to address. Solving the problem earned Haber and Bosch two Nobel Prizes in chemistry: Haber in 1918, Bosch in 1931. The problem with nitrogen is that, while it is abundant in the atmosphere, its triple bonds make the nitrogen molecule incredibly stable and therefore hard to fix.

Haber-Bosch process, a method of directly synthesizing ammonia from hydrogen and nitrogen, was developed by the German physical chemist Fritz Haber. He received the Nobel Prize for Chemistry in 1918 for this method, which made the manufacture of ammonia economically feasible. The method was translated into a large-scale process using a catalyst and high-pressure methods by Carl Bosch, an industrial chemist who won a Nobel Prize in 1931 jointly with Friedrich Bergius for high-pressure studies.

Haber-Bosch was the first industrial chemical process to use high pressure for a chemical reaction. It directly combines nitrogen from the air with hydrogen under extremely high pressures and moderately high temperatures. A catalyst made mostly from iron enables the reaction to be carried out at a lower temperature than would otherwise be practicable, while the removal of ammonia from the batch as soon as it is formed ensures that an equilibrium favoring product formation is maintained. The lower the temperature and the higher the pressure used, the greater the proportion of ammonia yielded in the mixture. For commercial production, the reaction is carried out at pressures ranging from 200 to 400 atmospheres and at temperatures ranging from 400° to 650° C (750° to 1200° F). The Haber-Bosch process is the most economical for the fixation of nitrogen and with modifications continues in use as one of the basic processes of the chemical industry in the world. See also nitrogen fixation.

The Chemical Engineering magazine web-link provides details about the Haber-Bosch process: https://www.thechemicalengineer.com/features/cewctw-fritz-haber-and-carl-bosch-feed-the-world/ .

As we turn the pages of history to the new global challenges associated with climate change, we see a global effort to utilize ammonia as a hydrogen fuel source that can significantly reduce the use of carbon generated by fossil fuels.

Egypt's legacy in green ammonia Continues: Egyptian wisdom once again becomes prominent in making green and blue ammonia as explained in the following summary: Interestingly, the production of green ammonia is not a new technology at all but was already commercial in 1921 by using hydropower! In the early years of ammonia production, ammonia-based hydropower reached a market share of around 30% in the early 1930's but was gradually replaced by the introduction of natural gas and naphtha afterward. In 1960, the biggest green ammonia plant built in the 20th century was realized in Aswan, Egypt. Fueled by hydropower from the Aswan dam, the facility produced 140-175 kt/a of NH_3 until recently, which is still a high capacity also with today's standards. Please read this interesting article by Kevin Rouwenhorst et al., if you want to know more about the history of green ammonia production: (PDF) 1921-2021: A Century of Renewable Ammonia Synthesis (researchgate.net). [16]

The global movement towards ammonia and hydrogen fuel sources that generate electricity and create hydrogen fuel is an "idea whose time has come".

The problems and challenges are quickly evolving globally by focus of professional associations, corporations, universities, scientists, entrepreneurs, government, industry, and public safety. The following is one of MANY examples of the trillions of dollars being invested for producing safe production, transport, storage and use of ammonia and hydrogen.
Honda and Mitsubishi to test data center powered by waste hydrogen, using recycled auto fuel cells. Honda will build a fuel cell power station, which will reuse fuel cells that have been retired, having been used in electric vehicles. Fuel cell electric vehicles (FCEVs) are an alternative to battery-powered cars, which run on electricity produced from hydrogen fuel cells. https://www.datacenterdynamics.com/en/news/honda-and-mitsubishi-to-test-data-center-powered-by-waste-hydrogen-using-recycled-auto-fuel-cells/

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, people 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.

https://www.epa.gov/sites/default/files/documents/ASHRAE_PD_Ammonia_Refrigerant_2010_1.pdf

CHAPTER 1: GROWTH OF AMMONIA IN THE U.S. AND GLOBALLY

1.1 Production, Transport, Transfer, Storage, and Use of Anhydrous and Aqueous Ammonia.

The hazards, risks, and threats of the loss of hazard containment events that occur in water-proximate locations can occur while transporting and/or transferring ammonia off-shore, at a pier, and in the major shipping channels that pass-through rivers, harbors, and shoreline communities.

The growth of ammonia production has grown at a slow but steady pace. That pace continued through 2022. In 2023 the level of ammonia production is beginning to increase dramatically because of the global acceptance of ammonia as an efficient hydrogen carrier and a carbon-free fuel that will replace hydrocarbons that are high global warming threats.

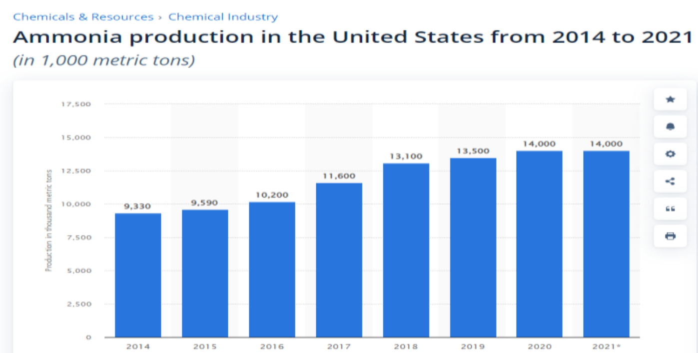


Figure 1-1 United States NH_3 Production

Note: The future ammonia production projections are changing dramatically as new global technology unveils better ammonia systems to create ammonia and systems to use ammonia as a fuel source. The current predictions could dramatically change.

In 2023 Asia Pacific (Australia, Japan, and Singapore) are considering the use of green and/or blue ammonia as their source of hydrogen fuel for power production. Japanese and U.S. ammonia energy associations are supporting innovative ways to produce ammonia-powered vehicles.
https://www.statista.com/statistics/1266392/ammonia-plant-capacities-united-states/

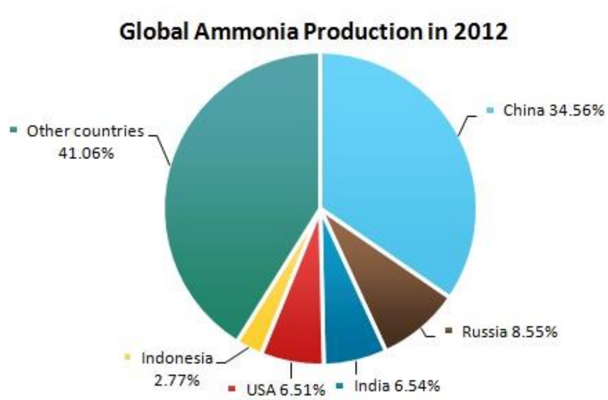


Figure 1-2 Global NH_3 Production – also see Figure 1-3.

The production of ammonia fuels began to expand to the Asia Pacific and throughout the world in 2023. The ammonia industry in the U.S. is beginning to grow with the creation of green and blue ammonia for sales and transport to help serve the fast-growing global demand for ammonia as a source of energy.

The Ammonia Market size is expected to grow from 184.96 million tons in 2023 to 202.98 million tons by 2028 (recent expectations estimate the growth of ammonia by 50 million tons by 2030)
. https://www.mordorintelligence.com/industry-reports/ammonia-market

The following article headline and picture are from an online news article from Yale Environmental 360. The title of the article is From Fertilizer to Fuel: Can 'Green' Ammonia Be a Climate Fix? It was published at the Yale School of the Environment. "Ammonia has been widely used as a fertilizer for the last century. Now, using renewable energy and a new method for making ammonia, researchers and entrepreneurs believe "green" ammonia can become a significant clean fuel source for generating electricity and powering ships." By Nicola Jones • January 20, 2022, Read the entire article at:
https://e360.yale.edu/features/from-fertilizer-to-fuel-can-green-ammonia-be-a-climate-fix
Similar articles about the future of ammonia energy can be found in newsletter format at: Ammonia Energy Association jatchison@ammoniaenergy.org

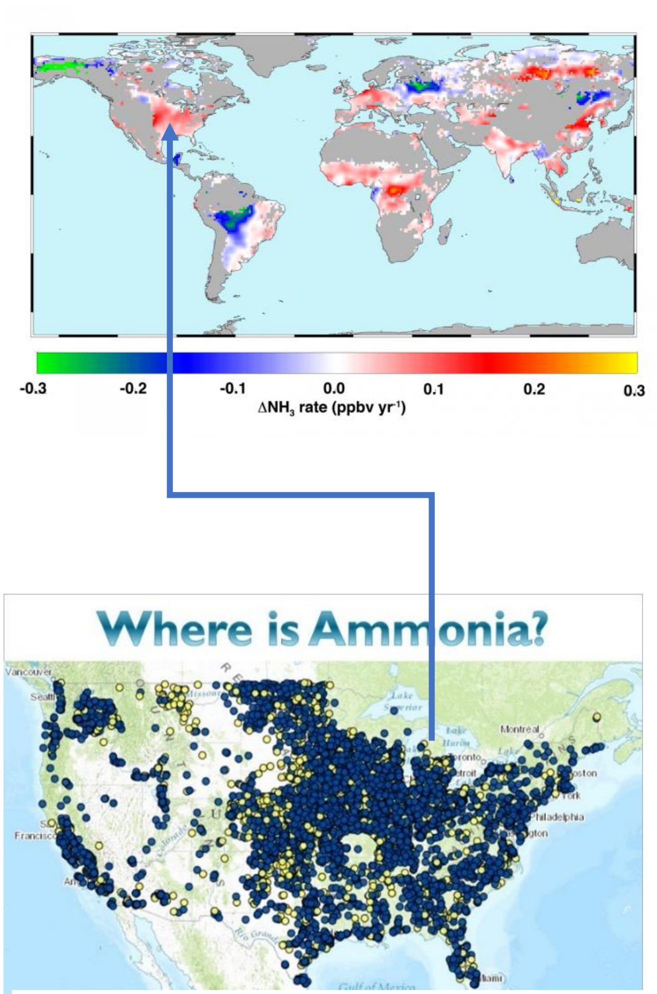


Figure 1-3 . A map showing average global concentrations of atmospheric ammonia between 2002 and 2016.

Hotspots of the atmospheric pollutant ammonia have been found over regions of the world dominated by intensive agriculture. The high concentrations of ammonia in the atmosphere were detected by infrared sensors from space by NASA satellites and published in the journal Geophysical Research Letters. The researchers also tracked the most likely sources of pollution, including farming and changes in atmospheric and soil chemistry. https://climate.nasa.gov/news/2565/nasa-satellite-identifies-global-ammonia-hotspots/

The concentration of registered (Risk Management Plans) and non-registered users of ammonia in the U.S. aligns well with the satellite imagery. About 85% of the ammonia used in the United States is for agriculture. Ammonia fertilizer is credited with saving one-third of the world's population from starvation. Industrial refrigeration is vital to support agriculture and other food production, so there are a lot of cold storage processing plants in the same location.

1.2 UNDERSTAND THE DIFFERENCE BETWEEN AMMONIA AND AQUA AMMONIA

1.3 Anhydrous Ammonia and Aqueous Solutions of Ammonia

Ammonia used for industrial refrigeration is over 99% pure with <1% water to help to prevent stress cracking when stored in a tank. Household ammonia is a diluted water solution containing 5 to 10 percent ammonia. Ammonia is a colorless, pungent gaseous compound of one nitrogen atom and three hydrogen atoms, (NH_3) that is highly soluble in water. Ammonia is formed naturally as a product of the microbiological decay of nitrogenous organic matter (animal and plant protein). Ammonia is also produced for use in fertilizers, or for use in the production of plastics, pharmaceuticals, and other chemicals.

Ammonia in groundwater is normal, due to microbiological processes. However, the presence of ammonia nitrogen in surface water usually indicates domestic pollution. Excess ammonia can damage vegetation and is incredibly toxic to aquatic life, especially at elevated pH and temperature levels.

Aqua Ammonia is used for various applications, it is ammonia dissolved in water to produce "aqua ammonia." Bulk aqueous ammonia (aqua ammonia) solutions are unstable, and the ammonia concentration may decrease during transportation or during storage. Therefore, delivered solutions are billed based on the ammonia concentration delivered to the facility or end-user. Aqueous ammonia is a compound containing one nitrogen and four hydrogen atoms (NH_4^+). While ammonia is a neutral non-ionized molecule (weak base), ammonium is an ion carrying a positive charge. In addition, ammonia emits a strong odor, but ammonium does not smell at all.

The major factor that determines the proportion of ammonia to ammonium in water is pH. The activity of the ammonia is also influenced by the ionic strength and temperature of the solution. It is important to remember that while molecular ammonia can be harmful to aquatic organisms, ammonium ion is basically harmless. In the water industry, it is important to know the concentrations of hydrogen bound nitrogen. Therefore, the terms ammonia and ammonium are used interchangeably, depicted as NH_3 -N or NH_4 -N correspondingly, and normally expressed in mg/L or PPM of N. The chemical formula for the relationship between ammonia and ammonium:

$NH_3 + H_2O <-> NH_4^+ + OH^-$

When the pH is low, the equilibrium is driven to the right and when the pH is high, the equilibrium is driven to the left. In general, at room temperature with a pH less than 6, the portion of ammonia-N as NH_3 is very low and almost all ammonia nitrogen is present as NH_4^+. At a pH of around 8, the portion of NH_3 is 10 percent or less, and at a pH slightly above 9, it is about 50 percent. Once the pH is > 11, all ammonium ions in the solution will be converted to the molecular form of ammonia. The activity of aqueous ammonia is much lower at low temperatures. The information provided on this page is summarized from:
https://uk.hach.com/parameters/ammonia#:~:text=Ammonia%20exists%20in%20water%20as,the%20ammonia%20exists%20as%20NH4%2B
https://www.cdc.gov/niosh/npg/npgd0028.html#:~:text=Anhydrous%20ammonia%2C%20Aqua%20ammonia%2C%20Aqueous,CAS%20No.&text=RTECS%20No.

1.4 A Sample of Hydrogen and Ammonia Fuel/Energy Advancements

Toyota To Develop Hydrogen Engine for Heavy Commercial Vehicles. July 9, 2022 (Railly News). Toyota is developing various engine options, including hybrid vehicles, fully electric vehicles, and fuel cell vehicles, in accordance with the energy conditions in different countries and different customer needs. Hydrogen engines stand out as one of these options. The hydrogen-powered Corolla, which has been used in some racing series in Japan since last year, is leading the development of this technology. The hydrogen-powered engine is sourced from the GR Yaris. a 1.6 liter, turbocharged 3-cylinder engine (video imbedded in the link) but the Corolla Sport was used as the base model in order to house the car's four hydrogen tanks and piping, derived from the technology used in the Toyota Mirai fuel cell electric vehicle. Efforts to reach the hydrogen community are accelerating with the increase in the number of partners in hydrogen production, transportation, and use. https://www.raillynews.com/2022/07/toyota-agir-ticari-araclar-icin-hidrojen-motoru-gelistirilecek/

Singapore to Explore Ammonia as a Clean Energy Source for Bunkering and Power Generation.

October 23, 2023 (EnergyPortal.eu). Jurong Island, Singapore - Singapore is set to embark on a groundbreaking project that aims to utilize ammonia as a fuel source for bunkering and power generation. **The country has already set a target to meet 50 percent of its energy needs with hydrogen by 2050, and ammonia is seen as a promising alternative to help achieve this goal.** The project, located on Jurong Island, will involve the development of an end-to-end ammonia solution to generate 55 to 65 megawatts of electricity. The imported low-carbon or zero-carbon ammonia will be used for direct combustion in a gas turbine or combined cycle gas turbine. In addition to power generation, the project will also focus on ammonia bunkering, with a target capacity of at least 0.1 million tons per annum. This will involve both shore-to-ship and ship-to-ship bunkering operations.

https://www.energyportal.eu/news/spore-a-step-closer-to-using-low-carbon-ammonia-for-bunkering-power-generation/382205/

Sunborne Systems is a green fuel technology company founded by Reaction Engines in the UK. The Oxfordshire-based company successfully demonstrated its ammonia cracking reactor's ability to produce a fuel blend capable of powering a 56 kW engine. The test program, performed at the Culham Science Centre in Oxfordshire, showed that the reactor has high thermal efficiency and the potential to be scaled into higher energy output for internal combustion engine systems.

CHAPTER 2: TRIPOD READINESS USES BOWTIE ANALYSIS

2.1 Strengthen the "prevent them all or stop them small" strategy.

Tripod participants (local, state, and federal) should collaborate to understand ammonia **H**azards, mitigate **R**isks, and prepare for **T**hreats (**HRTs**). The Tripod challenge is to strengthen the **lagging indicators** that must engage when a loss of hazard containment occurs. **The goal is to stop the loss of hazard containment** during the discovery and initial response stages **(first 30 minutes)**. If that fails, the event becomes a **"Top Event"** that is subject to control by tech-level command and response teams. They must understand how to safely engage **leading indicators** that mitigate, contain, and control risks and threats before high impact consequences occur.

Recognition and use of **lagging indicators** must include the trust and support generated by Tripod training and tabletop exercises. Industrial, government, and public safety lessons learned from historical loss of hazard containment events and from knowledge gained from understanding the chemical and physical characteristics of ammonia must be tempered with jointly accepted before an emergency event. When **leading indicators** reveal the escalating risk/threat factors the Tripod training should help the command team to respond to the early warning with a safely controlled escape from the isolation zone, awareness, and mitigation of sources of ignition, pressure management, liquid flow control, and ventilation of dangerous accumulations of ammonia. The Wolters Kluwer Bowtie analysis diagram shown in Figure 2-1 shows how hazards can create the potential to cause harm as ammonia escapes containment and develops a "threat line" that has pre-developed preventative barriers (lagging indicators) that prevent, mitigate, and prepare to stop an event before it transitions to a "Top Event" that can escalate to cause catastrophic impacts if not controlled and contained by emergency response forces. The success of the emergency response mode relies on addressing lagging indicators with recovery barriers such as ammonia detection and alert systems, high pressure cut-outs, pressure relieve valves, emergency ventilation systems, and planned emergency system control options. If the Event recovery barriers fail to contain and control the event a Top Event occurs. Leading indicators must be disclosed to the emergency response command team so that an incident action plan can be developed by using lead indicators that accurately acknowledge the safety and response protocols that a trained and equipped hazmat technician team

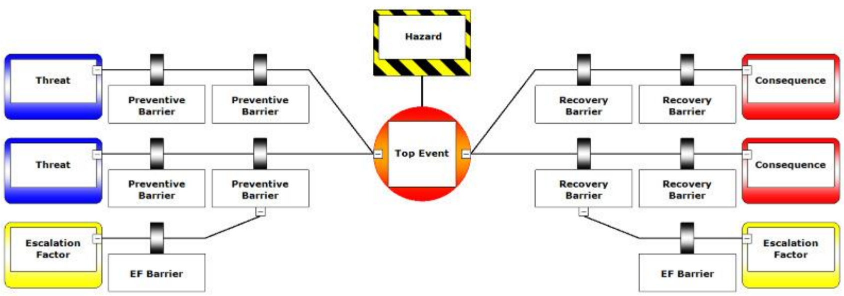


Figure 2-1 Bowtie Kluwer Diagram
https://www.wolterskluwer.com/en/solutions/enablon/bowtie/expert-insights/barrier-based-risk-management-knowledge-base/the-bowtie-method

must safely engage while working within the “hot zone” level of threat. **At this point, the reader should understand that the science-based lagging indicators that are used to set preventative barriers should strengthen as the lessons learned from applying conjecture-based leading indicators reveal success and failure.**

The U.S. Chemical Safety Board (CSB) investigates many catastrophic events that have occurred in the United States. Their reporting indicates that deviating from the safety norms is counter-productive and lack of safety and emergency response readiness causes much more expense. CSB investigations point out how a strong hazard can create a high-impact vulnerability. They are moving forward with an upgrade on their hazard assessment methods and practices. The following is a quote from the following: https://www.csb.gov/news/cdl-being-updated-/

The CSB is currently updating its Drivers of Critical Safety Change pages - the FY23 CDL items with subtopic areas that include the following (the bold blue font content was added by ASTI to further clarify the topic).

- **Process Safety Management:** system maintenance and operational controls that support safe operations and control of reactive hazards such as those listed on the last bullet point.
- **Risk Management Program:** Facility Siting, Offsite Consequences, Fenceline and Impacted Communities, and Information Sharing
- **Inherently Safer Design:** options such as high-pressure aerosol release mitigations, advanced ventilation technology, and hydraulic shock prevention measures e.g., hydraulic relief valves.
- **Emergency Preparedness:** Extreme Weather and other local area natural hazards
- **Reactive Hazards:** vulnerability for escalating factors due to chemical reaction e.g., trapped liquid hydraulic and/or hydrostatic pressure, flammability, mixture with water, etc.

2.2 The Use Of The Bowtie As It Relates To Emergency Response

Figure 2-2 ASTI Emergency Response Bowtie Diagram

There are many versions of bowtie hazard assessment diagrams. **The ASTI bowtie focuses on emergency response (Top Event)**. Each hazard has an initiating cause for a threat line that should include **lagging indicators** that provide early detection and preventative barriers to strengthen the early control of the event. The lagging indicators are set up on the **blue side of the bowtie** to provide prevention and preparation measures that will contain escalating risk factors when the event is small and easy to control e.g., **prevent them all or stop them small!.**

The emergency responders require a clear size-up. **CAN reports** are used to document ongoing situation status reports that help the command team assess the HRT concerns that impact future IAPs. The Incident Commander must understand the **Conditions** (current and anticipated status of the threat line impacts), **Actions** (related to control measures that address the escalating factors), and the **Needs** that address the safety and leading indicators of risk and threat that impact life safety, hazard containment, and control of the event. The Incident Action Plan and Safety Plan that results from understanding leading indicators (red side of the Bowtie) is vital for attaining containment and control of the Top Event.

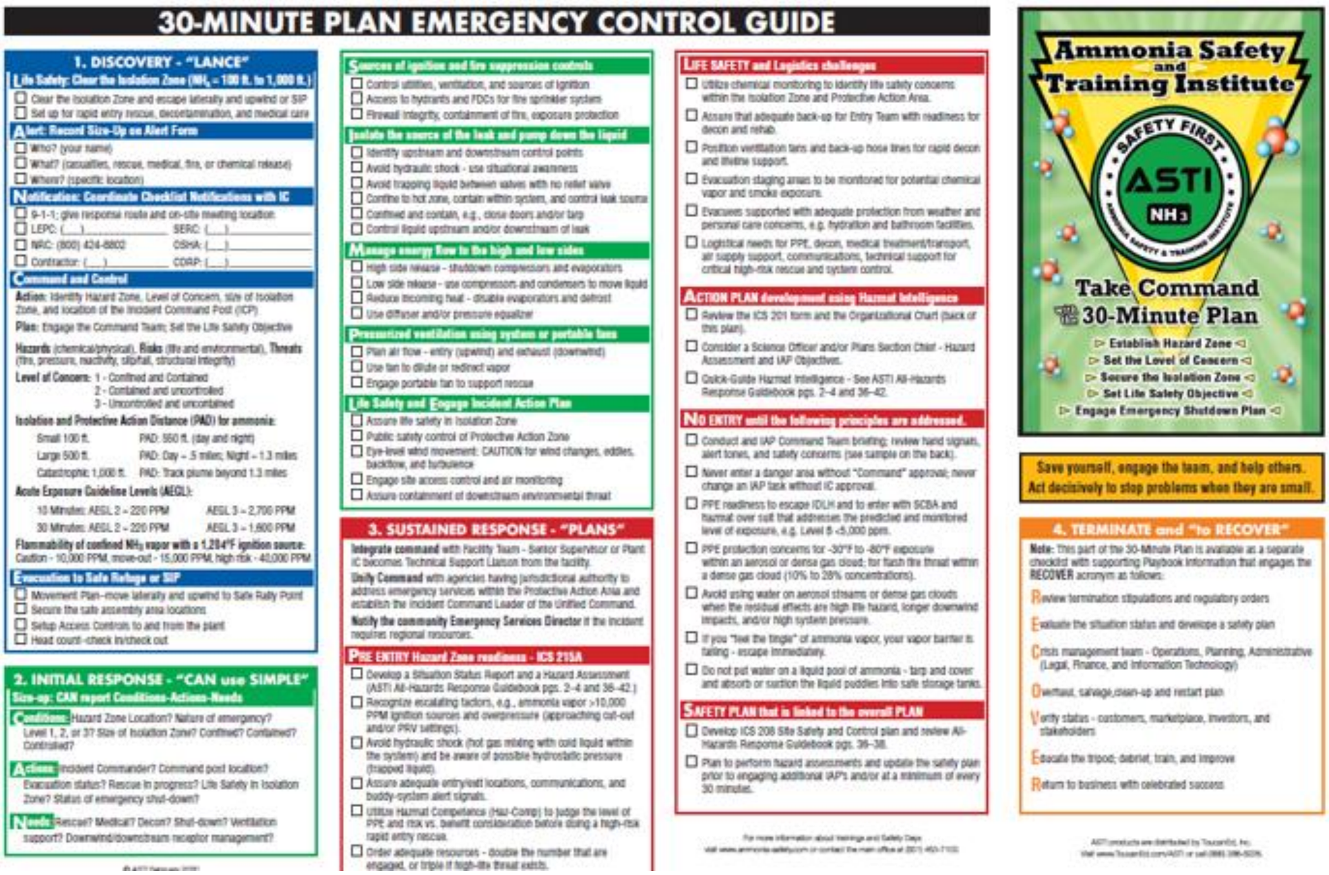


Figure 2-3 ASTI 30-Minute Plan

2.3 ASTI 30-Minute Plan - Based on EPA Integrated Contingency Plan "One Plan"

The One Plan (Integrated Contingency Plan) was published in the Congressional Record in 1996 https://www.nrt.org/sites/2/files/icppres1996.pdf and is the basis for all emergency plans. Published as a notice in the Federal Register at 61 FR 28642, June 5, 1996. available on the NRT Website at http://www.nrt.org and on EPA's Chemical Emergency Preparedness and Prevention Office Website at http://www.epa.gov/swercepp/pubs/oneplan.html .

The front page of the 30-minute plan has four stages of response checklists 1. Discovery, 2. Initial Response, 3. Sustained Response, and 4. Termination/Recovery checklist. The back page has a sample incident action plan, safety plan, and incident command system organization chart. There are three One Plan Response Goals that spin off the 30-Minute Plan.

The leading indicators and threat line mitigations are important for the command team's assessment needed for creating a safe and effective Incident Action Plan (IAP) that includes a safety plan, response objectives, and specific tasks that will contain and control the escalating factors that may become catastrophic to life, health, environment, and/or property.

One Plan Response Goal 1: A facility command team that is well trained on how to engage Discovery and Initial Response should be able to complete the checklist and engage planned mitigations and control measures so that the loss of containment of ammonia does not spread and grow.

One Plan Response Goal 2: The public safety Incident Commander may choose to integrate with the facility command team.

One Plan Response Goal 3: The collaboration between the public safety and facility command teams should result in the development of a written Incident Action Plan (IAP) and safety plan as the first step for engaging Sustained Response. Each IAP should not exceed 30 minutes of operational engagement.

The final stage of response is to terminate the emergency and begin the recovery stage. The recovery stage will continue to be subject to risks and threats of a damaged system that must be cleared by the Tripod command team and will require the technical expertise of ammonia system technicians to ensure that all damages and mitigation systems are up to the standard for a safe return to day-to-day service.

Contact ASTI by using their website www.ammonia-safety.com if you would like a copy of a template for creating a local area ammonia response concept of operations (CONOPS) that establishes how the command team, technical support services, operational response team must abide by the federal emergency response framework and implemented by the State Emergency Response Commission and the local **authority having jurisdiction**. ASTI emphasizes the importance of the CONOPS utilization of a "Tripod" approach between Industry, government, and public safety as they work together to address pre-event readiness, joint training, and integration of command when dealing with a loss of ammonia containment event that has a chance of becoming an emergency event.

Tripod command team CONOPS strategy should emphasize the need for immediate requests for the resources and personnel to **"go big early"** to prevent, mitigate, and prepare for the risks of a loss of hazard containment. Understanding hazards, managing risks, and assessing lagging and leading indicators is critical for hazmat command teams and responders. They will depend on technician specialists, emergency planners, and emergency managers to assess and define the threat line. This assessment begins with pre-event mitigations and preparation measures that fulfill the **"Prevent them all or stop them small"** strategy.

The 30-Minute Plan was designed by ASTI to aid ammonia emergency responders to maximize their pre-planned readiness for fast and effective engagement of the **Discovery and Initial Response checklists** within the first 30 minutes. The transition to Sustained Response should follow the emergency system control plan that was initiated during Discovery and Initial Response. The command team transition should include a well-explained situation status report and a sustainable safety plan that clearly explains the hazards, risks, and threats associated with the emergency event.

The strategy of the 30-Minute plan resembles the professional sports logic as follows:

- There are rules that set perimeters on how the game is played, to include safety gear and procedures that require coaching, referees, and player leaders. (Tripod rules of engagement)
- There are team assignments that include team leadership and specialty skilled performance for specific team tasks. (Rescue, Emergency System Control, Shelter-in-Place, etc.)
- There is a defensive and offensive coordinator with a game plan that is strategically mapped out in a playbook. The Playbook is summarized on a single sheet of paper that the head coach can review and coordinate with the team leaders and coaching staff. (the 30-Minute Plan)
- The winning team is physically fit, well organized, and well trained and equipped for delivering desired results on the play-by-play game plan (Incident Action Plan).

A well-trained facility command team will integrate command with public safety responders to engage a "clipboard" readiness action plan that safely engages a SIMPLE Initial Response plan During Sustained Response the leading indicators will involve the possibility of on-site/off-site consequences such as dangerous plume movement.
https://www.epa.gov/sites/default/files/documents/ASHRAE_PD_Ammonia_Refrigerant_2010_1.pdf

Figure 2-4 shows an example of an approved air purifying respirator designed to protect operators and maintenance personnel when they are doing work that has potential to release ammonia that presents a life safety threat. The canister attached to the bottom of the mask is certified for escaping immediately dangerous to life and health conditions e.g., 300 ppm for 30 minutes exposure.

https://www.cdc.gov/niosh/npptl/resources/pressrel/letters/respprotect/ca-2023-1067.html

The link to details about personal protective equipment for ammonia responders:
https://www.osha.gov/etools/ammonia-refrigeration/general-safety

Figure 2-4 Draeger 14G Canister mask

CHAPTER 3: AMMONIA HAZARDS, RISKS AND THREATS (HRTS)

3.1 Ammonia Chemical Hazards

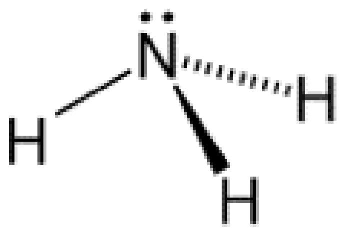
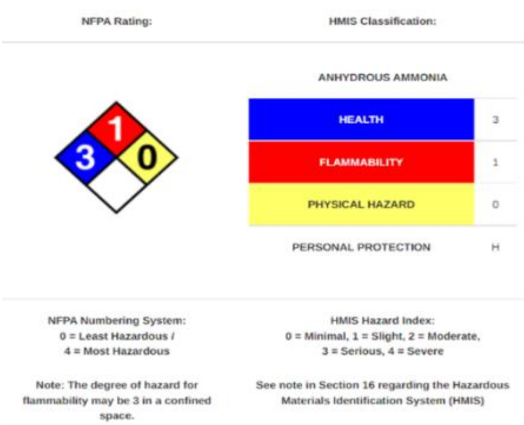


Figure 3-1 Ammonia summary from www.wikipedia.org

The ammonia molecule has a trigonal pyramidal shape with a nitrogen atom and three weakly bonded hydrogen atoms attached. An unshared pair of electrons are also attached to the nitrogen atom. An ammonia cluster is a few ammonia molecules held together by hydrogen bonds, a kind of interaction that is weaker than conventional chemical bonds. Ammonia is a colorless gas with a characteristically pungent smell. It is lighter than air, its density being 0.589 times that of air. It is easily liquefied due to the strong hydrogen bonding between molecules.



The NFPA 704 placard can be used by industry and public safety when approaching a hazard zone worthy of pre-warning...especially if the location requires going inside a building where the ammonia exposure and fire threats are greater. The fire rating of “1” (very low) moves to “3” when the ammonia is stored within a building or in a position where ammonia vapor can build up to the lower flammability limit. The U.N, # for anhydrous ammonia is 1005. The U.N.# for 19% aqueous ammonia is U.N.# 2672

AMMONIA, SOLUTION, WITH MORE THAN 10% BUT NOT MORE THAN 35% AMMONIA

Chemical Identifiers | Hazards | Response Recommendations | Physical Properties | Regulatory Information | Alternate Chemical Names

Chemical Identifiers

What is this information?

CAS Number
7664-41-7

UN/NA Number
2672

DOT Hazard Label
Corrosive

NIOSH Pocket Guide
Ammonia

International Chem Safety Card
AMMONIA (ANHYDROUS)

NFPA 704

Diamond	Hazard	Value	Description
	Health	3	Can cause serious or permanent injury.
	Flammability	1	Must be preheated before ignition can occur.
	Instability	0	Normally stable, even under fire conditions.
	Special		

(NFPA, 2010)

Figure 3-2 NFPA 704 Ammonia Warning Placard and Guidebook

Anhydrous ammonia is produced commercially at 95% to 99.98% pure with a small amount of water to reduce the potential stress cracking of ammonia tanks.

Aqueous ammonia is commercially produced at 20% to 30% (special orders for small amounts of 50% solution is used by chemist use in a laboratory). Aqueous solutions of ammonia that are generated by putting water on anhydrous ammonia during ambient environmental conditions can generate solutions that travel the same or more downwind (based on wind, environment, and volume of liquid released). The corrosive nature of aqueous ammonia results from a pH factor that ranges between 9 and 13. Eye, skin, and respiratory damage is accelerated due to the high ph. Aqueous ammonia solutions used for household cleaning are 2 to 3% mixture with water are sold in grocery stores. Ammonia also is effective at breaking down household grime or stains from animal fats or vegetable oils, such as cooking grease and wine stains. Because ammonia evaporates quickly, it is commonly used in glass cleaning solutions to help avoid streaking. https://www.chemicalsafetyfacts.org

NH_3 Thermophysical properties show that the pressure and temperature of saturated ammonia have a direct relationship as described in the Enthalpy Chart (Figure 3-6). (Ammonia vapor pressure at gas-liquid equilibrium (boiling point). The following properties of ammonia indicate the basic chemical characteristic risks associated with NH_3.

- Ammonia is a colorless non-flammable liquid
- Ammonia gas is lighter than air with a vapor density of 0.6 compared to air 1.0
- Ammonia has a high latent heat of vaporization. The heat of vaporization of ammonia is 23.4 kJ/mol which also relates to why it is difficult to generate the kilojoules per mole of heat flash off vapor that will ignite. The heat of vaporization for methane is 9.2 KJ/Mol.
- Ammonia is a colorless non-flammable liquid although dense gas clouds can ignite as follows: Ignition temperature 1204ºF (651º C) with an ammonia/air concentration between 15% and 28%.
- Corrodes galvanizing, Delete (cast iron,) copper, zinc, or their alloys
- Weight of liquid ammonia 5.15 pounds per gallon @ 68°F.
- Boiling point liquid ammonia at atmospheric pressure is -28ºF (-33.3 C).
- The volume ratio for ammonia between 100% liquid and 100% gas 850 gas to 1 liquid.

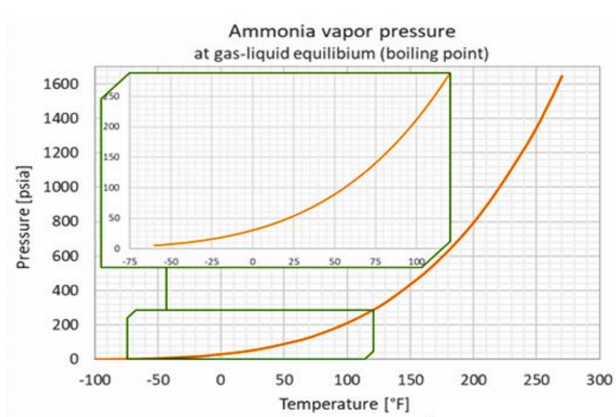


Figure 3-3 Ammonia Vapor Pressure

3.2 Storage Of Ammonia And The Types Of Release That Escape Containment.

Transport, storage, and transfer of ammonia and the types of release that escape containment. The maritime shipping and the onshore bulk storage of ammonia is generally in low-pressure tanks which operate at less than 1 psi above atmospheric pressure and between -27°F and -28ºF. The pressure in the gas space above the liquid in the tank is accurately maintained by a refrigeration compressor that receives low-pressure gas and condenses it to liquid via a condenser and then feeds it back into the bulk storage tank. When ammonia liquid is unloaded from a ship into an atmospheric pressure bulk storage terminal tank, the temperature of the ammonia to be off-loaded must be as close as possible to the temperature of the ammonia that is already in the tank. This is to avoid temperature inversion behavior also known as “rollover” occurring in the tank which can seriously damage the tank potentially causing a major release. The temperature difference must be controlled to less than 1°F.

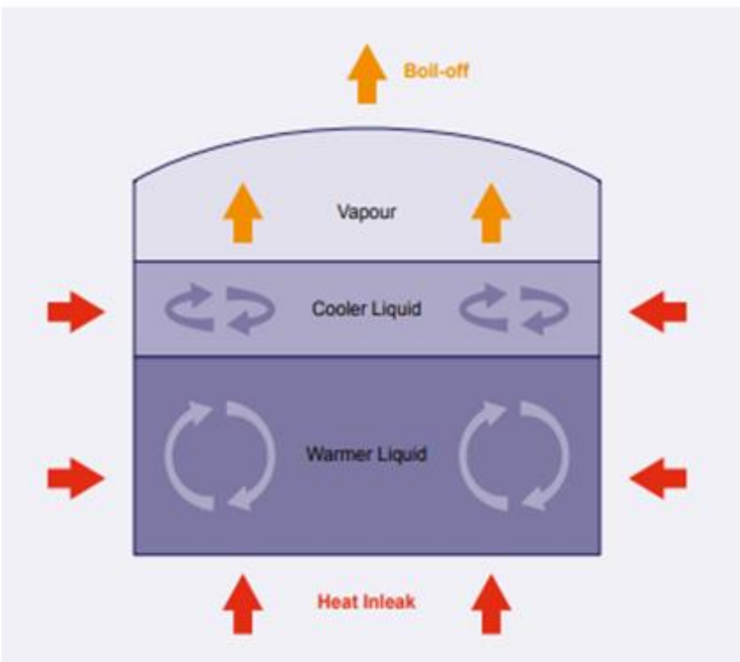


Figure 3-4 Rollover Consideration

Rollover Consideration The probability is low for a fully refrigerated (FR) bulk liquid ammonia tank may suffer a “rollover” phenomenon. Rollover occurs when a large portion of a warmer liquid rises from the bottom of the tank to the top, with a colder liquid at the top suddenly sinking to the bottom of the tank (shown in Figure 3.6). Ammonia vapor is released rapidly because of this spontaneous mixing of liquid ammonia with different densities in one storage tank. It occurs when a liquid body is stratified with a density inversion, which means a liquid layer just above its boiling point is covered by a cooler layer.

See Section 4.6 for a summary of the Lithuanian Ammonia Tank Failure that resulted from a rollover.

A rollover may result from pushing a huge quantity of slightly warmer liquid into the bottom of the tank. The lower warmer liquid density coupled with the potential formation of gas bubbles will drive the upward movement. The best way to minimize the risk of rollover is to ensure all ammonia fed into the tank is always within the very close temperature specification. The other problem with transferring a huge quantity of slightly warmer liquid into an FR tank is that the Boil Off Gas (BOG) generated may overwhelm the tank’s re-liquefaction refrigeration system and cause a rise in the top pressure. In this case, relief vents on the top of the tank could be lifted As shown in Figure 3.6, when there is little vertical heat or mass transfer in the storage tank due to hydrostatic pressure, both liquid layers establish their convection currents. The upper cooler layer releases vapor and loses heat, increasing its density. The lower layer has a higher temperature due to the heat absorbed from the surroundings, so its density decreases. The lower warmer layer will roll over the cooler upper layer resulting in heat release, and a large volume of boil-off gas will be generated rapidly. As a result, the tank is over-pressured, leading to the discharge of ammonia vapor through the relief valve, or in the worst case, causing structural damage to the tank.[12]

Water and ammonia have a polar atomic relationship and the mixing of the two liquids can result in a violent reaction because of the boil-off and flash-gas/vapor reaction.

Figure 3-5. Pure NH_3 2. Ammonia Mixes with Water 3. Aqueous Puff Cloud 4. NH_3 Liquid Vaporization

Picture 1: Anhydrous Ammonia is a clear liquid when it's at or below its boiling point which is -33ºC or -28ºF. Liquid ammonia will evaporate during ambient temperatures (above its boiling point). The ambient heat provides energy to vaporize the ammonia liquid which creates the ice build-up of water vapor in the air (which insulates the liquid). The surrounding ambient temperature (air and ground) can continue to provide heat of vaporization that drops ammonia liquid temperature to much lower than its boiling point. Colder liquid creates a more aggressive heat-of-reaction when water is introduced to the ammonia.

Picture 2: Cold ammonia liquid released from containment will aggressively boil-off. It sounds and looks like eggs frying in a very hot frying pan. Dense gas aqueous ammonia vapor move downwind.

Picture 3: When water is introduced to the very cold "sleeping ammonia liquid" the heat differential creates an immediate and very aggressive (high pH) dense aerosol vapor e.g., 60ºF water mixing with -41ºF ammonia liquid is a 100° differential.

Picture 4: The day's temperature was 60ºF (20.5ºC). The ammonia liquid surface ripple vapor was created by a 10 mph (16 Km per hour) wind. The downwind vapor production was minimal and non-detectible at 50 feet (15.2 meters) downwind. The Phillips engineers calculated the ammonia evaporation rate at 6.8 pounds (3.1 Kg) per hour for each square foot (929 square centimeters) of liquid surface.

The Isolation and Protective Action zones for anhydrous and 50% aqueous ammonia are about the same downwind distance. The most critical difference in risk and threats involves the vapor density of aqueous is heavier than anhydrous and aqueous ammonia is corrosive with a pH of between 9 and 13 when released to the environment (anhydrous has no pH until it finds moisture and transitions to an aqueous alkaline solution).

The term, pH, describes the extent to which a solution of material in water is acidic or alkaline. Anhydrous ammonia is not an ammonia-water solution. The term anhydrous means without water, and without water pH has no meaning; pH refers to hydrogen and hydroxyl ion concentration which results from disassociation in water. Aqueous ammonia is a solution of ammonia in water and therefore has "measurable" pH (a number from 0 to 14 that is based on a mathematical function of hydrogen ion concentration). A pH value of 7 is considered neutral, a pH value of less than 7 represents an acidic material, and a pH value greater than 7 represents a material that is alkaline or basic. Aqueous ammonia is a base, with a pH of about 11.6. All alkaline materials, including aqueous ammonia, are corrosive.

Adding water to a dense gas cloud will stop the white cloud condensation by absorbing the ammonia vapor into the water while at the same time warming the dense gas-to-air temperature differential which occurs as the ammonia is being absorbed into the water. water and ammonia mixture will then evaporate into a heavy invisible cloud of aqueous ammonia vapor that has a high pH that will impact the health and life safety of downwind victims who don't have respiratory protection or cannot shelter in place.

The volume of ammonia-to-water mixture materials is a critical factor for determining the level of pH damage that can occur to equipment (immediately corrodes copper, zinc, and their alloys), human tissue (especially the eyes and moist areas in the groin, neck, and underarms and the environment) leaching into groundwater to increase nitrate pollution or into biotic environments. The most serious damages can occur when water is applied to an aerosol and/or dense gas cloud with indiscriminate regard for containing and treating the aqueous ammonia until the pH is under 9 (it then can be received by a wastewater treatment plant if they are equipped and willing to permit the processing of the aqueous liquid waste via a permit. The Wastewater permit analysis provided by Monterey County Environmental Health to the State of California Water Quality Board was approved in 2007. The details of the process used to gain the permit approval are summarized in APPENDIX B: Ammonia Characteristics.

Anhydrous is a chemical term meaning free of water. Anhydrous ammonia is transported and stored with a small fraction of approximately 1% water present (to avoid stress cracking of vessels). Anhydrous ammonia is extremely hygroscopic, which is a chemical term used to describe a substance that absorbs moisture from the atmosphere and from surfaces that it may contact doing so without bonding. Anhydrous ammonia is also hydrophilic, which is a chemical term meaning it absorbs water and bonds with it on a molecular level. When ammonia dissolves in water ammonium hydroxide is formed. Ammonium hydroxide is also called aqueous ammonia or aqua ammonia (NH_4OH).

Anhydrous ammonia forms ammonium hydroxide solution when it contacts the mucous membranes of the eyes, nose, mouth, throat, and lungs. Ammonium hydroxide can cause corrosive injuries to the body. Because anhydrous ammonia is hygroscopic, it absorbs water from spills and releases clouds, forming ammonium hydroxide. Ammonium hydroxide is also corrosive to metals.

Water proximate threat impacts associated with transitions from anhydrous to aqueous ammonia, (during the production mode) need to be approached with caution. Aqueous ammonia is a weak base (alkaline).

Solubility

Water and ammonia are miscible in all proportions. When one refers to the solubility of ammonia in water, it is usually meant to be the solubility at a given temperature for which the vapor pressure is equal to atmospheric pressure.

Temperature °F	*Wt. % Ammonia Solubility*
32	47.3
50	40.6
68	34.1
86	29.0
104	25.3
122	22.1
140	19.2
158	16.2
176	13.3
194	10.2
212	6.9

Figure 3-6 Ammonia Solubility
https://airgasspecialtyproducts.com

A 5% mixture of ammonia and water (sold over-the-counter consumer packaging) creates an alkaline solution of 11.6 ph. A 17% solution of ammonia in water generates a 12.1 ph. Aqueous ammonia manufactured for industrial purposes such as De-NOx of power production is frequently manufactured at a 30% concentration in water yielding a pH of 13.5 which is the most concentrated aqueous solution that can be produced.

The solubility of ammonia increases as the water temperature decreases. The vapor pressure comment needs to be clear that the pressure is atmospheric for all temperature conditions of the blend. Also, note that increasing the temperature of aqueous ammonia will increase the rate of ammonia vaporization.

Review Figure 3-5 and note the rate of ammonia solubility increases as the water temperature decreases, (e.g., at 32˚ F the weight percentage of ammonia soluble is 47.3%, at which point the solution is saturated.) compared to ammonia mixed in boiling water, (212ºF) the resultant concentration is 6.9%. Commercial ammonium hydroxide generally contains 19-30% ammonia. Ammonium hydroxide solutions decrease in density as concentrations of dissolved ammonia increases. https://airgasspecialtyproducts.com/

3.3 Ammonia as a Maritime Fuel

The maritime shipping industry is seriously working on decarbonization of their heavy use of bunker oil fuel. The first ship running on ammonia (hydrogen fuel) have been launched. The Maersk Mc-Kinney Moller Center for Zero carbon shipping published the “Human Factors Considerations: Ammonia Fuel End-of-Stage Report https://www.preprod.lr.org/en/knowledge/research-reports/human-factors-considerations-ammonia-fuel-end-of-stage-report/

Typically, anhydrous ammonia is transported and transferred by ship and barge at or below its boiling point (-28°F). Highway and rail transport is done at ambient temperature conditions in large quantities as a saturated liquid with a pressure that corresponds to the liquid temperature. Highway and rail transport is done at ambient temperature conditions in large quantities as a saturated liquid at close to atmospheric pressure. Hence, it is important to understand its thermodynamic properties.

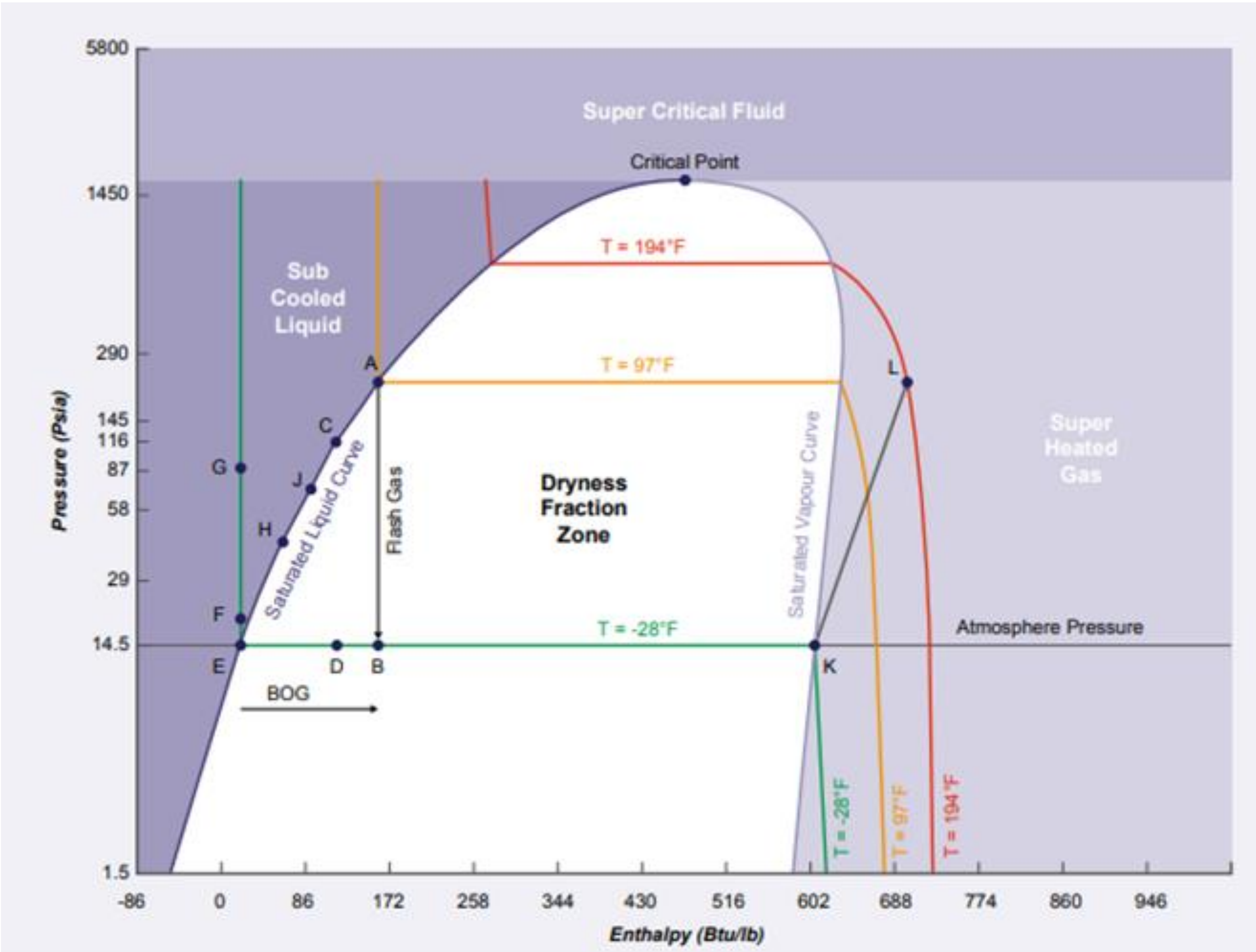


Figure 3-7 Pressure-Enthalpy Chart for Ammonia

The saturated liquid curve indicates 100% liquid at boiling point, and the saturated vapor curve line indicates 100% gas at boiling point. The horizontal distance between the two saturation curves measures the latent heat of evaporation. The evaporation process travels horizontally from the saturated liquid curve through the dryness fraction zone to the saturated vapor curve as heat is added, which may occur at constant temperature and pressure. Saturated liquid ammonia at a temperature of -28ºF and 14.5 psia is indicated as point "E" in the enthalpy chart. When heat is added at constant pressure, a phase change occurs as it moves horizontally to the right from point E to point K. In this case, when the added heat from the surroundings enters the -28ºF liquid ammonia, the resulting evaporated gas at point K is known as "Boil Off Gas" (BOG). Gas formed without pressure reduction is boil-off gas due to added heat (horizontal process in Figure 3-6). Flash Gas Phase change can also occur adiabatically if the pressure is reduced without adding heat. For example, saturated liquid ammonia at a temperature of 97°F and 202 psia is indicated as Point A in Figure 3-6. When pressure is reduced, a partial phase change occurs as it moves vertically down from Point A to Point B into the dryness fraction zone, with about 23% of the mass flow, instantaneously evaporating as “flash gas”. Flash gas will only occur with adiabatic pressure reduction (vertical process on Fig 3-7). The 23% vaporization of the liquid in the example explains what happens when the vapor pressure of liquid in a vessel is reduced (by a breach of the vessel above the surface of the liquid). The 23% of the liquid represents the change of internal energy of the liquid as its condition changes from a warm high-pressure fluid to a cold low-pressure fluid.

The transfer of large quantities of anhydrous liquid ammonia usually takes place at close to atmospheric pressure. Centrifugal pumps specifically designed to pump saturated liquids, are used for pumping saturated liquid ammonia while preventing cavitation. When pumping ammonia liquid from an atmospheric pressure tank, the height from the surface of the liquid to the centrifugal pump suction port is known as the “net positive suction head” (NPSH) when the vapor pressure of the liquid at the pump inlet is the same as the saturated vapor pressure of the gas above the liquid surface. Maintaining the correct NPSH according to the pump performance curve requirements is important to ensure no flash gas bubbles are formed in the pump suction due to pressure drops, which can cause cavitation. At the suction port of the pump, the ammonia condition will be very close to the saturation curve at slightly elevated pressure due to the NPSH requirement, which is indicated as point F in the sub-cooled liquid zone in Figure 3-7. At the discharge port of the pump, ammonia exists as a sub-cooled liquid, as indicated by Point G in Figure 3-7. Provided the transfer line is not too long (less than 3 miles) and is well insulated, the ammonia will predominantly remain as a sub-cooled liquid until it enters the receiving tank.[12]

3.4 Anhydrous Ammonia release threats can lead to four different phases of ammonia


Figure 3-8 Firefighter using a temperature probe to determine the coldest point in the aerosol cloud.

Ammonia stored in a pressure vessel can be released as a liquid, aerosol, vapor, dense gas cloud, or as an invisible gas if released from the gas space above the liquid level. The temperature at the transition point between aerosol stream and dense gas vapor cloud was -80°F. When saturated ammonia liquid under pressure at ambient temperature is discharged into the air as shown in Figure 3-7, it undergoes a significant pressure drop and most of the liquid instantaneously reduces in temperature to -28ºF which is the boiling point of ammonia at atmospheric pressure.

This temperature reduction means that sensible heat has been removed from the liquid and this heat has instantaneously caused a portion of the liquid to evaporate creating flash gas. The flash gas is formed in the pressure reduction orifice creating an extremely violent turbulence, atomizing the remaining liquid into an aerosol. After leaving the orifice, the aerosol cloud will further reduce in temperature due to the evaporative effect. The portion of the total liquid mass flow entering the orifice which changes to flash gas is dependent on the saturated liquid pressure driving it. This will usually be in the range of 10% to 25% and therefore the expansion ratio from liquid to gas will be in the range of 80 to 200 times. The exact percentage of the liquid mass flow that turns to flash gas can be determined by plotting the pressure reduction process on the enthalpy diagram in Figure 3-7 Aerosol/dense gas releases blend as visible white cloud plumes as the cold gas meets the warm air in the presence of humidity. Ammonia vapor moves buoyantly at ground level until ambient temperature and wind break up the dense gas to vapor that continues to evaporate to its gas density of 0.6, a little more than half the density of air at normal ambient temperatures; and even at its boiling point ammonia gas density remains less than that of air at ambient conditions.

However, if pressurized, and liquid ammonia is released accidentally, a portion of the mass flow will instantaneously form flash gas and violently propel an aerosol cloud of ammonia as described above. The density of this ammonia aerosol is typically about 3.5 times the density of ambient air, which is ~0.5 (air density varies with the pressure, temperature, and humidity. On a hot, muggy day, the air becomes "thinner" or less dense, and “thicker - heavier” in a cold foggy or high humidity circumstances.

The challenge is for the first responder command team to determine the isolation and protective action zones based upon weather, wind, plume movement. This is a critical decision when victims do not have respiratory protection or rescue assistance needed to safely escape.

Aerosol stream generated within the pressure vessel: There are three ways that pressurized liquid anhydrous ammonia transitions to other types of release. The release begins with a jet stream of very cold aerosol droplets that transitions into dense vapor/gas plume (absorbing more atmospheric heat) and moves downwind. The environmental heat and wind break up the dense gas into an invisible vapor that continues to track on the cooled ground that the driving aerosol created. Wind, humidity, vegetation, bodies of water, and ambient heat moves to the cooler ammonia plume as it transitions to invisible vapor (0.6 vapor/gas density) and rises into the upper atmosphere where the ammonia breaks down chemically (generally in less than a week) without doing harm to the earth’s ozone. Ammonia has a Global Warming Impact (WPI) of less than 1 because it separates into harmless hydrogen and nitrogen atmospheric compounds.

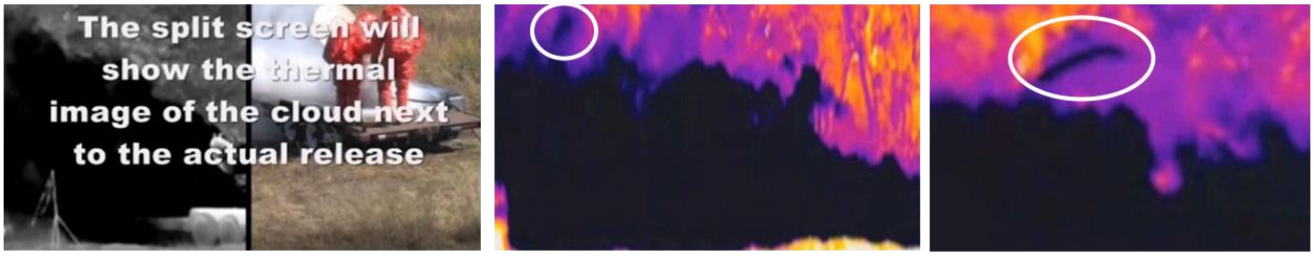


Figure 3-9 ASTI Training Release Infrared Pictures of Aerosol “Liquid Globules”

Left Picture: Aerosol stream from a 5,000-gallon bobtail delivery truck feeding a 5/8” orifice (outlet) located in a railcar pressure hood. The split screen will show how the extremely cold aerosol (black infrared part of the picture) grows, while also giving off dense gas (pink infrared).

Middle Picture: The liquid aerosol stream forms aerosol globules and droplets that expel out of the aerosol stream and boil-off and flash into dense gas as the remaining liquid glob arcs back into the plume.

A high pressure and high-volume release e.g., from a rail tank car (33,000 gallons) or semi-road trailer (10,000 gallons) can generate aerosol streams that can reach 50 to 100 feet (15 to 30 meters) before they begin to transition to dense gas clouds.

Right Picture: Ammonia globules boil-off flash-off dense gas (pink infrared) as they dive back into the plume.

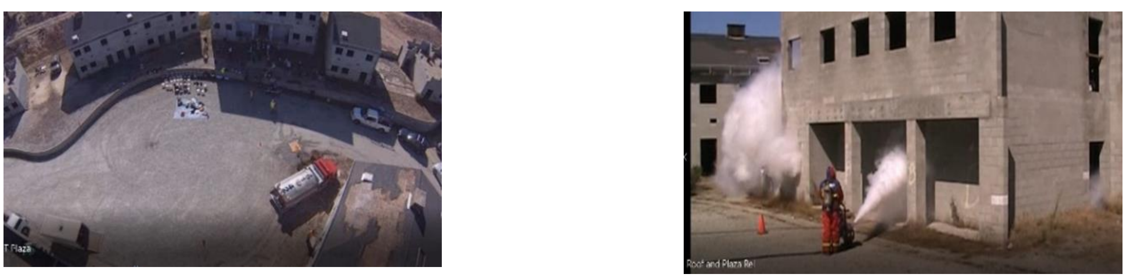


Figure 3-10 Fort Ord California Bay Area ASTI 32 Hour Course with Live-Ammonia Training.

Left Picture: The Military Operations in Urban Terrain (MOUT) Plaza wind direction.

Right Picture: NH_3 release through a 5/8” orifice supplied by a 5,000-gallon (18,929 liters) tank at 110 psi. The temperature of the Plaza was approximately 68ºF (20ºC) and wind speed was low, ~5 to 10 MPH. The 3-story cinder-block building has open windows and doors and has an open stairwell within 10 feet of the doorway that is receiving the ammonia.

The cold ammonia aerosol moved with the mild westerly wind that entered the building on the right side of the building. The plume filled the bottom story of the building and vented out of the opening on the left side of the building. Less than 200 ppm moved up the stairwell to the second-floor ammonia was detected on the third floor. The cold dense gas cloud moved swiftly out of the exit doorway and windows on the downwind side of the building. Figure 3-10 shows how the dense gas cloud hit the plaza buildings on the downwind side and the cloud began to swirl. The atmospheric heat energy provided power to the swirling ammonia cloud that was strong enough to resist the downwind movement. Instead, the dense gas vapor moved upwind towards the student assembly area. The Safety Officer called for the ammonia supply to be shut down. The dense gas lost the volume and heat differential that had sustained the “tornado” type of swirl that moved the impact area in a circular pattern throughout the Plaza area.

Figure 3-11 ASTI Aerosol Release training at the Fort Ord, California MOUT Facility Plaza

Left Picture: The dense gas cloud moved towards the downwind Plaza building wing.

Middle Picture: The cold dense gas cloud hit the warmer building and deflected.

Right Picture: At that point, the dense gas cloud began to spread and show signs of upwind movement. The plaza was evacuated, and participants watched as the cloud lost energy and faded away into invisible vapor. All this occurred within 5 minutes.

Lessons Learned: The movement of ammonia moved out the windows and doors laterally with the wind direction rather than upward into the second floors. Low-speed winds can allow the cold ammonia vapor to transition as a cold gas without the overpowering impact of moderate to high wind conditions. Ammonia’s attraction to moisture (atmospheric and vegetation moisture) and/or bodies of water must be considered when planning for evacuation, SIP, and command team incident command post location.

Low wind (< 6 mph = < 10 km/h)		Moderate wind (6-12 mph = 10 - 20 km/h)		High wind (> 12 mph = > 20 km/h)	
km	(Miles)	km	(Miles)	km	(Miles)

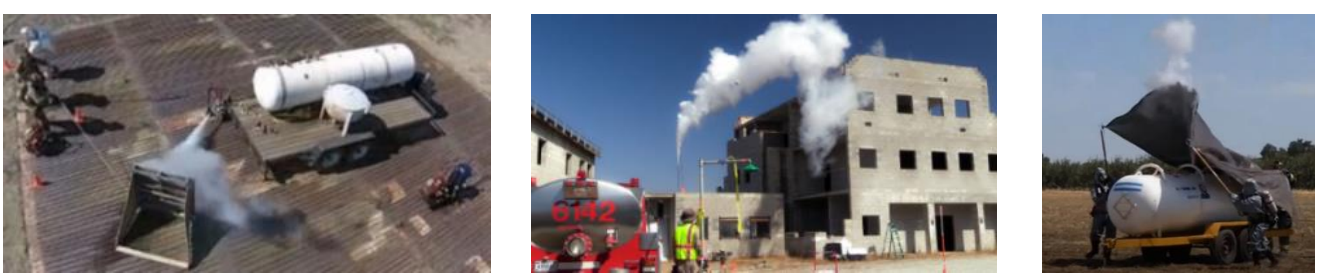


Figure 3-12 ASTI Aerosol and Plume Movement at the Fort Ord

Left Picture: If the aerosol cloud is blocked by buildings or any other solid object the ammonia aerosol plume will lose its downwind acceleration. The blocking of the ammonia-dense gas causes a turbulent ball of energized dense gas that creates a much smaller downwind impact of ~300 feet (91.4 meters).

Middle Picture: Notice how the cold dense gas cloud deflects off the corner of the much warmer building and heads for the cooler air between the two buildings. The rest of the cloud will disperse downwind in the direction that a roof top windsock would show. The ammonia vapor that disperses at ground level will move with ground level wind movement which can be at an opposite direction than the roof top windsock would reveal because the wind deflection around buildings is very different than free flowing wind at the roof top.

Right Side Picture shows the effectiveness of covering an ammonia release with a poly-vinyl tarp. An unmitigated free-flowing aerosol stream can launch dangerous downwind vapor for up to 1,000 feet (304 meters) of isolation zone followed by a protective action zone that can extend to up to a mile (1.6 kilometers). The blocking created by the plywood barrier will deflect the aerosol stream and reduce the downwind velocity of the stream.

Figure 3-13 ASTI Fort Ord MOUT Plume Movement in A Wet Field Environment as explained below.

Left Picture: An ammonia aerosol release during low wind speeds in an environment of very moist ground vegetation.

Middle Picture: The ball of energized dense gas rolls around like a mini-cyclone.

Right Picture: The dense gas begins to escape to form a cold trail for the vapor to move until a wind shift occurs that can flip the plume in an opposite direction. The buoyant ball of gas is easily turned during variable wind conditions...especially with low and variable wind speeds. A moderate wind moved the plume 90º into the swamp of reeds and the plume continued to ball-up over the reeds.

Figure 3-14 Howard Co. Maryland Fire Training Wet Day Release.

Left Picture: An ammonia aerosol release during low wind onto speeds in an environment of very moist ground vegetation.

Right Picture: The aerosol release will linger as a puff cloud and mix with the swamp reeds and water. The invisible vapor will be moving away from the main body of the plume as aqueous ammonia vapor that will have a pH factor that will sting with alkaline corrosive impact.

Figure 3-15 Dry Day Releases-double 7/8” Nozzles at 125 psi 68ºF and 5 to 8 mph wind

Top Left Picture: The release begins when one of the 5/8” nozzles opens to release an aerosol/dense gas cloud that begins to form a cold trail for the rest of the escaping ammonia plume to follow.

Top Middle Picture: The left flank of the plume moves into the trees and breaks up the dense gas vapor, allowing ammonia gas to move freely up the hill through the trees and vegetation.

Bottom Left Picture: One 5/8” nozzle opens forming an aerosol/dense gas cloud followed by the opening of the second 5/nozzle. Notice how the first plume is loosely connected to the double nozzle (much stronger) aerosol/dense gas plume. The first plume head’s visible dense vapor cloud splits between a small group of oak trees and quickly diffuses into invisible gas that disperses up into the atmosphere; NOT TO SAY that some of the invisible gas will be at ground level for a hundred feet.

Bottom Middle Picture: The two-nozzle release is the only visible vapor cloud. The wind has increased its impact on the plume so that it moves into the trees and disperses as it moves up the hill through trees and vegetation.

Right Side Top and Bottom Picture: The “Tarp and Cover” team moves in with a right and left flank anchor emergency responders wearing firefighter turnouts and self-contained breathing apparatus. They are trained to stay out of the visible dense gas while placing the tarp. The goal is to block and contain the aerosol dense gas jet stream. Dense gas that escapes the edges of the tarp is inconsequential, in that the dense gas quickly transitions to invisible gas and moves up into the atmosphere.

Left Picture: Steady high-pressure aerosol stream released in a moderately high level of wind and humidity. The downwind threat of highly irritating (high pH) vapor can extend for a mile (150 meters).

Middle Picture: The aerosol stream has been covered with a tarp which stops the aerosol stream plume, and only allows a ball-shaped dense gas dense gas to dissipate into vapor. The attraction to moist ground vegetation will keep the ammonia-dense gas cloud circulation into the wet environment which generates an exothermic reaction with water.

Figure 3-16 Wet Release from a 5,000-gallon skid tank at Hydro Care in Landskrona, Sweden (described below.

Right Picture: Dense gas transitions to invisible vapor as the ammonia plume moves downwind. It is critical to have plume models that consider the fluctuation intensity associated with attractive forces such as water, wind, humidity, water, and cooler temperatures. Lessons Learned: A wet ground keeps the aerosol vapor cloud low to the ground and tightly contained for a long downwind distance. The containment of the aerosol with a basic (hardware store-purchased vinyl tarp) reduces the downwind impact significantly to 300 to 500 feet or 100 meters.

See the Plume Model Comparison to the discussion that occurs in section 4.7 Desert Tortoise at the Nevada Test Site: Dry Lake-bed on page 78.

You will see that the first 15 seconds of the Figure 3-15 aerosol jet stream is beginning to move exactly like the Desert Tortoise release. The characteristics of plume models will give similar characteristics that can be considered for much larger release.

3.5 Ammonia Flash Fire is A Rare Experience

The flammability of ammonia is a possibility at any time that a dense gas concentration of ammonia can reach its Lower Flammability limit of ~15% (150,000 ppm if it doesn't exceed its upper flammable

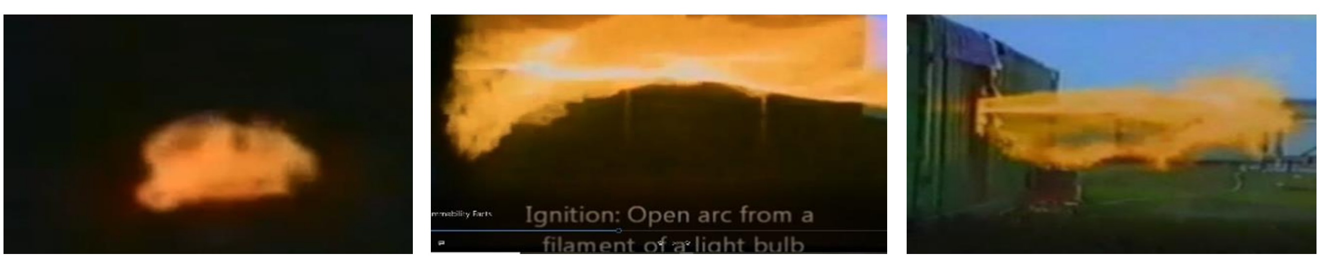


Figure 3-17 Infrared picture of a flash fire within a wooden crate.

limits of 28% AND when a source of ignition that is at least 1200°F is available within the vapor within its flammable limits (an electrical spark or filament to a light bulb can generate 1200°F (651°C).

Left Picture: A spark from a filament of a light bulb ignites with a small initial fire. The initial ignition would resemble the left picture Figure 3-16.

Middle Picture: The fire immediately flashes as the heat of ignition burns all the vapor within the room.

Right Picture: The flame spread generates a fast and powerful heat plume that blows through the plastic-covered window and spreads from the ceiling to the floor with high energy impact.

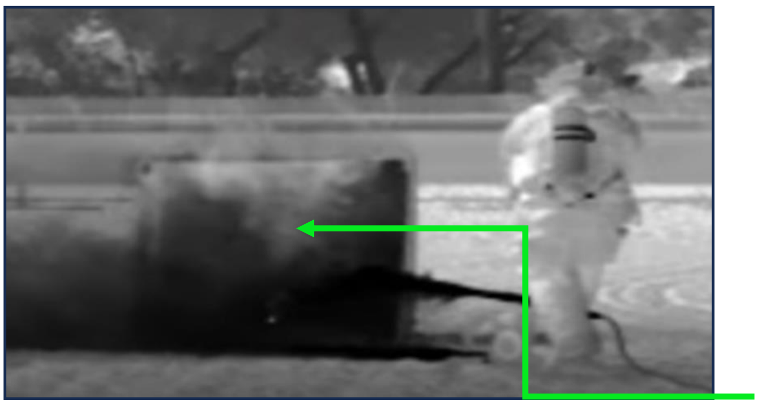


Figure 3-48 Ammonia Flash Fire within a Wooden Apple

ASTI conducted a test with a lighted flare placed within a 4-foot by 4-foot wooden box that was also 4 feet deep. The flash fire occurred suddenly when the vapor mix reached the lower flammable limit (15% (150,000 ppm). It flashed quickly (1 to 2 seconds) without sound or concussion. It could only be seen through an infrared camera. The sudden flash fire is the lighter v-pattern within the wooden box.

Structure fire within a facility that has an ammonia system presents a lower level of overall threat if the fire has vented and the ammonia mixes and burns with fire flame and smoke plume.

Figure 3-19 Salinas Fire Chief Samuel Klemek and his Command Team Debriefing on the Taylor Farm

Left Picture: Taylor Farms structure fire burns through the warehouse roof and vents the smoke and hot gases. The roof failure also causes the ammonia evaporator coil to collapse and ammonia vents as a bright white (cold smoke) cloud https://abc7news.com/taylor-farms-fire-salinas-evacuation-shelter-in-place-california-ammonia-explosion-risk/11747214/ Notice how the right side Infrared picture is dark colored, indicating that it is a cold gas. The ammonia gas rises into the heat plume and up into the atmosphere as it transitions to nitrogen and hydrogen.

Middle Picture: Salinas Fire Chief Sam Klemek and his command team worked the fire for several days. Toxic smoke from the fire included multiple gases e.g., ammonia, chlorine, lab gases and a high fire load of combustibles. A shelter in place order extended for a one-mile downwind urban area.

Right Picture: Infrared camera picks up the venting of ammonia liquid aerosol and gas (white-circled) into the plume after a portion of the roof collapsed and an evaporator coil breached and vented.

Figure 3-20 A Very Rare Ammonia Flash Fire Event

ASTI's team has investigated ten structure fires that have vented similarly to the Taylor fire, and we consistently find that relief valves and system controls reduce the potential for a boiling liquid expanding vapor explosion (BLEVE). Releases of ammonia that are not vented to the outside do have potential for flash fire as was shown in figure 3-17.

It's very rare to develop conditions where a flash fire of ammonia vapor would occur in an outside release. We did find a rare occasion when a sudden large puff cloud did ignite. It happened on an early, cool, and foggy morning (May 1987) an anhydrous ammonia truck with a fully loaded (10,000 gallon) MC 331 trailer was headed east on Interstate 80 towards Sacramento, California.

As the driver entered the exit ramp overpass ramp that led to Interstate-5 he lost control and hit the overpass ramp guardrail. The truck and trailer hung up on the rail while the driver exited the truck. The driver was walking away from the truck when it suddenly broke through the ramp and crashed and fell 175 feet onto the street below the overpass (see top two pictures in figure 3-19). The hydraulic shock and weight of the impact of the fall caused the end of the MC 331 trailer to detach. The tank launched at high speed and powerful force into the underside super-structure of the bridge overpass as the metal peeled off the bridge girders and the ammonia tank. The release of 10,000 gallons of ammonia resulted in a puff cloud that mixed with the cold and humid morning air. Drivers on I-80 saw a ball of fire about 150' high flash into the dark morning sky. The driver died with severe third-degree burns on his back. The bottom two pictures show evidence of fire to the underside of the overpass and the charred cable insulation. Sacramento Fire Station was close to the event. The firefighters were awakened by the sound of the tank explosion. They suddenly couldn't talk because they had unknowingly driven into the invisible vapor as they approached the wreckage...they continued to drive by the wreck to get clean air.

Figure 3-21 Phillips 66 Cactus Plant Etter, TX. April 1965 and ASTI Infrared Dense Gas Flash

Left Picture: Ammonia liquid will boil off from surrounding ground and atmospheric temperature and then be stable unless water is added, or new heat is applied. A burning fuel-soaked rag wrapped around the end of a long stick is thrown into the one ton of contained liquid and is quickly extinguished by the cold and high concentration of pure ammonia liquid and the vapor concentration was above the upper flammable limit.

Middle Picture: Water sprayed on the liquid pool causes a flash of dense gas. Aqueous ammonia vapor seems to add more potential for flash fire; an ammonia vapor mixture holds within the flammable limits for a longer time.

Right Side Picture: Stick flare thrown about 10 to 15 feet downwind of the dense gas cloud momentarily ignites. This reveals the fact that the aqueous ammonia vapors are within the flammable limits of ammonia combustion. The burning vapors resemble the way that a wet wood campfire will put out a lot of smoke that will flame at the edges because of the fuel, heat, and air mixture.

Water placed upon liquid ammonia creates visible and invisible alkaline vapor that will be much more irritating than anhydrous ammonia. This is why coveralls and full-face respirators are very effective for escaping anhydrous ammonia vapor.

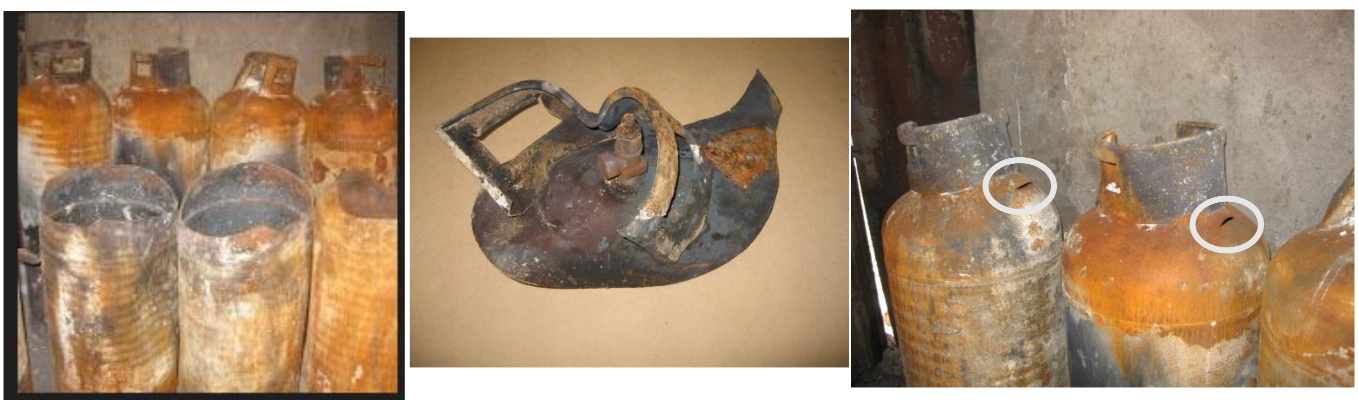


Figure 3-22 Fire in a Ammonia Cylinder Storage Warehouse – 150 pound or 680.4 Kilograms

Left Picture: The cylinders were properly stored, chained in place before the fire started.

Middle Picture: A piece of the top of one of the cylinders that lost the top of the tank (second row).

Right Picture: All the cylinders stored along the top row opened with a small slit near the top of the valve housing (see the slit within the white circles).

Here's the question: Which of the cylinders were full and which were partially full? Think about it…if the cylinder expanded and went liquid full there wouldn't be any vapor pressure to the excessive pressure would split the cylinder at the weakest weld point. The release would be a very high pressure liquid release but there would not be any vapor pressure behind it to have the force that would tare the entire top off of the cylinder. The partially filled cylinders had more vapor pressure behind the slug of ammonia that blew the tops off the cylinder.

3.6 Ammonia and the Purposeful Use of Water

The purposeful use of water on ammonia must consider the overall impact of mixing water with anhydrous ammonia. During emergency response event there are no "never use water" rules of engagement when dealing with the need to protect life, environment, and property. The purposeful use of water on ammonia or on ammonia systems is a "risk versus benefit" decision. The responder must have a clear understanding of the positive and negative impacts to people, environment, and property BEFORE applying the water.

Use of Water Objective	**Risk vs. Benefit Consequences**
Reduce impact of an NH_3 cloud	Creation of aqueous ammonia vaper that will develop high pH and increase flash fire threat.
Cooling of system components	Water that is cooler than ambient temperature or much cooler than the system component is okay.
Improve visibility in an NH_3 cloud	Knocking down ammonia vapor to see a valve or to access a rescue victim will temporarily work in an outside environment but creates foamability threat and corrosive impacts when used inside a room.
Dilute (wash-down) NH_3 liquid	NOT recommended – the consequences of creating aqueous ammonia clouds outweigh benefits and there are better alternatives e.g., let the liquid evaporate, suction the liquid into an ammonia cylinder, or absorb the NN_3 with chemical absorption pads.
Hydraulic Ventilation	Very effective when the ventilation plan includes the safe recovery of aqueous ammonia run-off.
Water curtain to reduce NH_3 threat	Will work for odor control (which generally is non-life threatening. Contained run-off may accumulate to form high-threat aqueous vapor.

Alternative Options that should be considered when determining the risk versus benefit of using water on an ammonia release.

1. An aerosol cloud can be covered with a tarp to reduce the downwind impact of an aerosol release.

2. Block an aerosol jet stream to break the downwind flow of the dense gas cloud. This would increase the puff cloud impact at the block point. A properly trained and equipped hazmat team could cover with the puff cloud with a tarp to reduce the dense vapor impact.

3. System mitigations are available to reduce system pressure so that ammonia release is easy to ventilate with a fan.

4. Immediate use of a fan to supply fresh air to a rescue victim. ASTI trainer Bob Cole is credited with saving a life because an industrial response team used his recommendation to save an operator who went down while trying to escape an ammonia release. The fresh air supported his ability to escape.

5. Fire ventilation fans used to supply Positive Pressure ventilation https://www.firerescue1.com/fire-products/ventilation/articles/ventilation-fans-6-types-to-consider-vMAtRZfJftDY1209/

6. Cover (contain) a large liquid surface are of a pool of NH_3 liquid with plastic balls and/or PVC tarps to reduce vapor off-gassing.

Improper use of Water: A dense gas cloud of ammonia in the compressor room. was knocked down with a fire hose line without any mitigation of the run-off water:

5,500 fish (two species of bass) were killed. The fire department and the ammonia facility were fined and required to pay for restoring the fish population.

Proper use of Water: The Las Vegas fire department, under the command of Hazmat Incident Commander William Grass made the decision to ventilate a cold room by using hydraulic ventilation. Arrangements were made to contain the aqueous water run-off within a catch basin of the storm drain system.

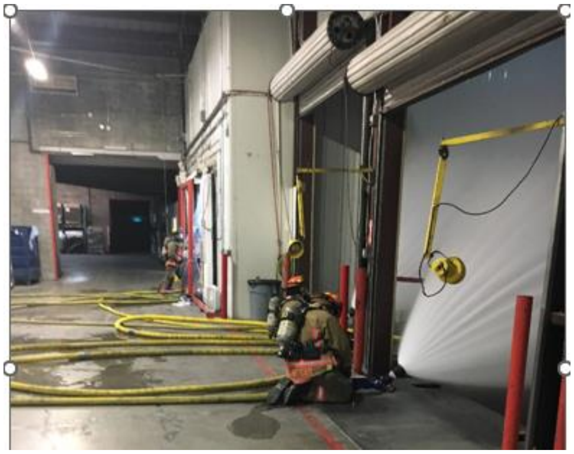


Figure 3-23 The Problems and Purposeful Use of Water on Anhydrous Ammonia

Rescue victims are down in an aerosol cloud. Firefighters approach and rescue with the assistance of a fan. They will perform a rescue while wearing their firefighter ensemble (firefighter turnouts provide full skin protection) and self-contained breathing apparatus with a personally fit tested positive pressure mask that ensures that no contaminants enter the mask. The firefighters will use high-power blower/fans to move the aerosol dense gas away from the victim so that the firefighters can safely make the rescue.

Figure 3-24 Using a powered blower to Divert an Anhydrous Ammonia Aerosol Jet Stream for a Rescue

Left Picture: The aerosol dense gas release is covering a rescue manikin with dense gas vapor.

Middle Picture: Firefighters direct the blower/fan at the aerosol stream so that the cone of high pressure ventilation air moves the plume 90 degrees away from the victim.

Right Picture: There are many blower/fan companies that now sell light weight battery operated fans that are quick and easy to operate for rescue and for vapor/smoke ventilation.

An aqueous ammonia vapor cloud can be dangerous: On a foggy morning in August 2009 in South San Francisco 200 pounds (91 kilograms) of ammonia leaked from a rooftop evaporator. The system operator used water to wash away a puddle of liquid ammonia on the roof. The aqueous ammonia vapor cloud rolled off the compressor room roof and dropped to ground level as the foggy weather carried the dangerous aqueous ammonia vapor into the business district.

A call for evacuation occurred and people were exposed to the aqueous ammonia vapors as they escaped their cars and buildings. 17 were hospitalized, one was a bus driver who had exited his bus to pick up a group of children within the Genentech facility that was located across the street and several hundred feet away. The driver was walking to get the children when he suddenly was overcome with aqueous ammonia gas and fell to the ground and couldn't move. Police officers drove car next to the bus driver and tried to rescue him. The officer couldn't breathe and got back into his car and escaped. Genentech employees watched from the windows inside the building without any discomfort from the ammonia exposure.

SAN FRANCISCO (AP) — The owners of a South San Francisco salami plant will pay nearly $700,000 and overhaul its refrigeration system as part of a federal judgment stemming from an ammonia leak that sickened almost four dozen people.

The U.S. Environmental Protection Agency and Department of Justice say Columbus Foods will pay the penalty for the August 2009 gas release without acknowledging wrongdoing. The sausage maker also agreed to spend $6 million upgrading its refrigeration system and improving emergency notification procedures. https://www.impomag.com/maintenance/news/13205859/salami-plant-to-pay-700k-for-ammonia-leak

Left Picture: A small puff cloud of aqueous ammonia aggressively flashes from water being placed into about five gallons (18.9 liters) of liquid ammonia that was sitting as a stable liquid at about -40°F (which is also -40°C). The water is 50°F (10°C); that would be a 90°F heat differential.


Figure 3-25 Puff Clouds – **left picture** Water on NH_3 forms a small aqueous puff cloud.
Right picture 7,500-gallon MC 331 trailer crash with a trailer carrying a scoop-loader causes a Puff cloud (with no water impact) on the I-5 freeway near Fresno CA. The orange circle shows the location of the tank puncture.

Right Picture: The vapor pressure was approximately 90 to 100 psi. The puff cloud came from the scoop-loader puncture that released the tank vapor pressure within the first minutes. Notice the ice buildup on the lower third of the MC331 tank. The liquid that sat very stable in the tank.

Lessons Learned: This incident shows two key issues: 1) avoid putting water on liquid ammonia (cover it, let it evaporate, or have hazmat-equipped personnel soak it up and remove it safely. 2) Use caution when advising people to **evacuate from a safe inside rally point** into a dangerous outside isolation zone impact area. Shelter in place within a vehicle or building is safer than exiting into an ammonia vapor cloud.

Viability of Water Curtain Protection The logic for mitigating ammonia release vapor risks with water curtains began to intensify in the late 1990's mainly for large bult tank storage of low-pressure liquid ammonia. The following "Science Direct" article link will explain the historical development of water curtain technology: https://www.sciencedirect.com/science/article/abs/pii/S0957582018300855

The ASTI concerns about the use of water on ammonia leaks relates to two significant concerns

(1) **When the temperature of the water that is played upon a leaking ammonia tank and/or system is warmer than the ammonia stored within the tank (or system) pressure will rise.** The continued use of water will prevent liquid ammonia within the tank from dropping in temperature and pressure so as to not self-refrigerate into a stable liquid. In most cases venting vapor pressure without adding more heat could save at least a third of the tank's liquid from escape; especially when the vapor release is contained with a tarp, because the contained vapor will be much colder that the atmospheric temperature.

(2) **If the water curtain is close to the leaking tank or tank bund (containment area) the water's off-spray will mix with the ammonia liquid and/or vapor to form aqueous ammonia.** Aqueous ammonia

liquid and vapor will be corrosive and very irritating to the downwind environment and human exposure (respiratory, eye, and skin damage). Aqueous ammonia run-off will increase the threat of contamination to live bodies of water. The aqueous solution will increase the growth of algae that will rob the water of oxygen content needed by fish. Corrosive aqueous solution will corrode copper and brass, e.g. electrical systems, motors, and computer systems.

3.7 Teutopolis crash, spilling anhydrous ammonia

Effingham County, Ill. Two miles east of Teutopolis, Illinois I-40 crash – a semi-tanker crashed into a ditch because of a reckless driver trying to pass the ammonia truck that was carrying 7,500 gallons of anhydrous ammonia. The first arriving fire responders saw a "big cloud" of ammonia moving to the southwest. The fire crew that arrived backed out of the area where ammonia vapor was present.

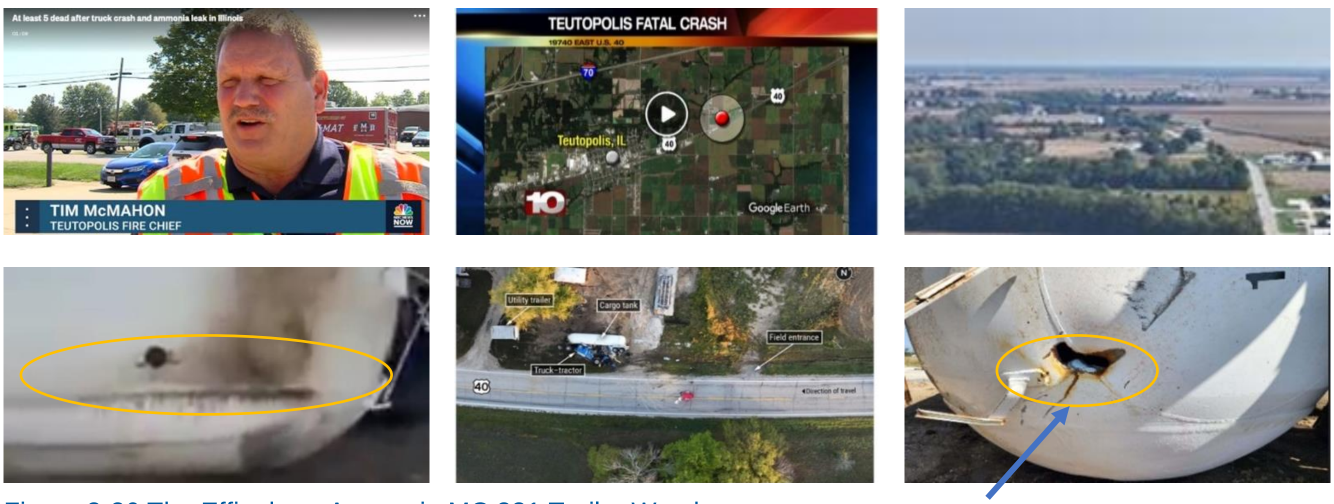


Figure 3-26 The Effingham Ammonia MC 331 Trailer Wreck

The bottom left picture shows the ice line (circled) that indicates the remaining liquid in the tank, as the ammonia vapor had escaped, and the ammonia laid at rest (minimal threat) until the hazmat team placed a magnetic patch over the tank rupture area (bottom left). This caused pressure to build up again.

The bottom right picture shows the ammonia MC 331 trailer jackknifed after being forced off the side of the road by a reckless driver trying to pass him. The forward end of the tank was punctured by a trailer hitch of a utility trailer causing about a 2" by 6" hole in the head of the tank. Approximately 3,500 gallons of ammonia escaped and caused a puff cloud. Officials evacuated approximately 500 people within a one-mile radius of the crash, including northeastern parts of Teutopolis.

Five deaths occurred during the evacuation. Two died when they left their vehicle to try to escape by moving through the dense ammonia gas cloud, instead of sheltering-in-place within the vehicle. Three deaths occurred when a father collapsed while checking out the evacuation route. His two children left their home to attempt to help their father back into the home. They all died; most likely they couldn't breathe as they were attempting to move their father. Your muscles need oxygen to provide strength.

ASTI Tech-Forum Discussion with Charles "Chip" Day of Specialized Response Solutions

Chip Day worked with Chief Tim McMahon to create an incident action plan and safety plan. Each step of the process was set with a clear task order and safety plan. The goal was to eliminate the ammonia vapor pressure from the damaged tank so that it could be safely right sided for ammonia transfer to a recovery ammonia 331 trailer that was standing by.

The Effingham FD hazmat responders had patched the damaged tank hole with a magnetic patch. This had to be removed to allow the tank to de-pressurize. The escaping vapors were diffused by natural air currents. A video shows the ice formation at the liquid level of the tank lying on its side.

The tail end of the damaged trailer was not damaged. It was an older trailer that had rear loading and ammonia liquid transfer capability with supply lines and an on-board pump.

Figure 3-27 Transferring Ammonia Liquid

The recovery tank had to be prepared for receiving the ~4,000 gallons of ammonia from the damaged trailer. The vapor pressure of the empty recovery tank was ~110 psi. The recovery tank had to be de-gassed to 0 psi to be set up for receiving the cold liquid from the damaged trailer.

Chip Day lives in Texas and was online with communications with the hazmat incident commander (IC) who supplied pictures and video views of the damaged tank. Chip worked with the hazmat IC to set up an action plan that clearly laid out each step of the liquid transfer. He also created a safety plan that points out the leading risk indicators for potential transfer flow problems. The plan worked without any unforeseen challenges.

The action plan that Chip laid out displays the professional insight needed to ensure the safe transfer of ammonia liquid from the de-pressurized damaged tank and shows the value of the recovery tank being empty and de-gassed so that the transfer pump could draft the liquid into the recovery tank without having to overcome internal pressure within the damaged tank and the recovery tank.

In situations where the damaged tank is under pressure and the ammonia is being transferred to empty recovery tanks, secondary blocks may be needed on the internal excess flow control valves. The team leader conducting the transfer would need to establish an action plan and safety plan that considers the leading risk indicators associated with blocking the excess flow valves so that they are closed and prevented from shutting down while the liquid is flowing. The procedure for correctly blocking the check valve with secondary blocks requires an experienced hazmat technician who has performed ammonia liquid transfers and is familiar with the consequences of over-riding the check valves. The industrial ammonia suppliers and/or CHEMTREC will have emergency response contractors like Chip Day available for local use.

Heavy-duty wreckers (tow trucks) were used to upright the damaged tank trailer. Paul Horgan and Chip Day discussed the value of a wrecker with a rotator crane when up righting a damaged ammonia transport tank trailer. More details are available in Section 3.8 (next pages)

3.8 ASTI Recommendations for Emergency Response and Recovery Vapor Management

ASTI demonstrated an innovation called the LIQUIDAT-R designed and engineered by Frank Wewers, who is an ASTI Board Member and owner of Fli-Tech Consulting - https://www.zoominfo.com/c/fli--tek-consulting-llc/542398331 designed a fast and effective system for reducing system pressure within an industrial fixed facility ammonia system.

Figure 3-28 LIQUIDAT-R that will transition an aerosol release into a very light and invisible vapor that rises harmlessly into the atmosphere.

The LIQUIDAT-R will receive an aerosol dense gas release and dry out the liquid and then vent the high-pressure fan is linked to an accelerator that aggressively vents the dense gas into the atmosphere.

Left picture: An aerosol release that is an unmitigated aerosol/dense gas release.

Right picture: Several seconds after engaging the LIQUIDAT-R the aerosol/dense gas cloud transitions to invisible vapor that harmlessly travels up into the atmosphere. the invisible gas into the atmosphere. The ASTI team could not find any evidence of ammonia vapor at the ground level as the LIQUIDAT-R vented the gas up into the atmosphere.

The infrared picture shows the immediate reduction of visible aerosol as it transitions laterally. The aerosol release sends the liquid to a recovery tank as the LIQUIDAT-R continues to aggressively vent

The liquid recovered from the release can be pumped back into the system. A long-term release would vent minimal vapor as compared to the potential that the recovered liquid would develop if not mitigated.

Figure 3-29: A 4” Diameter Vent Stack to Release Ammonia liquid and Dense Gas aerosol Supplied by a 7,500 Gallon Ammonia Delivery Truck MC-331 Trailer.

Two 20-foot 4” PVC Pipe vents secured with guy lines set up by Paul Horgan in about 30 minutes. This is valuable when dealing with an ammonia pressure vessel is damaged and the pressure needs to be reduced to the appropriate pressure for liquid transfer (or no pressure if the removal is by pump that is using a suction transfer).

Containment and control of a leaking valve on a semi MC331 trailer or rail car can be unsafe to access and often includes dense vapor clouds that makes valve accessibility difficult (can’t see the valve and the dense gas will be very cold to put an improper insulated gloved hand into the pressure head).

The ASTI team also demonstrated how a **high-powered leaf blower** could move the dense gas surrounding a leaking valve within a railcar pressure head. The blower will clear the air and make the valve more visible with less exposure to the responder's gloved hand when they reach in and close the leaking valve.

Figure 3-30 High-powered leaf blower

Chip Day and the other 15 ASTI Tech-Forum members reviewed the October 2023 live release innovations that support the opportunity to reduce tank pressure. The venting was supplied by a Hill Brothers 10,000-gallon ammonia delivery truck.

The vapor pressure from the Hill Brothers 7,500-gallon ammonia delivery truck was delivered through a 1” vapor supply line the vent stack. The hose line was connected on the downstream side of a high-capacity leaf blower that supported the ventilation system to add ventilation air to the ammonia aerosol release within the stack. The fan heated and accelerated the aerosol-dense gas so that the released gases dispersed faster into the upper atmosphere.

Figure 3-31 Venting the Dense Gas From A Rail Car Pressure Hood Training

The response team showed how to handle a leaking valve from a railcar pressure dome. The ground-level fan moves the leaking vapors downwind as the responder approaches with a leaf-blower fan to clear the visibility and access to the leaking valve. The method was performed and witnessed by experienced emergency responders from BNSF and Canadian Pacific Railroads. They were very impressed with the safety and effectiveness of the ventilation of vapors for safe access and control of a leaking pressure dome valve.

3.9 Ammonia Emergency Risk and Threat Impact Vulnerability on Health and Life Safety

The local ammonia response concept of operations (CONOPS) must have pre-event training and response wisdom to recognize the lagging and leading ammonia hazards, risks, and threat indicators that may impact workers, emergency responders, and the public. The local Tripod relationship should result in a CONOPS that has defined the mode of response for each of the five levels of complexity. Each of the five complexities would pre-set the notifications of local, regional, state, and federal agency support.

Most frequent lagging and leading indicators that relate to hazards, risks, and threats to water proximate events:

System overpressure is one of the highest threat concerns. An Overpressure lagging indicator would occur when a high-pressure event exceeds the high-pressure set-point warning. If the warning is ignored a higher-level leadership lagging indicator threat would exist. Normalizing deviance is a serious safety consciousness culture threat. The risk versus benefit of normalizing deviance is a costly and very dangerous leadership trait. Productivity and profits are proven to be exceptional when the leadership builds a strong Tripod relationship that emphasizes safety and emergency response readiness. The training, PPE, working environment, and employee pride becomes a countermeasure that beats back any thought of normalizing deviant safety measures.

Water proximate critical threats are directly related to ammonia liquid, aerosol, dense gas, and vapor exposure(s). The most distinctive difference between the threats of anhydrous and aqueous ammonia is the fact that aqueous ammonia includes a mixture of ammonia and water that produces an alkaline liquid and vapor with a pH range between 11 to 13. Additionally, a concentrated mixture of aqueous ammonia vapor is heavier than air and will travel low to the ground for longer distances before the vapors escape into the atmosphere.

Ammonia's characteristic odor creates a natural source of fear for those who do not understand its impact. The odor threshold for Ammonia typically begins for humans at 5 parts per million (ppm). The exposure typically does not become a risk factor until the 15-minute Time-Weighted-Average (TWA exceeds 35 ppm. For example, a short-term exposure, 3 minutes to seek fresh air or shelter location) from a release of 150 ppm of ammonia would result in an exposure of 30 ppm calculated for the 15-minute period. The human body metabolizes ammonia from the air we breathe, food that we eat, and many other natural and man-made sources to break down the food and water that we need in our bloodstream to survive. https://www.ncbi.nlm.nih.gov/books/NBK207883/

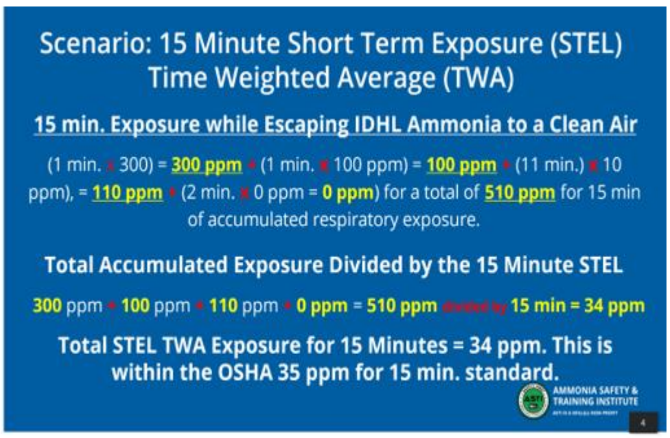


Figure 3-32 Calculating Time Weighted Average (TWA) for 15 min. Short Term Exposure Level (STEL)

Exposure 1 = 300 ppm for a one-minute entrapped in the hot zone.

Exposure 2 = 100 ppm for a one-minute escape to a Rally Point.

Exposure 3 = 110 ppm for ten minutes at 10 ppm at a Rally Point off-gassing.

Two min. 0 ppm to complete the 15-minute STEL period.

Total Exposure for 15 min. STEL = 300+100+110 = 510 ppm divided by 15 = 34 ppm.

The victim would not be likely to have any serious health effects, regardless of age. The AEGL-1 is the airborne concentration (expressed as ppm or mg/m3) of a substance above which it is predicted that the general population, including susceptible individuals, could experience notable discomfort, irritation, or certain asymptomatic non-sensory effects**.** https://www.cdc.gov/niosh/docket/archive/pdfs/NIOSH-010/0010-101603-Morawetz_J_Presentation.pdf

In 1993 the National Academy of Sciences published the "Guidelines for Developing Community Emergency Exposure Levels for Hazardous Substances." https://www.epa.gov/aegl/history-acute-exposure-guideline-levels-aegls The guidelines are very conservative and can apply to the general public (young, old, and infirm). AEGLs are laid out in three categories AEGL 1 low threat, AEGL 2 potential injury, and AEGL 3 (severe injury and potential death). AEGLs describe the human health effects from a once-in-a-lifetime, or rare exposure to airborne chemicals. AEGLS are used by emergency responders when dealing with chemical spills or other catastrophic exposures, AEGLs are set through a collaborative effort of the public and private sectors worldwide.

Ammonia 7664-41-7 (Final) - Expressed in PPM					
	10 min	30 min	60 min	4 hr.	8 hr.
AEGL 1	30	30	30	30	30
AEGL 2	220	220	160	110	110
AEGL 3	2,700	1,600	1,100	550	390

Figure 3-33 EPA Created TWA Acute Exposure Guideline Levels

The AEGLs are designed to be calculated with a Time-Weighted-Average (TWA) for time frames that begin at 10 minutes and extend to 8 hours of respiratory exposure. AEGL-1 is the airborne concentration above which it is predicted that the general population, including susceptible individuals, could experience notable discomfort, irritation, or certain asymptomatic, non-sensory effects. The effects are not disabling and are transient and reversible upon cessation of exposure. AEGL-2 is the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience irreversible or other serious, long-lasting adverse health effects or an impaired ability to escape. AEGL-3 is the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience life-threatening health effects or death.

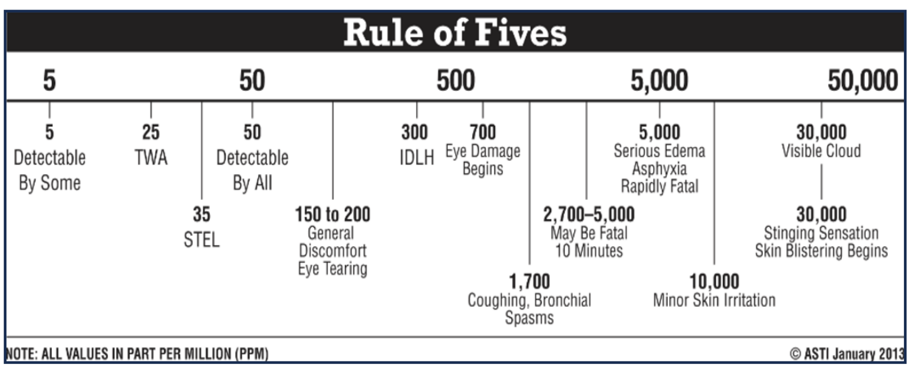


Figure 3-34 Summary Estimated Ammonia Exposure Threat Created by

The Rule of Fives table is a quick guide developed by ASTI to provide consequences of acute short-term (first 10 minutes) ammonia exposure on a table of multiple fives: 5, 50, 500, 5,000, and 50,000 ppm. The table will help first responders determine the immediate triage and medical threats for victims escaping an ammonia release. The medical and toxicological impacts on an individual must be estimated by medical treatment professionals. They will use advanced information based on the age and physical condition of the victim. https://www.atsdr.cdc.gov/ToxProfiles/tp126.pdf

3.10 Safely Escape, Evacuate, or Shelter-in-Place

Figure 3-35 ASTI team performing a Shelter-In-Place Demonstration.

The Tech Forum discussed the challenge of addressing the immediate life hazards of ammonia-dense gas vapor. The ASTI team has performed numerous evaluations of the benefits of sheltering in place rather than escaping into an ammonia-dense gas cloud. The survivability of Shelter-in-Place (SIP) clearly outweighs moving through a dense gas cloud. The wall of the building is about 60 degrees warmer than the very cold approaching dense gas cloud. The vapors deflect and move up into the atmosphere. It takes a while (based on environmental factors) for the ammonia gas to equalize in temperature with the SIP location. At that point, the deflection of vapor movement is less of a factor. This is why windows, doors, and ventilation systems must be closed off during an SIP event.

Understanding When and How to Escape, Evacuate, and/or Shelter in Place (SIP) will generally begin with the facility first responder command team; for transport emergencies the person in charge of the transported ammonia will announce his or her recommended movement plan, e.g., move lateral and upwind to safe refuge (inside or outside). The facility command team leader is responsible for employees and visitors at their plant. He/she will make sure that an Access Control Officer is appointed at the designated entry point for public safety responders. This occurs as the evacuation protocol is initiated. The ammonia event escape plan will be coordinated by the IC appointed Evacuation Supervisor. Each facility established Hazard Zone within the facility will have appropriate inside and outside rallying point locations, and those who are already safely sheltered in place will be accounted for in the PAR. An evacuation "sweeper" position is often used to ensure that all employees, contractors, truck drivers, and other visitors are accounted for.

The facility response team and all supervisors and employees should be trained and ready to engage Discovery and Initial Response procedures. The Incident Commander must be briefed with a Conditions Actions and Needs report (CAN Report) during the Discovery stage of the emergency event. The decision for 911 dispatch should include a pre-determined policy on responding to the level of complexity of the incident. The FEMA levels of complexity are designed to provide five options.

FEMA complexity levels https://www.fema.gov/sites/default/files/documents/nims-incident-complexity-guide.pdf

The evacuation pre-plan for escaping an ammonia release is contingent on the wind direction, ammonia plume status, and the **FEMA level of Complexity** (**Complexity level 5** is fixable by maintenance within an hour, **Complexity 4** is fixable but needs emergency services backup, **Complexity 3** requires immediate local public safety response**, Complexity 2** will require regional support, and **Complexity 1** is a declared disaster).

The fire escape plan is NOT dependable for ammonia release because fire and smoke have distinct characteristics than ammonia vapor movement. The fire evacuation team can be trained to use ammonia evacuation protocol to safely move people to safe rally points and the evacuation team would be expected to consider the higher level of impact from invisible ammonia vapor movement as opposed to the fire and smoke spread.

Generally, the public safety command team officer-in-charge assumes command after receiving a **Conditions, Actions, and Needs (CAN) report** from the facility emergency manager. The facility evacuation group supervisor will manage the safe movement from the Isolation zone **(Immediately Dangerous to Life and Health >300 ppm)**. The overall evacuation plan should be well rehearsed so that all employees, supervisors, and evacuation team members know the safe refuge areas and the methods of determining eye-level wind impacts for a safe movement action plan to safe shelter and staging areas.

The public safety Incident Commander (IC) will immediately ask for a **Personnel Accountability Report (PAR)** from the facility emergency manager in charge. It's important to be accurate with the communications exchange. In the early stages it is okay to indicate that the status of the PAR is not complete because the evacuation procedures are currently being accomplished. Ensure that the facility command team has priority is to provide a PAR status for all personnel that were in or near the Isolation Zone. The overall PAR status will be accounted for as the rally point supervisors report their PAR count.

The Public Safety IC will update the **size and location of the Isolation Zone (High Life Threat - AEGL 3) and Protective Action Zones (AEGL 2 and 3)** and will issue Shelter-in-Place or evacuation movement plans for all downwind life safety concerns. The local Emergency Manager and law enforcement agency are often appointed to coordinate with the Incident Commander to oversee the of-site evacuation.

The initial stage of an emergency event is accomplished by first responders. The U.S. Department of Transportation (DOT) created an Emergency Response Guidebook (ERG) for transportation incidents that involve hazardous materials. The DOT Guidebook is especially useful during the initial phase of any emergency event that may impact the community. of a response following discussion about escaping ammonia is taken from the 2020 Emergency Response Guidebook

We suggest that you download the DOT ERG while reviewing the following discussion about community evacuation/SIP details.

https://www.phmsa.dot.gov/sites/phmsa.dot.gov/files/2020-08/ERG2020-WEB.pdf

The challenge is for the first responder command team to determine the isolation and protective action zones and whether the victims have respiratory protection or rescue assistance needed to safely escape. We are concerned that an "Evacuation" order can be misapplied when evacuating the public into an Isolation and/or Protective Action Zone. The ASTI team is currently reviewing the **2020 DOT Emergency Response Guidebook pages 285 to 289** for the action plan advisories for first responders who are summoned to an incident that poses a high immediate toxic air life threat.

Page 286 from the 2020 DOT Emergency Response Guidebook: They create tables of distances that are useful for the command teams to use when protecting people from vapors/gases resulting from spills involving materials that are considered toxic by inhalation, materials that produce toxic gases upon contact with water, and chemical warfare agents.

DOT Emergency Response Guide page 288: "Shelter in in-place is used when evacuating the public would cause greater risk than staying where they are, or when an evacuation cannot be performed. Direct the people inside to close all doors and windows and to shut off all ventilating heating and cooling systems." This information should be a priority message to the first responders and the emergency broadcast system within the community. This is why the local law enforcement and the community Emergency Manager coordinate with the Incident Commander's advisory **for SIP, escaping the Isolation Zone, and a Protective Action Zone when conditions are safe to do so.**

The Isolation Zone defines an area surrounding the incident which people may be exposed to dangerous (upwind) and life-threatening (downwind) concentrations of material.

The Protective Action Zone defines an area downwind from the incident in which people may become incapacitated and unable to take protective action and/or incur serious or irreversible health effects.

Evacuation for fire is designed to address movement from a quickly spreading fire. A fire in a structure that has reached the free-burning stage can spread at a rate of 50 times its size every minute. The smoke particles are the result of incomplete combustion. Heated smoke that not properly ventilated by firefighters can flash-over with the force that will lift the roof and break windows as it gains more air to become completely involved throughout a structure.

Evacuation for ammonia requires victims that are in the room where the ammonia is releasing to use the safest escape route e.g., moving lateral and upwind of to an employee rally point or evacuation staging area inside or outside of a building that is not near the ammonia release point (hot zone. The victims of a fire or ammonia leak that are trapped must communicate their situation to those in command.

A call to 911 that indicates the victim status will quickly be communicated to the incoming public safety responders by the 911 dispatcher via radio to all responding units (fire, police, medical).

Worst-Case Catastrophic Accident For worst-case scenarios involving the instantaneous release of the entire contents of a package the distances may increase substantially. For such events, doubling the initial isolation and protective action distances is appropriate in the absence of other information.

ID No.	Guide	NAME OF MATERIAL	SMALL SPILLS (From a small package or small leak from a large package)			LARGE SPILLS (From a large package or from many small packages)		
			First ISOLATE in all Directions	Then PROTECT persons Downwind during		First ISOLATE in all Directions	Then PROTECT persons Downwind during	
				DAY	NIGHT		DAY	NIGHT
			Meters (Feet)	Kilometers (Miles)	Kilometers (Miles)	Meters (Feet)	Kilometers (Miles)	Kilometers (Miles)

TABLE 3 - INITIAL ISOLATION AND PROTECTIVE ACTION DISTANCES FOR LARGE SPILLS FOR DIFFERENT QUANTITIES OF SIX COMMON TIH (PIH in the US) GASES

	First ISOLATE in all Directions		Then PROTECT persons Downwind during											
			DAY						NIGHT					
			Low wind (< 6 mph = < 10 km/h)		Moderate wind (6-12 mph = 10 - 20 km/h)		High wind (> 12 mph = > 20 km/h)		Low wind (< 6 mph = < 10 km/h)		Moderate wind (6-12 mph = 10 - 20 km/h)		High wind (> 12 mph = > 20 km/h)	
	Meters	(Feet)	km	(Miles)	km	(Miles)	km	(Miles)	km	(Miles)	km	(Miles)	km	(Miles)
TRANSPORT CONTAINER	**UN1005 Ammonia, anhydrous: Large Spills**													
Rail tank car	300	(1000)	1.9	(1.2)	1.5	(0.9)	1.1	(0.6)	4.5	(2.8)	2.5	(1.5)	1.4	(0.9)
Highway tank truck or trailer	150	(500)	0.9	(0.6)	0.5	(0.3)	0.4	(0.3)	2.0	(1.3)	0.8	(0.5)	0.6	(0.4)
Agricultural nurse tank	60	(200)	0.5	(0.3)	0.3	(0.2)	0.3	(0.2)	1.4	(0.9)	0.3	(0.2)	0.3	(0.2)
Multiple small cylinders	30	(100)	0.3	(0.2)	0.2	(0.1)	0.1	(0.1)	0.7	(0.5)	0.3	(0.2)	0.2	(0.1)

Figure 3-36 small and large Spills of anhydrous ammonia

The information in Figure 3-36 relates to small and large Spills of anhydrous ammonia and commercial grade aqueous ammonia (50% solution) create the same sized **Isolation Zone**, considered to be IDLH (300 ppm) or greater, and Protective Action Zone, considered to be less than AEGL 2 (220 ppm). Most cigar-shaped plume models provide three color codes as follows: **AEGL 3 Isolation Zone, AEGL 2 Protective Action Zone, and AEGL 1 also in the Protective Action Zone** but specifically color-coded to the 8-hour permissible exposure level (PEL). When judging exposure threat to individuals and the community the AEGL considerations should be based upon Time-Weighted- Exposure.

The ASTI team spends a lot of time evaluating serious injuries and deaths associated with victims who chose to escape through ammonia dense gas rather than shelter-in-place. Critical life safety choices occurred during the Minot in North Dakota train derailment, where fifteen rail cars hauling anhydrous ammonia derailed and released 240,000 gallons of anhydrous ammonia released to soil and air creating a vapor plume that covered the derailment site and drifted toward Minot; a SIP order was put in place. https://ebrary.net/131238/health/minot_january_2002_train_derailment_anhydrous_ammonia_release Only one death occurred when a young couple decided to leave their home and drive through the cloud. The husband drove their vehicle into a tree, his wife escaped to a nearby house and survived. He got out of the vehicle on the other side and could not find a shelter location he fell to the ground and died.

1975 Houston Texas I-610 An Ammonia Truck-Trailer Crash In (with the same size load as Effingham). https://www.chron.com/news/houston-texas/houston/article/In-1976-an-ammonia-truck-disaster-claimed-the-12906732.php

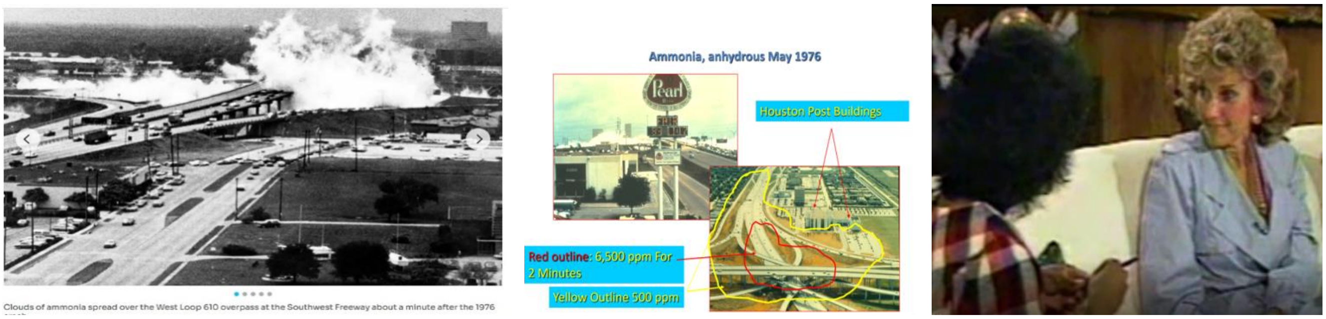


Figure 3-37 Mickey Johnson Explains How She and Her Two-Year-Old Son Survived by Sheltering-In-Place in Her Care, Even Though the Ventilation System was still on.

Mickey Johnson stayed in her car with her son and survived the dense gas cloud (even with her car's ventilation system on). She put a coat over her young son and laid over him. She suffered a long-term respiratory injury. It would have been better if she had placed the coat over herself and her son so they could both breathe cleaner air. The people in the car in front and behind Mickey's car decided to run from their cars through dense gas. Unfortunately, they fell to the ground and died. This is another good example of the value of securing a shelter location rather than step out into a cloud of ammonia to escape.

3.11 Threats to Downwind Populations

Aqueous ammonia will occur anytime that anhydrous ammonia mixes with water. The general lower concentration of solution (less than 10% mixed with ammonia) range of a water stream into ammonia results in a pH is 9 to 11. The toxicity to humans and aquatic organisms is significant if the exposure exceeds the AEGL time-weighted average. Victims may rarely have any more than a tingle on their skin, especially in areas that have more moisture e.g., neck, armpits, and/or groin. When mixing anhydrous ammonia with water an exothermic reaction will occur that raises the water temperature. The warmer the aqueous ammonia solution the higher the volume of aqueous ammonia off-gassing occurs. The following is a list of examples of how aqueous ammonia builds in solution threat:

1. Off the shelve ammonia cleaner is 2 to 3% ammonia.
2. Water used to knock down a dense gas cloud of anhydrous vapor will generally produce aqueous ammonia run-off at a pH of 9 to 11. The ambient temperature aqueous solution mix will generally not exceed 10% to 20%.
3. Commercially produced aqueous solution is generally 30% ammonia shipped in plastic ammonia totes or aqueous ammonia tanks that meet DOT standards. Special orders of higher concentration (50% solution is rare and generally only for laboratory use) are a much higher threat to

manufacture, requiring more heat management, production safety, and storage tank requirements. Note: NEVER put anhydrous ammonia into a tank that has been used for aqueous solutions; the water in the aqueous solution will absorb the anhydrous ammonia which can cause a tank implosion.

The low-lying corrosive vapors from aqueous ammonia that is greater than 20% is just as dangerous as anhydrous ammonia, or more because of the immediate alkaline impact on skin, eyes, and respiratory system. The same increased corrosive impact occurs to brass, copper, and their alloys. Caution must be taken when using ammonia, make sure that the benefits outweigh the long term impacts.

Download a free PDF copy of the ERG at https://www.phmsa.dot.gov/sites/phmsa.dot.gov/files/2020-08/ERG2020-WEB.pdf The 2024 version of the DOT Guidebook will be published no later than mid-2024.

3.12 Understand How to Read a Plume Model

The ammonia emergency first responders to a release event may not have a plume model available to help them to understand the challenges of the invisible ammonia vapor that is moving downwind. Instead, they will consider wind direction provided by roof and eye level wind indicators and estimate (guess) the impact of the ammonia release and visible dense white vapor. That can be difficult on a hot dry day because dense gas isn't as visible when water vapor (humidity) isn't available.

Most fire service in the U.S. carry Thermal Imaging Cameras (TIC) to track the heat of a fire. ASTI will be doing more investigation on how a TIC can help track the movement of an invisible dense gas cloud.

ASTI recommends that a worst case and/or most likely case plume model be pre-developed for each facility hazard zone that contains dangerous chemicals e.g., ammonia, chlorine, sulfur dioxide. This will

Figure 3-38 ALOHA Plume model-Cigar-shaped (3 degrees of release), Confidence and Steady State lines

help the first responders assess and anticipate probable movement of the ammonia cloud on-sight and within the downwind community. The next challenge will be to ensure that the responders understand the information provided by plume models.

Red, Orange, and yellow cigar shaped plumes represent the plume designer's predicted level of threat e.g., AEGL-3 (red - >300 ppm), AEGL-2 (orange – <220 ppm), and AEGL-1 (yellow – < 25 ppm. The plume modeler can change the color codes to show different levels of threat. **Yellow Confidence lines**

forms the fan-shaped yellow line that indicates 90% accuracy of the lateral sway due to wind change for downwind impact. **Steady State** is the predicted end point of the plume (based upon the data used to build the plume e.g., pressure, size of release opening, and volume of chemical feeding the release.

Low wind (< 6 mph = < 10 km/h)		Moderate wind (6-12 mph = 10 - 20 km/h)		High wind (> 12 mph = > 20 km/h)	
km	(Miles)	km	(Miles)	km	(Miles)

Figure 3- 39 Wind Speed

The left-side model shows a **low wind speed** (< 6 mph) that reveals a 90% confidence perimeter for the cigar-shaped plume will remain within the yellow line perimeter a plume (shows a 180^{o} confidence line perimeter). A low wind generally will not have the strength to keep the plume from wandering left or right. A strong wind increases (narrows) the confidence line perimeters, as is shown in the right-side picture in Figure 3-38.

The right-side Model shows a 15-mph wind that keeps the 90% confidence spread on a smaller spread. The Steady State confidence line will recede as the pressure and volume of the release reduce. Advanced plume models will give a time that the plume will recede to a pre-determined set point. This gives the command team a chance to anticipate containment and control concerns.

EPA – CAMEO/ALOHA computer aided management of emergency operations the methods of developing, reading, and understanding plume model specifics. https://www.epa.gov/cameo Another great source for public safety chemical emergency computer aided management is the FEMA ChemResponder program. https://www.youtube.com/watch?v=smpOWW6DwgQ FEMA also provides emergency responders access to advanced plume modeling created by the Interagency Modeling and

Atmospheric Assessment Center (IMAAC)

https://www.fema.gov/emergency-managers/practitioners/hazardous-response-capabilities/imaac

This access is 24-7 and 365-day access to advanced modeling with higher levels of atmospheric, topography, and intelligence on the details of the plume such as the time frame to be expected for a release to go to Steady State and the timing and concentration changes as the plume recedes to the location of the source of release.

FEMA offers a free ChemResponder web-app service that is only available to public safety The web-app platform provides the command team with a system that monitors the situation status and provides an opportunity to upload facility information and access to other technical services that aid in the creation of safe and effective incident action plans and safety plans. See the following link for more details.

https://www.fema.gov/sites/default/files/2020-07/fema_cbrn_chemresponder_fact-sheet.pdf

3.13 Personal Protective Equipment and Ammonia Monitoring.

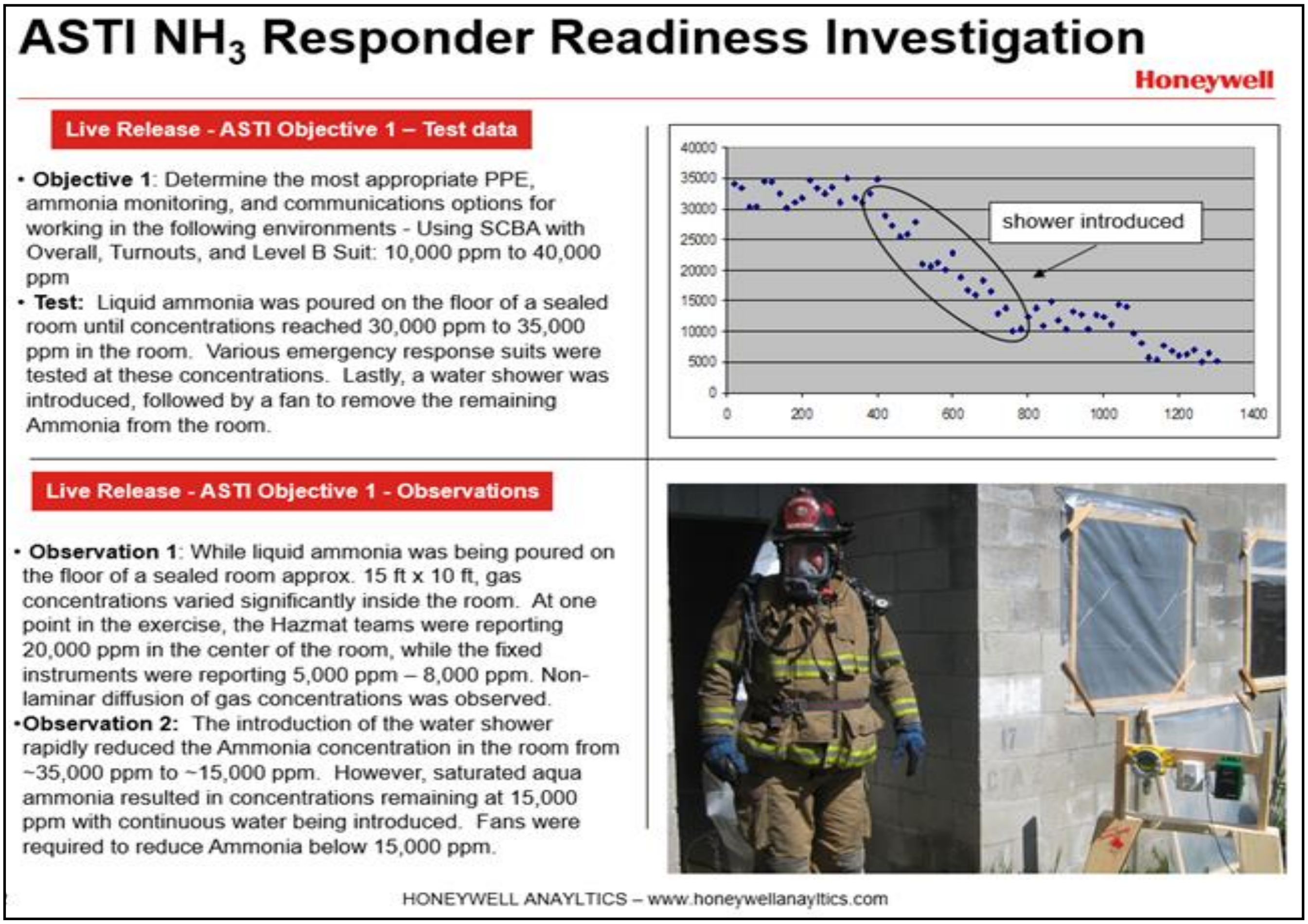


Figure 3-40 Personal Protective Equipment Ammonia Exposure Testing

The test results show that the water shower temporarily reduces the level of ammonia vapor within the room. The downside is that the ammonia vapor becomes alkaline and evaporates aqueous gas that has a higher potential for a level of human (high pH) and environmental impact (nitrates into water).

The safety of emergency responders depends on an accurate assessment of the level of ammonia threat that exists for two locations: 1) A personal ammonia detector located on the entry team leader, and 2) an ammonia detection system that monitors the room or area where the entry team is working. The two points will link to the need for personal protective equipment (PPE), backup support, and the length of time that operators and responders will work in the ammonia-monitored location.
The infrared detector had better serviceability than the catalytic sensors. They stood up well for 20 minutes in a 40,000-ppm environment and did not over-range when returned to zero. The infrared detector was 20 seconds faster than the catalytic bead sensor. The movement of cold ammonia vapor will be repelled when it meets a warmer outer wall of a building. The same is true for ammonia vapor that meets a vehicle, or even a human body. Initially, the vapor rebounds by emitting heat from warmer bodies.

3.14 The Comparison of Using Water or A Fan to Mitigate Ammonia Threats

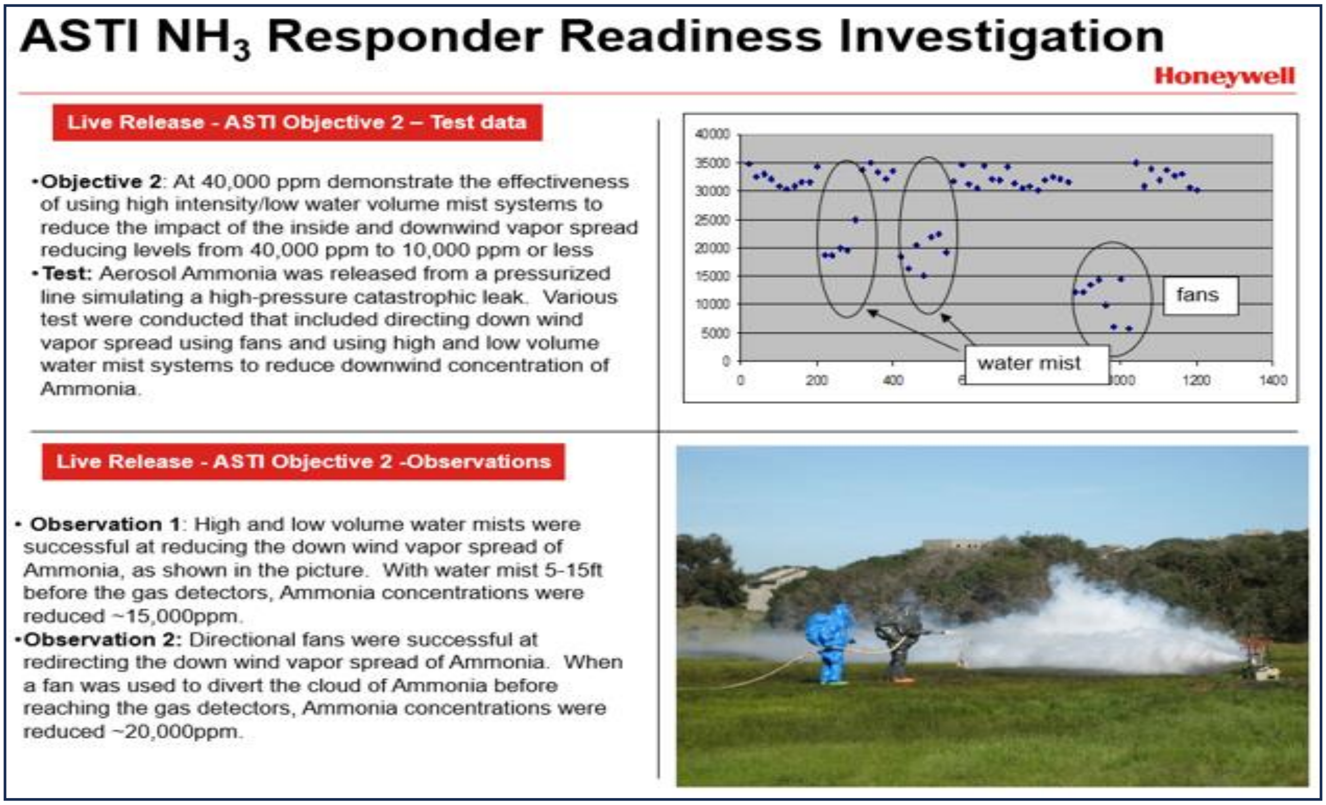


Figure 3-41 Evaluation of the effectiveness of the use of water streams on aerosol/dense gas.

Utilizing water to mitigate aerosol vapor will create alkaline water runoff: The test results show that the two water streams move the same amount of ammonia out of the plume as does one fan. The fan breaks out the same amount of ammonia vapor from the plume and moves the vapor further away from the plume than water. Further, the fan will vent the vapor to the atmosphere while the aqueous ammonia generated with water soaks into the wet ground and evaporates as a corrosive gas, soaks down to the water table, or flow into a body of water that may kill fish and bio-organisms.

Positive Pressure Ventilation for Clearing Ammonia Vapor from Inside a Building: Introducing a clean air plume that covers the entire vent opening will pressurize the room with fresh air that must be vented from a downwind vent of equal size to the entry air flow opening. This process of ventilation is called “Positive Pressure Ventilation” or PPV.

Figure 3-42 Lessons Learned Regarding Shelter-in-Place Within a Structure or an Automobile.

Left Picture: The temperature within the building is 67ºF (19.4ºC). The building has plastic sheeting that is duct taped to the window openings.

Middle Picture: The release lasted for about 2 minutes. The temperature of the wall decreased by 5ºF and there was only 5 to 10 ppm of ammonia entering the building.

Right Side Picture: The ammonia jet stream of aerosol dense vapor cloud was released from a ¾" open orifice at 100 psi from about 20 feet (6.1 meters). The aerosol dense gas cloud played upon the vehicle for about 90 seconds. The level of ammonia that entered the vehicle was under 500 ppm and very survivable. The aerosol was cold enough to crack the windshield. A shield (rag, towel, piece of clothing) over the nose and mouth will help the victim survive.

Future Concern: The ASTI Team has performed three live releases with vehicles exposed to an ammonia release; one within a dense gas cloud of more than 10,000 ppm for three minutes the ammonia level within the pickup was 300 ppm which is very survivable. The second and third release was with direct aerosol jet streams aimed at the driver's seat door. The release was approximately 2 minutes, and the amount of ammonia vapor did not exceed 250 ppm.

The ASTI team will be doing more testing and will be creating a preparatory checklist to be used by the emergency management team when communicating the vehicle shelter-in-place best practice during an ammonia release.

The Minot N. Dakota Train Derailment resulting in over a million pounds of ammonia released during a cold snowy night:

On January 8, 2002, at 1:34 in the morning nine rail cars of ammonia (240,000 gallons) breached when the train crashed off the rails near the city of Minot, North Dakota. The level of ammonia kept people in their homes until about 5:30 in the morning when the sunrise began to lift the cloud of ammonia. Only one death occurred when a man and his wife decided to get into their pickup that was in the garage. They crashed out through the garage door and tried to drive away...they hit a tree because the ammonia cloud made it hard to see. The couple left their vehicle...the wife went towards a house and pounded on the walls, the residents let her into their home, and she survived. Her husband went the other way and eventually fell to the ground and died.

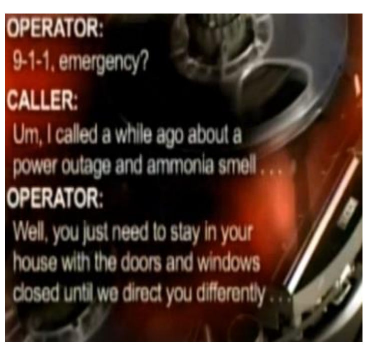


Figure 3-43 Minot, N. Dakota

The 911 operators were the only resource for information because the emergency broadcast system was not accessible…it was covered by a dense ammonia gas cloud.

CHAPTER 4: Maritime and Water-Proximate Events

Introduction: The influence of water-proximate events examined in these situations will address transport, transfer, storage, and/or on-site dispensing of ammonia that become water-proximate top events. Each of the case studies will show the value of plume modeling for emergency managers and responders.

The ASTI team will work with the CRADA team to continue to study the impacts of the releases shown in Chapter 4. We will utilize Bowtie hazard assessments supported by a higher level of scientifically created technical research findings that show how the loss of hazard containment of trigger "Events" that

Future Concerns: The future assessment will also include information that supports a higher level of preparedness to use incidental control standards engaged by trained engineers, operators, and emergency responders to stop and event when it' small. This will require effective detection and ammonia monitoring readiness by maintenance, operations, and emergency first responder readiness to contain and control the loss of hazard containment before the "Event" triggers a "Top Event" (emergency) that create life threatening escape and emergency response forces that foresee the emergency threats and safely use emergency system control and containment methods to control the Top Event before significant threats to life, property, and/or environment.

The next phase of our research will include a deeper look at two catastrophic ammonia events that were not water proximate. The research will include the following events:
Dakar ammonia accident in Senegal. This incident has a very good report prepared by Seshu Dharmavaram and Venkat.Pattabathula about the Dakar event that has been portrayed as being the worst ammonia release in history Dakar and Seshu presented their report to the American Institute of Chemical Engineers (AIChE) in 2023. https://www.aiche.org/sites/default/files/cep/20230747.pdf

Potchefstroom vessel failure in South Africa. In 1973, a major release (estimated at a total of 38 tons) of anhydrous ammonia occurred at a fertilizer plant in Potchefstroom, South Africa. There were 18 fatalities. In this article, the authors offer some comments on the emergency response to the accident, without prejudice to the actions taken at the time, to illustrate how present-day practice, standards, legislation may help to alleviate the effects of similar accidents.

https://lenniegouws.co.za/ammonia-explosion-in-potchefstroom/

must be detected and mitigated with built-in control measures.

The Emergency Event Case Studies are presented to explain the following types of release.

- Ammonia released directly into a body of water.
- Ammonia plume that moves over a body of water.

- Ammonia puff cloud occurring from a sudden system failure due to hydraulic shock or hydrostatic pressure.
- The impact of the application of water on ammonia release.

The Case Studies discussed in Part 4 will provide experiential evidence that will link to Part 5 of this report where the emergency response challenges and gaps in knowledge related to water-proximate releases are summarized.

4.1 Case Study Incident #1: Kwinana Australia (near Perth)

Figure 4-1 Kwinana (near Perth) Western Australia: The incident occurred on Saturday, July 21, 2018, at 10:30 am. It was a cool day, 5ºC or 41ºF with cloud cover and occasional rain.

Figure 4-2 Kwinana Port Site Pictures. See Figure 4-3 to see how ammonia traveled 900 meters across the sea to Wells Park (parking lot).

On July 21, 2018, an incident occurred at CSBP Limited's import facility in Kwinana, Western Australia, that resulted in the accidental release of ammonia vapor.

A thorough investigation identified the causes of the incident, which resulted in the quick connect/disconnect coupler disconnecting from the ship manifold flange, releasing approximately 1,000 kg of ammonia. Thankfully no one was injured, but the incident provided key learnings for CSBP and industry on how to safeguard against similar incidents occurring in the future.

Author: **Naresh Patel** [13]

The release occurred at the end of a hot gas purge of the loading arm that was used to connect the ship to an on-shore pipeline that fed the ship's ammonia delivery to an on-shore storage tank.

Event Summary: While completing the off-loading of liquid ammonia from ship-to-shore storage tanks a valve that was supposed to be open was closed, which set up a condensation dead end in the piping resulting in high velocity reverse-flow of liquid surges against the loading arm articulating joint. The volume of the high-pressure gas collapsing at an 850:1 ratio caused the liquid to fill the low-pressure void left by the absence of gas. The mechanical damage was caused by the sudden stopping of the moving liquid as it came against the loading arm joint. This pressurize-collapse-slam action is repeated until the loading operator shuts down the supply of high-pressure gas.

Event Details: The hot ammonia vapor used to purge the loading arm is supplied from the ship's ammonia compressor 1st stage-discharge—designed at press 5.2 bar (77 psig). temperature 107ºC (224.6ºF) temperature. The discharge vapor is superheated, not saturated. The operator noticed the field reading was 5ºC (41ºF) on the loading arm with a pressure reading of 4.5 bar (65 psig). As per the vapor pressure curve, at this pressure saturation temp is -5 degrees C (28ºF). It means, there was no liquid present due to superheated ammonia.

The delivery line purge process and accidental release based on the description by the tank farm manager:

- The pump process (mechanical pumps or gas pressure increase over the liquid surface of the source tank) stops when the delivery of the cold liquid to the storage tank is completed.
- The primary delivery valve (PDV) at the wharf end (perhaps aboard ship) of the pipe is closed and the smaller shunt valve (SV) that connects around the PDV is opened and set at 1.5 turns open.
- All the main delivery valves from the PDV (including the one at the root station) downstream to the storage tank are open.
- Discharge gas is routed into the liquid delivery line onboard the ship downstream of the ship's main line isolation valve. The condition of the gas is 65 psig and superheated significantly (design is 224°F – may be cooler but still well superheated). The 65-psig saturation temperature is 44°F. The gas flushes the liquid in the delivery arm through the SV and sweeps the liquid downstream to the storage tank.
- Hot gas continues until operations determine that the entire delivery line is void of liquid. Some of the discharge gas condenses inside the main line but continues toward storage tank 2 with the cold liquid inside the pipeline.
- Hot gas injection stops. The pressure in the main line is still approximately 1 psig.
- The main line valve at the root station is closed to isolate the wharf side loading arm back to the ship side isolation valve (that is closed) upstream of the QCDC.

- The short section of the line is purged with nitrogen to make it safe to disconnect the arm and the QCDC.

The deviation of procedure:

- Hot gas is injected into the main line by the ship's refrigeration system.
- The main valve at the root station that is manually opened by hand-jack slips closed before the main line was adequately flushed of liquid. This creates a dead-end from the ship's isolation valve to the root station and the inner walls of the pipe and valves are very cold – approximately -28ºF.
- The main line is dead ended now with a temperature well below the 44° saturation temperature of the hot gas being supplied. As a dead end with a cold internal surface, the pipe all the way to the improperly closed root station valve is now a condenser that is working on the injection gas from the ship.
- The gas that is metered through the SV superheats and begins to condense on the cold walls of the main pipe and valves including the QCDC.
- The pressure downstream of the SV drops significantly as the specific volume of the supplied hot gas because of the collapse of hot gas into liquid. The gas pressure in that section of the main line drops into a deep vacuum that causes a reverse flow from the main line that accelerates with mechanical velocity.
- The slug of liquid slug rushes back from the downstream piping and slams against the QCDC and the PDV (dead end) which caused the loading arm gimbles to fail (QCDC and wharf side gimble joint).
- The liquid occupying the main line between the improperly closed root valve and the PV escapes suddenly – since hot gas was not simultaneously terminated the gas served to propel the liquid release up in the air instead of seeing the liquid drop to the wharf and bay.

Puff Cloud Release: The ship's ammonia delivery was completed, and the loadmaster called for the hot gas purging of the ship's loading arm to begin. This would clear the liquid from the loading arm and downstream pipeline. The objective was to push the liquid past the first pipeline shut-off valve, but that turned out to be closed. Initially, the hot gas procedure was proceeding as normal. It was not recognized that a downstream pipeline valve had been incorrectly closed. The hot gas condensed the trapped liquid creating increased vapor pressure. The vapor pressure met the closed valve and pushed the one-ton slug of anhydrous ammonia liquid back to the ship's manifold. The liquid slammed the loading arm knuckle joint connection to the ship's manifold and broke open releasing a one-ton liquid aerosol and dense gas puff cloud.

The visible cloud slowly dispersed over the wharf where the ammonia ship was moored. The cloud moved downwind over the ocean water. See Figure 4-3 on the next page for a picture of the release location.

Five (5) victims suffered respiratory stress and were transported to the hospital.

One victim was next to the loading arm on the ship, two others next to the loading arm on the jetty, and two were located on ground level 300 meters away. Paramedics on-site assessed all ammonia injury victims, and one was taken to hospital for precautionary assessment. No one had life-threatening. Minor Injuries included eye irritation and respiratory discomfort.

Figure 4-1 Kwinana Western Australia Ammonia

One visitor at Wells Park noticed the vapor cloud approaching. He moved into his car watching the cloud approach land. He smelled the odor of ammonia and rolled up his window as he watched the cloud pass over his vehicle. He mentioned that saw droplets landing on his vehicle windshield, which could have been rainfall and/or ammonia picked up as the plume moved over the seawater.

Naresh Patel mentioned that he has witnessed high-pressure aerosol ammonia releases over seawater. He thought that the aerosol plume could draw the seawater into the plume, but he was also quick to mention that he had not found any scientific evidence of how the mixture of ammonia and seawater would occur.

Effectiveness of Detection and Incidental Control Measures: The compressor was shut down within a few minutes. The vapor pressure was vented, and the event was controlled within about 20 minutes.

Efficacy of ATD (Atmospheric Transport and Dispersion) modeling benefits for emergency managers and responders. We will finish our investigation of the conditions associated with the event and then build a plume model that would indicate how the plume moved. CSBP Limited Dispersion of **Ammonia**. Welles Park is 990 meters/3,248 feet away from the jetty. During a heavy wind event, we can see droplets landing on the seashore structures, moving toward land with the wind. At this distance, it was not possible to differentiate between ammonia and water. The cold aerosol/dense gas ammonia release that was tracked on the surface of the seawater was picked up and condensed with some warmer seawater.

4.2 Case Study #2: Chilean - Magallanes Incident

Ammonia Release Directly into a Body of Water. The impact of releasing ammonia into water relates to the boil-off pressure and boil-off gas developed from the phase change transition from liquid ammonia to an aqueous aerosol, dense gas, and a vapor plume.

Figure 4-2 Diagrams and Pictures Location of Puerto Mejillones

Location, date/time, setting, and weather conditions Chilean port release where ammonia spilled from a ship into the water and an aerosol dense gas vapor cloud formed as the ship's cold (sub-cooled) ammonia liquid hit the water and flashed off as an aerosol dense gas cloud. According to the port captain, Cristian Peña, the accident occurred around 5:20 p.m. on November 25, 2016, within the maritime terminal at Magallanes, Chile.[10]

Initial Loss of Hazard Containment: During an offloading maneuver, a liquid hose line breached. The breach was thought to have occurred from a break in a coupling, although it was still connected to the ship's ammonia storage tank. The liquid ammonia leak continued for 5 minutes until the crew activated the emergency shut-off system. https://www.youtube.com/watch?v=Kl-aaUFOD2g

The massive product leak occurred at 5:20 p.m. at the ENAEX Company maritime terminal during the discharge of liquid ammonia. The product was being unloaded at -33°C from the Liberian-flagged vessel "Sanko Independence".

At 5:20 pm, the vessel's manual coupling system separated from the unloading hose that transported the product from the Sanko Independence vessel to the Enaex Company's terminal. Automatically the vessel's excess flow valves activated, and the product transfer stopped.

The amount of chemical remaining inside the discharge hose spilled into the sea for a period of approximately two minutes, generating a cloud of product because of the fast expansion of ammonia from its liquid phase to its gas phase, accelerating the normal phase transition process of the product due to the thermal impact that affected the product when contacting the surface of the sea. The approximate temperature of the sea was 17.5^{o} Celsius.

The prevailing strong wind in the sector at the time of the accident was northerly. A northly wind at that time of day was most unusual. The prevailing wind normally blows in the direction of the city - East / Southeast). The ammonia cloud did not reach the coastal land because quickly dispersed as the ship headed out to sea.

Boil-off Heat Energy Caused by a Loss of Hazard Containment Triggering Event: When the flexible hose line that joins the discharge terminal was decoupled, the residual ammonia fell to the sea for about 2 minutes. It is estimated that the entire incident occurred in about 5 minutes [11].

Figure 4-3 Diagrams and Pictures Location

Effectiveness of Detection and Incidental Control Measures:

Figure 4-5 shows that the dense gas cloud lies flat on the ocean for about 300 feet (91.5 meters) before it begins to thin out into a vapor that evaporates into the atmosphere.

The Chilean Navy investigated the incident. Their findings revealed three circumstances that reduced the impact of the emergency release.

1. There was no crew on the deck area of the ship. The captain had called for all crew members to shelter within the ship's quarters; this procedure was followed appropriately, and no one was injured.
2. The emergency shut-down valve worked correctly, only producing a spill from the ammonia supply line between the shut-down valve and the loading arm connection.
3. The meteorological conditions, especially the strong wind, and the mixture of the ammonia liquid into the ocean water generated a reaction between ammonia and water, (ammonium ions), to move some of the ammonia to mix with the seawater.

Top Event Energy that Creates Significant Threats to Responders and the Community:

The ammonia plume, in large part, was mitigated by a strong wind as the Ship's Captain moved the ship into the wind and further out to sea to protect his ship's crew and the shoreline community from the escaping ammonia vapor.

The overall response to the release mitigated most all of the ammonia impact to the industrial zone or the community of Mejillones.

Water Proximate Ammonia Release Impact on Transportation, Transfer, Storage, and/or Dispersion of Ammonia.

The following discussion presents **"conjecture-based observations"** from the Desert Tortoise ammonia water proximate release that should be science-validated to improve the lagging indicators" that will be used to formulate improvements for designing more effective preventative barriers and better leading indicators insight for emergency response leadership when they create action plan/safety plan readiness for containing and controlling ammonia releases.

The estimated loss of ammonia liquid was about 425 to 530 gallons (1.6 to 2.0 cubic meters). There are concerns about the impact on the Chilean mussel sector. The Chilean environmental teams will be monitoring the potential impact on the future of the mussel sector. The temperature differential between the liquid ammonia is -33^{o} C and seawater 17.5^{o} C seawater -27.4^{o} F and 63.5^{o} F = 90^{o} F differential which would flash off vapor that would otherwise mix with the seawater as an underwater plume. For this reason, the impact on the mussel sector is likely to be negligible.

Efficacy of ATD (Atmospheric Transport and Dispersion) modeling benefits for emergency managers and responders. For this part of the Report, we decided to analyze the cloud movement dynamics that were revealed in the early evaluation of water-proximate ammonia releases.

4.3 Case Study Incident #3: New Hampton Iowa Submerged Railcar Release into Water

Location, date/time, Setting, and Initial Weather Conditions Sunday, August 29, 2021, six locomotives and eleven Canadian Pacific (CP) rail cars derailed due to the failure of a railway trestle during a major rainstorm and flood that occurred near New Hampton., Iowa. Canadian Pacific reports that one car carrying anhydrous ammonia was derailed into floodwaters and leaked product. The following is a summary developed from news reports and personal interviews with CP Railroad officials and two presentations that Canadian Pacific command team members and tech responders gave in 2022 and 2023 to the ASTI 32-Hour ASTI students in the Monterey Bay area in California.

Thank you to Dale Buckholtz, Ed Dankbar, and Nick Willis from CP Railroad for providing the additional details that properly focused the response, cleanup, and mitigation of this event.

Figure 4-4 Location of New Hampton Train Derailment

The incident happened on Sunday at 4:07 p.m. about three miles southwest of New Hampton. The weather on August 28th a major rainstorm flooded the New Hampton area.

A record level of rainfall resulted in about 22” of rainfall over a 24-hour period of time.

Figure 4-5 Sunday August 29th Weather Report

At about 6 am on August 29th, the rainfall began to diminish. The impact of the 24 hours of heavy rain created a wall of water that drained from the agricultural fields and created a raging wall of water that took out the railroad crossing.

The rainfall and high temperatures continued but the wind levels dropped during the evening and into the night.

Initial Loss of Hazard Containment

The ammonia railcar was at the bottom of the flooded area and was breached by one of the 6 railcars piled on above, which caused a 6” X 3” hole to puncture at the end of one of the ammonia railcars. The railcar emptied the 33,000 gallons of ammonia. Most of the ammonia moved out with the fast-rushing (1900 cubic feet per second) flood water. The ammonia rail car release and diesel fuel from the locomotives prompted an evacuation of area residents. KWWL-TV reported the leak led to evacuations near the derailment site approximately 3 miles southwest of New Hampton. As of Sunday afternoon, the Chickasaw County Emergency Management Agency reported those who had been evacuated were being allowed to return home, and that current weather modeling showed no danger to New Hampton residents.

There never was any significant (health or life-threatening sign) of ammonia odor or environmental impact associated with the response and recovery from the 33,000 gallons of ammonia released underwater. The incident debriefing from CP railroad indicated that the volume of flood water moving fast and aggressively diluted the underwater ammonia plume and the steady high-speed wind (15 mph) diluted the ammonia vapors quickly into the upper atmosphere.

Canadian Pacific RR, along with the New Hampton and Ionia Fire Departments, Chickasaw rescue, ambulance, and the sheriff's office worked very well together to mitigate and recover from the incident.

Summary of the New Hampton Event: https://www.kimt.com/news/iowa/anhydrous-ammonia-and-diesel-fuel-leaked-from-ne-iowa-train-derailment/article_72c8aa17-457e-532f-a2af-47b58e2a8e1b.html

Some families near the derailment site had been evacuated, but a few residents refused to evacuate.

News Header: "CHICKASAW COUNTY, Iowa - Emergency management in Chickasaw County is asking the public to avoid an area where a train derailment took place."

https://starshazmat.com/2022/09/06/september-6-2022-freight-train-derailed-in-hampton-iowa/

The locomotive crew escaped the train without injury. The conductor and engineer from the incident were both taken to Mercy One New Hampton as a precaution and were treated and released. No other injuries have been reported.

https://www.kaaltv.com/archive/nearly-5000-gallons-of-ammonia-removed-from-from-ne-iowa-train-derailment-site/

8/31/21 – Crews continued to work throughout the night to remove 4,900 gallons of aqueous ammonia from a damaged tank car. Aqueous ammonia does not pose a threat to public health. The ammonia water was relocated for hazardous materials disposal. Four remaining tank cars of anhydrous ammonia are intact and staged for their content removal. Iowa DNR and EPA will continue to monitor operations. Should the situation change in the future, local responders will be back on the scene to support operations and provide public updates.

The high winds helped to dissipate the escaping vapor. Pockets of ammonia remained in the soft mud surrounding the release. The vapor reaching the New Hampton community ranged between 2 to 5 PPM. The high volume of on-going fresh water flushed and diluted the ammonia without any significant life safety or environmental damage.

https://www.kaaltv.com/archive/nearly-5000-gallons-of-ammonia-removed-from-from-ne-Iowa-train-derailment-site/

8/30/21 5:30 p.m.- According to the New Hampton Fire Department, crews are making significant progress removing cars. The railcar of concern has been evaluated and is not deemed to be a hazard any longer. https://www.kimt.com/news/iowa/around-5-000-gallons-of-ammonia-removed-from-ne-iowa-train-derailment/article_e7a02a8b-bde8-5956-8555-c867f41d3038.html

Canadian Pacific reports that one car carrying anhydrous ammonia derailed into floodwaters and leaked the product. “Supporting and working closely with local emergency response officials, our priority is protecting public safety and the environment as we continue our coordinated response.,” the railroad said in its statement. “CP sincerely appreciates the efforts of local First Responders for their quick and ongoing response.”

Figure 4-6 The left side picture is the damaged railcar that released the 33,000 gallons of ammonia into the turbulent floodwaters.
The Right picture are the railcars and locomotive that landed on the damaged railcar.
spread of ammonia vapor impact.
Pockets of ammonia entrapped within the mud would occasionally vent from workers and from moving out the railcar debris.

Summary Points about the Emergency response: The following are high point emergency concerns:

1. The flushing of very high volumes of fresh water, high wind, and warm temperatures significantly reduced the impact of losing 33,000 gallons of anhydrous ammonia into the flood waters.
2. Responders discovered pockets of ammonia as they worked in the mud and slush left by the receded flood waters.
3. Continuous hazard and damage assessment was vital to maintaining on-scene safety. All responders had proper PPE, including escape hood respirators should an ammonia pocket open and cause a respiratory threat.
4. The entire contents of the railcar that was punctured were released into the flood waters...there was minimal vapor production and only one tree suffered some defoliation.
5. Water and plume modeling was an ongoing support for judging the vapor and water threats.

4.4 Case Study: California Ammonia Company (CALAMCO), Stockton California

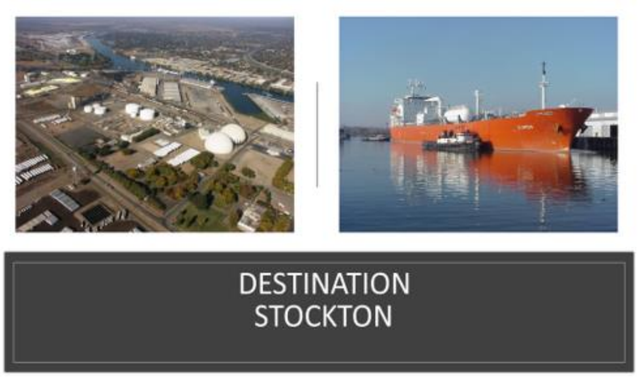


Figure 4-7 CALAMCO Ammonia Delivery to CALAMCO

CALAMCO is a California-based cooperative made up of over 900 grower members from throughout California, as well as fertilizer dealers. https://calamco.com/about.php Since its inception in 1957, Best Fertilizers Co. in 1932, Lowell W. Berry had the vision to form California Ammonia Co. (CALAMCO), a joint venture involving The Best Fertilizers Co. and a group of California farmers.

CALAMCO was incorporated in 1957 for the principal purpose of manufacturing and selling anhydrous ammonia to its own stockholder-patrons in accordance with their preferred patronage rights. They are located in the Port of Stockton in a high-security location.

CALAMCO ammonia capacity is 40 thousand tons, stored in two 20,000-ton atmospheric tanks that sustain at 0.25 psi vapor pressure. They also have 500 tons of ammonia stored in 7 pressurized vessels at 60 to 160 psi. Their throughput of ammonia is 160,000 tons of ammonia per year. The ammonia supply is shipped and delivered from their supplier in Trinidad. The ammonia is off-loaded from the ship into a 14” insulated pipeline that is 2,200 feet in length (50 tons of ammonia when full). The off-loading occurs at 1,500 tons/hour.

Figure 4-8 Left Pressurized bullet tanks (500 tons capacity); Right One of two Low pressure (0.5 psi) low pressure ammonia 20,000 tons of ammonia storage.

Ammonia is delivered predominantly to agricultural customers by truck, rail, and nurse tanks. The ammonia is used for the vegetable, fruit, and nuts supplied by California to the U.S. and globally. The use of ammonia as a fertilizer increases crop output at a pace that has saved a third of the world’s population from starvation.

Figure 4-9 CALAMCO Ammonia Delivery to Customers

CALAMCO has a very good safety record. They have two very capable full-time Safety officers and two trained operators who are equipped to oversee the safety, security, and emergency response readiness 24 hours a day 365 days a year. They have experienced two non-injury releases of ammonia that could have been significant if they hadn't responded with appropriate measures.

The following pictures are not CALAMCO incidents. The CALAMCO team investigates accidents that occur when using ammonia that they supply. Notice how the covered skin reveals undamaged skin (short pants rolled up and sock slid down). The value of full skin protection and goggles when working near NH_3.

The CALAMCO safety team provides support to any ammonia user who is experiencing an emergency

Figure 4-10 Left Trapped liquid blows the liquid line; Right Tank Failure due to Aqueous Mixing with Anhydrous NH_3

or critical safety challenge. They use these insights to train responders with a deep level of understanding of how and why emergency events and accidents occur.

CALAMCO has experienced two significant ammonia releases over the past 50 years. Both had the potential to develop serious impact but neither reached that level of concern because the on-site team and the CALAMCO used the lagging (preventative barriers and system controls) to reduce the impact of the release and then joining with the fire responders to use leading indicators to develop an effective incident action plan and safety plan to contain and control the release.

CALAMCO Release 1: In 2003 a 7,000-gallon release of 20% aqueous ammonia occurred when the tank was over-filled. The vapor space was reduced to the point that hydrostatic pressure built up in the dome of the tank caused a small split at a weld, releasing 7,000 gallons of aqueous ammonia. The left picture is a mapped location showing the location of the aqueous ammonia tank (white circles) as it relates to the downwind community. The right-side picture shows a closer look of where the small tank of aqueous ammonia was contained within a bunded area. The thin red line is a mile mark (1.6 kilometers). The red circle is the location where incoming fire responders stopped because of a strong odor of ammonia. They re-routed and came into the plant from the upwind side.

Figure 4-11: Top pictures show the Aqueous Ammonia Tank location (white circles). The right-side picture is a closer look at the tank location in the Bunded containment area. The bottom-right picture shows the stormwater pump.

The CALAMCO team used a storm water pump to remove the 7,000 gallons of aqueous ammonia in the bunded containment into MC331 transport trailers. The potential contamination of aqueous ammonia was evaluated and deemed safe for agricultural use.

CALAMCO Release 2: In 2016 a valve was closed as they were moving an ammonia supply from a 14" (35.6 centimeters) liquid line. The trapped liquid built-up hydrostatic pressure that blew a gasket on the 14" control valve that was shut off.

Figure 4-12 Circle left picture is Fire Command; middle upper circle is the MC 331 trailer at the loading terminal; circle that links to the right side picture is the 14-inch pipeline valve with a blown blown gasket.

The CALAMCO team coordinated with the fire responders to develop a plan to transfer some of the trapped liquid into MC 331 ammonia trailers. The problem was solved, and the valve was replaced.

Figure 4-13 left Key points on vulnerability and partner relations, right top-rated risk, and threat concerns.

The CALAMCO team certainly doesn't rely on their long and very good history of no serious emergency events as a reason to flatten out safety and emergency response efforts. Instead, they apply extra effort to set high safety standards to sustain (normalize) those standards by continuously engaging training with the emergency services and building-in mitigations and preventative safety barriers that would allow for a "stop them small" approach to any loss of hazard containment. Their inspection and services are also motivated by continuous improvement that is promoted by governmental and insurance audits.

The bottom line is that CALAMCO is very aware of the vulnerability of an ammonia emergency for the community, emergency responders, stockholders, and for their customers as the only bulk storage supplier of ammonia on the West Coast. The CALAMCO team, from top to bottom of the organization, understands the value of NOT deviating from the safety and proper ammonia system "norms" that they set.

4.5 Port Neal Fertilizer Plant Ammonia Nitrate Explosion

https://en.wikipedia.org/wiki/Port_Neal_fertilizer_plant_explosion

At approximately 0606 hours on December 13, 1994, an explosion occurred in the ammonium nitrate plant at the Terra International, Inc., Port Neal Complex. Four persons were killed as a direct result of the explosion, and 18 were injured and required hospitalization. The explosion resulted in the release of approximately 5,700 tons of anhydrous ammonia to the air and secondary containment, approximately 25,000 gallons of nitric acid to the ground and lined chemical ditches and sumps, and liquid ammonium nitrate solution into secondary containment. Off site ammonia releases continued for approximately six days following the explosion. The following video describes the actions that led to the ammonium nitrate explosion: https://www.youtube.com/watch?app=desktop&v=zfdRPmJX_x4

Chemicals released because of the explosion have resulted in contamination of the groundwater under the facility. The U.S. Environmental Protection Agency (EPA) developed a detailed report that explained the cause of the ammonia nitrate explosion. The report bibliography also provides several related information and news coverage details.

https://archive.epa.gov/emergencies/docs/chem/web/pdf/cterra.pdf

The Terra Incident at Port Neal, Iowa occurred on December 13, 1993. A 15,000 metric ton ammonia tank was punctured by a piece of metal shrapnel that resulted from an ammonium nitrate explosion that drained 5,700 tons of ammonia liquid into the bunded area. The temperature was 30^{o}F with light snowfall with a high 22 mph north wind.

The Terra facility was sold to CF Industries and has operated very successfully for the last 30 years.

Figure 4-14 Ammonia Nitrate Explosion Shrapnel Punctures an Ammonia Liquid Tank

Left picture: A 15,000-ton low pressure anhydrous ammonia tank (identified with a white circle) was pierced by a piece of steel shrapnel from the ammonium nitrate explosion. A 15,000 tank on the bottom row of tanks a metal shrapnel.

Middle Picture: A current picture of the ammonia tanks today (white circle shows where the damaged tank was removed. Notice the blue circle location that has an imprint of the original damaged tank.

Right Picture: The bunded area where the second 15,000-ton tank still sits.

The ammonia release caused several challenges for the emergency responders, summarized as follows:

1. 5,700-tons of ammonia leaked from one of the two 15,000 metric ton storage tanks because of damage caused by shrapnel from the ammonium nitrate explosion. The tank was contained in the bunded area where the two. The ground temperatures were very cold, so the initial flash gas was not a significant problem.

2. The primary immediate concern was to isolate the second 150,000 metric ton tank located adjacent to the punctured tank. The second tank was designed to flow automatically to the adjacent tank (that was punctured) to sustain an on-going supply for off-loading for transport. The only way to stop the flow was to shut down the valve on the 14-inch supply line the connected the two tanks. The liquid ammonia had filled the bund, so it was difficult for the hazmat team members to get to the control valve. They used a flat bottom rowboat. The density of the ammonia liquid (5.5 pounds per gallon) is significantly less than water (8.3 pounds per gallon), so the stability of board and the freeboard between the gunnels of the boat and the liquid ammonia was very small. The hazmat team member did get to and closed the valve.
3. An ice cap formed as atmospheric air (20ºF to 30ºF with a 15-mph wind) blew over the subcooled ammonia liquid located in the bunded containment area. ASTI sent two instructors (Jim Ennis and Michael Chambers) to Port Neal to investigate the incident. They found out that the first responders (volunteer firefighters) were instructed by the EPA Incident Commander to put water on the ice cap that covered the bunded ammonia containment. The objective was to melt it and use water to dilute the liquid ammonia. The heat of reaction created an aqueous ammonia dense vapor cloud that traveled downwind, causing significant community impact.
4. The impact of the initial ammonia nitrate explosion caused ammonia vapors and the aqueous flash gas plume to impact the community downwind population for several miles. The sound of the explosion was heard 30 miles away. Windows broke in the community within 6 miles of the plant.

Figure 4-15 Terra Explosion Impact on the community - CF Industries Rebuilt in July 2016.

Left Picture: Six-mile downwind impact area between Homer and Sioux City Iowa.

Right Picture: In 2016 CF Industries invested 1.7 billion dollars to expand and update the system mitigations and standards of operation. The training and readiness of the on-site responders has improved significantly. The ability to sustain the preventative barriers and the ability to read leading indicators for a potential emergency impact has also improved significantly.

4.6 Lithuanian Ammonia Tank Failure

Rupture of a cryogenic ammonia tank March 20th 1989 Jonova Lithuania (USSR)

ICHEME SYWOSIUM SERIES NO. 124: The following report is authored by Bengt Orvar Andersson and is available at the following website location: https://www.icheme.org/media/10446/xi-paper-02.pdf

Note: Bengt Orvar Andersson was the lead instructor at the NORSK HYDRO fertilizer plant training site in Landskrona, Sweden during the late 1980s. The ASTI team worked closely with Bengt doing live ammonia releases in Sweden as well as at the ASTI Headquarters in Watsonville, California ASTI Headquarters. We attained a lot of very good information about anhydrous ammonia while working with Bengt and his team of instructors.

The following is an edited summary of key issues associated with the Jonova Lithuania

The results of the failure of a t0,000-ton unpressurized ammonia tank. The ammonia gas released caught fire and ignited fertilizer store containing 15,000 tons of NPK (N for nitrogen. P for phosphorus. K for potassium fertilizer). The ammonia vapor and fertilizer decomposition products formed a 400 km contamination zone. There were 7 fatalities and 57 injuries.

The accident took place at the Azotas Fertilizer plant, 12 km (7.5 miles) from Jonova, a town of some 40 000 inhabitants. The plant has 5, 000 employees and manufactures fertilizers. The plant was built in 1969 and, apart from the accident, the area made a generally good impression with the visitors. Maintenance, however, seemed to be somewhat neglected.

The ammonia tank surrounded by a retention wall of reinforced concrete with thickness of 400 mm (15.7 inches) and height of 14.l meters (46 feet), was situated quite close to a fertilizer factory, where NPK 11-11-11 was produced. This product was conveyed by rubber belt to two store houses (15,000 tons and 20,000 tons capacity). Adjacent to these was also a storehouse for 20,000 tons of ammonium nitrate. All these stores were nearly full at the time of the accident.

The ammonia tank was supplied with ammonia from an ammonia factory, some 600 m (657 yards) from the tank. The tank was of Japanese design and built by Soviet personnel in 1978. It had a capacity of 10 000 tons unpressurized liquid ammonia (-33º C or -28ºF) and contained 7,000 tons when the accident occurred. It was equipped with everything necessary for safe operation:

- Two ammonia storage cycle piston compressors wfth.th@ capacity of 323 m^3/h, one with electric motor drive and the other one with diesel engine.
- Two safety valves with capacity of 4 200 m3/h each

- Two breathing valves in case of vacuum conditions
- One torch with capacity of 500 kg/h

The control room from which loading of railway tankers was also supervised.

Figure 4-16 Jonova, Lithuania Ammonia Release and Ammonium Nitrate Fire and Explosion.

The tank was single walled and surrounded by perlite insulation, kept in place by an outer steel shell for weather protection. External diameter 30.3 m, height 21.3 m and internal diameter 28.9 m, height 19,9 m. The tank rested on a concrete foundation of pillar design, to which the tank was anchored by 36 straps (1400 x f40 x10 m) fastened to the outside of the cold wall by a welded device and penetrating through the tabletop of the foundation. The straps were fixed in place beneath the "tabletop" by four crossed wings welded to each strap.

Liquid ammonia (-33^{o}C) flows into the tank bottom and is also extracted from the bottom by centrifugal pumps to railway tankers.

The following description of the accident is a summary of the official investigation report, made by the Lithuanian authorities.

On March 20th, one of the compressors in the ammonia plant was in durable repair and the second was stopped at 10.00 a.m. for a short-term repair. The start-up of the ammonia storage piston compressor for drawing off ammonia gas was delayed because of a difficulty with opening the gate valve in the water delivery line for cooling the compressor. The pressure in the tank was 700 mm (27.6 inches) of water. An operator began the operations of stopping the reception of cold ammonia from the plant and of opening the exhaustion of ammonia gas to the torch. The filling of the railway tankers was stopped.

Between 11:00 to 11:15 a.m. the ischemic tank destroyed itself.

Suddenly the tank opened on one side between wall and bottom, ammonia rushed out through the leak. At the same time the whole tank was dislodged from the foundation and smashed with great force through the surrounding wall of reinforced concrete on the side opposite to the leak. It finally landed about 40 meters (131 feet) from the foundation. The bottom of the tank remained on the foundation.

Devastation around the tank was enormous and liquid ammonia around the fertilizer factory and stores was in places 70 cm (27.5 inches) deep. Copious quantities of ammonia evaporated and suddenly the ammonia gas caught fire and the whole area (control room, fertilizer factory, belt conveyor, and loading site) was engulfed in flames. The burning belt conveyor fell into the fertilizer store containing 15,000 tons of NPK 11-11-11 and self-sustaining decomposition was initiated.

The ammonia vapor and the fertilizer decomposition (nitrous fumes) spread up to 35 km forming a contamination none with an area up to 400 km^2. At 5 km the cloud had the height of 100 m: at 10 km up to 400 m: and at 20 km up to 800 m.

After 12 hours all the ammonia had evaporated but the fertilizer continued to burn (decompose) For three days wolving great quantities of nitrous fumes.

To protect the operators and employees of the plant, the Population of Jonova and adjacent regions, the measures were taken as follows:

- Warning and emergency evacuation of employees from the plant.
- Gradual evacuation of community residents from hazardous rare. In total 32,000 people were evacuated.
- Permanent information for the community was distributed.
- Protection of water sources was put into place.
- The rescue work continued for three days, and the official number of fatalities was 7, and 57 injuries at the time of my visit (May 1989).

Clearing up and deconstruction had at that time not yet started, but an ammonia tank identical to the one wrecked in the accident was about to be started up. Operation of this tank and the NPK plant has however been stopped by the Lithuanian authorities.

Causes of the failure according to the official commission of inquiry in USSR:

l) The tank did undergo an overpressure.

2) This overpressure was due to following events:

- Delivery of 14 tons "warm ammonia (+l0°C or 50°F) at the bottom of the tank because of an operating mistake in the ammonia plant.

- This "warm' ammonia accumulated at the bottom of the tank in the form of “lenses” or a layer of warm unstable ammonia. It did not evaporate at once because of the hydrostatic pressure.
- This layer or these lenses tilted over the surface of the liquid
- Then this warm liquid ammonia evaporated to lower its temperature to -33^{o}C (-28^{o}F).
- This sudden evaporation caused the overpressure.

3) All refrigeration compressors were out of operation.

4) ammonia did catch on fire.

The detailed description of the incident by the Ministry in charge of the environment - DPPR / SEI / BARPI occurred in 2007. A very good follow-up to the ICHEME SYWOSIUM SERIES NO. 124 report by Bengt Orvar Andersson Report. The details have been well studied and carried in the report located at: https://www.aria.developpement-durable.gouv.fr/wp-content/files_mf/FD_717_jonova_1989_ang.pdf

There is also an excellent video discussion about the event located at the following link: https://www.youtube.com/watch?v=pUMs6zNH1dk

4.7 Desert Tortoise at the Nevada Test Site: Dry Lake-bed

Sponsored by the Department of Energy and Lawrence Livermore, U.S. Coast Guard, The Fertilizer Institute, and Environment Canada, https://www.osti.gov/biblio/6393901

Two 10,960-gallon (41.5 m^3) capacity highway tanker trucks from California Ammonia Transport were specially modified to permit high discharge rates via a 4" port at the bottom of each tanker. These four-inch lines were connected to a six-inch diameter spill line having a remotely operated spill valve, flow meter, temperature and pressure transducers, and an orifice plate at the end. Although the ammonia at ambient temperature before testing was self-pressurized to several hundred psia, additional gas from a high-pressure gaseous nitrogen tube trailer was used to maintain the tank pressure to continuously force the NH_3 out of the tanker trucks at a constant rate.

The series of plume movement pictures shown on the next page shows how a high-pressure aerosol jet stream of aerosol/dense vapor plume will travel downwind and across the lakebed that has about 8 to 10 inches of water (due to a recent large rainstorm). The table (figure 4-6) located on the next page will depict the key points associated with an ammonia-release plume that is released over water. The table of events will explain how the ammonia plume develops from the start of the release followed by a minute-and-a-half aerosol/dense vapor release that unfolds. An excellent summary of the Desert Tortoise release is available on line at:file:///C:/Users/MSI/Downloads/Evaluation_of_the_Desert_Tortoise_ammonia_field_te.pdf Evaluation of the Desert Tortoise ammonia field tests with the FLUENT CFD model using unsteady RANS by Christopher G. DesAutels and Lloyd L. Schulman - TRC Companies, Inc, Lowell, Massachusetts, USA. lschulman@trcsolutions.com

Figure 4-19 (the Green Box Concerns listed below), relates to cloud movement across water. The four sections begin with a picture that shows the cloud movement during each of the four stages.

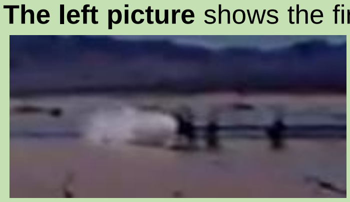
Each of the plume movement stages shows how the cloud disperses. The Green Box Concerns will also indicate further investigation and explanation needed.

The Chemical Research and Development Agreement (CRADA) between the Department of Homeland Security (DHS) Chemical Security Analysis Center has been extended for another year, ending in February of 2025. The CRADA team will work on all Green Box concerns in Figure 4-17 and in Chapter 5 of this document.

The goal is to evaluate the empirical data (based upon professional observation that is NOT backed up with technical research and scientific validation. The results of the CRADA evaluation will lead to a higher level of lagging indicator evidence used for mitigating threats. The evaluation will also lead to a high level of leading indicator awareness so that emergency managers and responders can be prepared to effectively project the risks and threats of the fire/chemical sustained response. ASTI will update this report with a planned date of February 2025.

1. Green Box Concern 4-2: Left picture - release begins - Right picture - 15-second point.

The left picture shows the first seconds of the release. **Right side Picture**: The head of the aerosol sets the water surface pathway that the rest of the aerosol plume will follow.



Why does the head of the release taper upwards as it connects with the rest of the jet stream of aerosol?

The head of the ground-level movement will set the pattern (cold trail) for the rest of the plume for as long as the aerosol release continues to be driven by the tank pressure that feeds the liquid/aerosol jet stream into the open and unimpeded atmospheric flow.

If the aerosol is blocked the aerosol cloud will be temporarily balled up into a puff cloud unless the dense vapor buoyancy catches a good wind to move it back to the water's surface as a meandering dense gas cloud.

Observation: The first 15 to 20 seconds of the release the aerosol droplets will likely drop into the water and expand to a warmer dense gas. At 30 seconds the tapered head plume section transitions from dense aerosol/vapor to dense gas and the plume lengthens accordingly.

2. The left picture is at 15 seconds **The right picture is at the 30-second point.**

Notice that the vapor space under the head of the release has a wider vapor gap detachment from the water. The cold ammonia dense vapor and gas within the plume's head begins to transition to dense gas.

Question 1: How does the cold trail created by the plume impact the lengthening of the plume?

Question 2: Does the polar attraction of ammonia to water offset the impact of the cold trail?

Question 3. Why does the aerosol/dense vapor plume form a sectional connection (like a caterpillar)? One thought is that the high-pressure release that was driven by high-pressure nitrogen caused some "liquid sloshing" as described below.

3. Left picture is at 45 seconds **Right picture is at the 1-minute point.**

Observation and Question: The head of the release transitions from a tapered vapor cloud to a longer and more slender vapor cloud. Notice that the transition between the body of the plume slowly transitions from the body to a long slender dense vapor nose on the end of the cigar-shaped plume head. The long nose lengthens as the release approaches the 1-minute mark. The body of the aerosol cloud begins to shorten as the nose lengthens.

Question 4: Does the change to a long narrow nose on the cigar shaped plume signal that the release is nearing its steady-state phase?

Question 5: How does the long nose head (instead of the blunt tapered head) differ with the heat of reaction and attracting forces of ammonia to water?

Question 6: Do plume modelers consider the transition of the plume tapered head to the long nose version of the plume?

Question 7: Does the longer nose lengthen the dense gas part of the plume and does this phenonemen apply more of the heat energy that resides in the body of the aerosol/dense gas plume body?

4. Picture is at the 1 minute and 30-second point (which is the last available picture)

Observation: The body of the plume is shorter as the long slender head lengthens. The connection and transition between the slender nose head to the plume body is a sudden and very blunt change.

Question 8: How does this version of the plume differ from a similar release on dry ground?

The differences between a dry bed and a wet bed release might reveal more information about the factors that differentiate plume movement on water.

Question 9: Would the cigar-shaped plume be more like a cigar with a large ash that continues to cool as it approaches the very hot nub-end of the cigar?

Question 10: How would a large volume of water (hose stream) at the hot nub end of the cigar impact the overall intensity of and growth of the release?

Question 11: How would blocking the vapor cloud with a big tarp reduce the downwind impact of the plume?

Question 12: Would the water applied to the snub end of the dense vapor release cause the incoming vapor to ball up into a puff cloud, or would the release continue in the same shape as a downwind heavy aqueous vapor? How would the length and toxic impact of the plume change when using water mitigation and a blocking mitigation?

Other points of concern that relate to the comparison of information presented in the 1983 Nevada lake bed Desert Tortois release compare to information deducted from the need to be considered:

- How does the initial release of an aerosol jet stream create blobs of liquid ammonia that drive forward and create additional ground and or water flash gas and atmospheric cooling?
- Recent Desert Tortoise ammonia release events have shown pockets of ammonia that burrow into the ground within the immediate area of the aerosol stream event. It would seem that the same phenomena would occur when the plume moves across surface water…or does the surface water temperature repel and disperse the liquid droplets immediately into the very cold aerosol?
- If the Desert Tortoise release was blocked with a wall for a similar lateral release (or from a topside release hitting a ceiling) disperse differently than a release into the ground or if it vented upwards how would the transition of the puff cloud differ from the plume that releases directly into the ground?
- At what point within the plume does absorption of vapor become impacted with a stronger level of absorption?
- The head of the aerosol stream tends to slant upward as it drives downwind…is this the beginning of the dense gas mixing with water as colder ammonia continues to drive the plume downwind without intensive absorption into the water?
- Why does the front of the plume thin down at about 30 to 45 seconds after it's released across the water?
- Why does the frontal plume thinning increase in length as the plume moves further downwind/downstream?
- Does the plume begin to go to "steady-state" at about the 1-minute time frame?
- The dynamics of an ammonia release vary, based upon the ammonia release pressure, size of the opening, volume of release and interaction with the surrounding atmospheric conditions, terrain, and the temperature differential between the body of water and the ammonia liquid and/or aerosol dense gas plume that would ride along the surface of the body of water.
- It is imperative that the chemical and physical analysis of ammonia absorption with water considers the difference between:
- Ammonia cloud traveling across water – tends to absorb with a consistency between the volume, vapor temperature, and the continuation of the driving forces that move the aerosol e.g. the continued pressure

exerted from the source of the aerosol plume…stop or contain the aerosol source and the vapor cloud becomes less of an absorption impact as the warmer water temperature would drive vapor upward when NOT in a concentrated on-going pressure driven aerosol release.

- Ammonia leaking directly into water will generate an underwater plume that would change the state of the anhydrous ammonia to aqueous ammonia. The molecular polar strength of an aqueous ammonia solution would reduce the movement of ammonia gas to the surface of the water to evaporate.
- **Ammonia** from a submerged pipeline or storage tank would release as a plume that would stay together for the time, distance, and temperature differentials that impact ammonia dilution and evaporation.

Figure 4-17 Desert Tortoise Ammonia Release Analysis for Judging Water Proximate Releases

4.8 Jack Rabbit Dry Bed Releases of Clorine and Ammonia

The video link (above) is an excellent review of the difference between the ammonia and chlorine plume movement. The video also shows how a high volume and high pressure release into the ground can form a puff cloud that eventually grows to a mushroom cloud that travels downwind in accordance with the upper atmospheric wind and weather conditions.

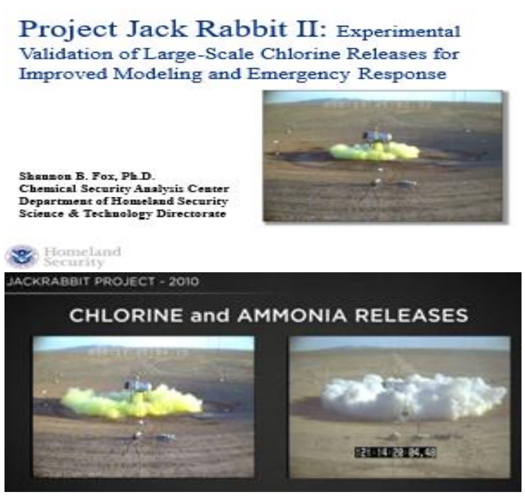


Figure 4-18 Jack Rabbit II Ammonia and Chlorine Release

The early discovery of the type of release will have substantial impact on the emergency response operations e.g., recognizing the need for immediate shelter in place for high-risk movement plans and evacuation staging area alternatives.

Figure 4-20 shows clips from this video link: https://www.youtube.com/watch?v=AQk_vdjq7lw

After watching the video review the following bullet points about chlorine and ammonia releases.

- The lagging indicators should give the emergency responder a good expectation of how the puff cloud of aerosol stream deflects off the ground (similar to the lateral blocking of an aerosol jet stream.
- At his point you should consider the leading indicators about how the jet stream launched upward would differ from the ground deflected puff cloud.
- Chlorine has a Vapor density of 2.5 (over twice as heavy as air). Ammonia is 0.6 vapor density.
- Chlorine IDLH (Immediately Dangerous to Life and Health) is 10 ppm (parts per million). Ammonia IDLH is 300 ppm.
- Chlorine Boiling Point = -29.3ºF or -34.6ºC. Ammonia boiling point is -28ºF.

The following are lagging and leading indicators that emergency responders should always remember:

Lagging Indicator: When liquid or aerosol solutions of ammonia and chlorine mix they produce nitrogen trichloride and hydrogen chloride that form chloramines that are very toxic and potentially explosive.

Leading indicators: The mixture of gaseous forms of ammonia and chlorine are less toxic and rarely explosive concerns than liquid mixtures of ammonia and chlorine.

Rescue of of toxic victims of chloramine poisoning can be considered by first responding firefighters in full bunker gear and self-contained-breathing- apparatus if explosive factors are mitigated.

4-8: Debunking the Myths About Ammonia Releases

Mythe 1: Illinois State Trooper Dies Trys to Rescue a Victim in an Ammonia Dense Gas Cloud

The following is a summary of events that turned a very good Illinois State Patrol training video into a mythical story about a vehicle accident on an country road between a pick-up hauling a 1,000 gallon agricultural nurse tank of anhydrous ammonia. The ASTI team was not convinced that it was real. We met with Sgt. Kelly Hulsey with the Illinois State Police and found out the following:

Photo Description	Informational Summary Associated with the Photo
	The video begins as Sgt. Hulsey is dispatched to the vehicle accident. His patrol car camera covers the actions taken when Sgt. Hulsey attempts the rescue. https://www.youtube.com/watch?v=4q7EotI_5kk
	Sgt. Hulsey approaches the victim. In reality this is the point where the invisible ammonia vapor would be approaching 500 to a 1,000 ppm. He would begin coughing and his eyes would start to itch and alkaline tears would begin to impact his vision.
	Sgt. Hulsey is speaking to the victim trying to arouse him. In reality Sgt. Hulsey would not be able to talk and would have a hard time breathing. His esophageal airway would shut down and he would not be able to breath.

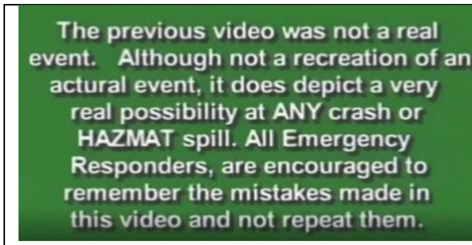
	Sgt. Hulsey met with the ASTI team and did a pod-cast for an ammonia Safety Day in the Chicago area. He explained that someone had copied the video and anonymously uploaded it onto the internet. They left out the ending of the video that Sgt. Used for training purposes.
	An interesting side note associated with the work that the ASTI team and Sgt. Hulsey revealed many law enforcement agencies have placed an air-purifying respirator in the trunk of their car. The purpose for the multi-gas full face respirator was for dealing with terrorism and riot events. Many law enforcement officers are not aware that the respirator is an excellent protection for escaping immediately dangerous to life and health (IDLH) ammonia vapor. Firefighters arrive with self-contained breathing apparatus and full skin protection. They are equipped with 30 to 45 minutes of air to perform rescue.

Figure 4-19: Myth About State Trooper Death While Attempting a Rescue

Myth 2: West Texas Ammonium Nitrate Explosion was Falsely Blamed on Anhydrous Ammonia.

The following is a full account of the West, Texas Fertilizer Grade Ammonium Nitrate Explosion created by the U.S. Chemical Safety Board (CSB).

Accident Occurred On: 04/17/2013 | **Final Report Released On:** 01/28/2016. The video link to the CSB findings: https://www.csb.gov/west-fertilizer-explosion-and-fire-/

Accident Type: Chemical Distribution - Fire and Explosion

Investigation Status: The CSB's investigation was approved by a unanimous board vote at a public meeting in Waco, TX, on January 28, 2016.

	A massive explosion at a fertilizer storage and distribution facility fatally injured twelve volunteer firefighters, two members of the public and caused hundreds of injuries. The West Texas firefighters were gallantly battling a fire in an agricultural supply warehouse. They were very aware of the anhyrous ammonia tank storage located outside of the warehouse. They were protecting the 10,000 gallon high pressure ammonia tanks with water. They had no information about the fact that ammonium Nitrate fertilizer was stored inside the warehouse until a visiting Dallas Fire Captain warned them of the dynamics of the fire.

<table>
<tr><td></td><td>12 Firefighters killed in the West, Texas ammonium nitrate explosion. One of the 12 was a fire captain from Dallas Texas who was performing a local area Emerngency Medical Technician course. He responded to the scene and recognized that the flame dynamics indicated a potential ammonium nitrate explossion.</td></tr>
<tr><td>
</td><td>The West Incident Commander (I.C.) was concerned about the high pressure ammonia tanks and wasn't aware of the hazards of ammonium nitrate. The Dallas Fire Captain convinced the West I.C. to abandon the fire attack and to evacuate the area for a minimum of 1,000 feet. The evacuation had begun when the ammonium nitrate suddenly exploded with a shock waveequal to 15 to 20 thousand pounds of TNT, similar to a 2.1 magnitude earthquake.</td></tr>
<tr><td>
</td><td>The news coverage on the West, Texas incident immediatelly went global. Many major news networks searched for technical advise about what caused the explosion. Astro Physist Michio Kaku explained that Ammonia nitrate is set off in two ways: "Ammonia nitrate added with fuel oil can set off a tremendous fertilizer explosion and here we think there was anhydrous ammonia (in gas form), which can be set off with water"

https://www.cbsnews.com/news/west-texas-explosion-explaining-the-physics-behind-blast/</td></tr>
<tr><td></td><td>The Chemical Safety Board investigation revealed the facts about the West, Texas ammonium nitrate explosion. It all began with the fire spreading throught the wood frame storage building. The Ash and charcoal debris from the wood structure and wooden storage bin seperation walls covered the ammonium nitrate which caused pockets of nitrate gases to trigger a highly flammable oxidizer supported fire that eventually generated enough heat to explode the 40 tons of ammonium nitrate.</td></tr>
<tr><td colspan="2">  

None of the high pressure ammonia bullet tanks contributed to the West, Texas explosion. Flames impinged on the dne of several ammonia tanks and on the many 1,000 gallon nurse tanks (circled in white) used for delivering anhydrous ammonia for field ammonia fertilizer injection survived with little or no damage.</td></tr>
</table>

	**Local investigators, the State Fire Marshal, and Federal Agencies (CSB and ATF) spent over 20,000 hours of investigation** and delivered the final report. The report revealed that anhydrous ammonia had no impact on the West Texas explosion.

Figure 4-20: Myth About Ammonia Explosion at West Texas

Anhydrous ammonia storage had an EPA required Risk Management Plan (RMP) that the West Texas Fire Department was aware of…they new about the stored ammonia and were attempting to cool exposed ammonia tanks. The storage of ammonium nitrate does no require a RMP plan. The RMP requirements would have given the local emergency responders and regulators a better level of understanding about the threats of Ammonium Nitrate. The lack of understanding about the stored ammonium nitrate could have contributed to the lack of knowledge about the existence of the ammonium nitrate by the West, Texas command team.

https://www.claimsjournal.com/news/southcentral/2014/08/11/253079.htm

4-9:Facts about Anhydrous Ammonia Used for Industrial Refrigeration.

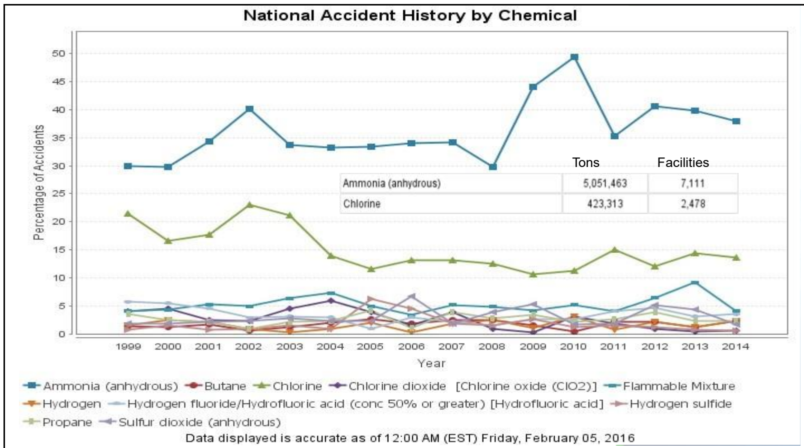
Ammonia has an odor that instinctually generates fear. The smell triggers the brain to react with a sense of awareness that danger lurks nearby. The odor of urine is a clear signal of the presence of ammonia because the brain is stimulated to release the ammonia that enters the blood stream and settles in the liver for urination, sweat, and/or feces.

The same warning doesn't exist for other types of refrigeration, such as freon or flammable hydrocarbon refrigerants. The victims will succumb to the non-threatening odor (or lack of odor such as carbon monoxide that is one of the biggest silent killers of humans) of chemicals that smell like almonds or other sweet-smelling odors...because they aren't aware of the impact.

John S. Bresland was appointed by George W. Bush as chairman and chief executive officer of the U.S. Chemical Safety Board (CSB) in March of 2008. One of his many initiatives involved an analysis of emergency events involving the industrial refrigeration use of anhydrous ammonia that resulted in injury or death. His concern was that there was a high number of incidents reported by OSHA yet none that warranted a full CSB investigation. He wanted the CSB to examine the potential for catastrophic events that could occur in the communities hosting ammonia refrigerant.

The following is a summary of his findings, followed by information about the amount of ammonia used in the U.S. by EPA. Kent Anderson, President Emeritus of the International Institute of Ammonia

Refrigeration (IIAR) and past chair of the Ammonia Safety and Training Institute did a thorough analysis of the CSB and EPA data that evened the playing field by revealing the number of events as compared to the number of facilities and amount of ammonia uses when compared to the other toxic inhalation liquified gases that were analyzed by EPA and CSB.



EPA data reveals anhydrous ammonia as the most popularly used toxic inhalation liquified gas (5,051,463 tons) and 7,111 facilities as compared to chlorine about 423,313 tons at 2,478 facilities.

The other chemicals listed are butane, hydrofluoric acid, hydrogen sulfide, and sulfur dioxide.

Comparable Risk

Chemical Name	AEGL – 10 Min. Exposure	Flammability	Special Hazards
Ammonia	AEGL 1 = 30 PPM AEGL 2 = 220 PPM AEGL 3 = 2,700 PPM	Flammable Gases – Category 2 Flammable Range: 15% to 28% Ignition Temperature 1204 F	Acute toxicity Category 4* Corrosive skin irritation beginning at 10,000 ppm Aquatic hazard – Category 1 May cause frost bite
Chlorine	AEGL 1 = 0.50 PPM AEGL 2 = 2.8 PPM AEGL 3 = 50 PPM	Oxidizing gas Category 1 May cause or intensify fire	Acute toxicity Category 2 Aquatic hazard Category 1 May cause frost bite
Sulfur Dioxide	AEGL 1 = 0.20 PPM AEGL 2 = 0.75 PPM AEGL 3 = 30 PPM	Non-applicable	Acute Toxicity Category 3 Skin corrosion/irritation Category 1
Methyl Chloride	AEGL 1 = NR (insufficient data) AEGL 2 = 1,100 PPM AEGL 3 = 2,700 PPM	Flammable gas – Category 1 Flammable range: 7.6% to 19% Extremely flammable gas Explosive mixture with air	Colorless and extremely flammable gas with a mildly sweet odor Acute Toxicity Category 4** Carcinogenicity Category 2 Target organ toxicity Category 2

*SDS Category 1 is the highest level of concern and 4 is the lowest

** Methylene Chloride in paint stripper (smells like paint thinner) killed 13 in 2012.

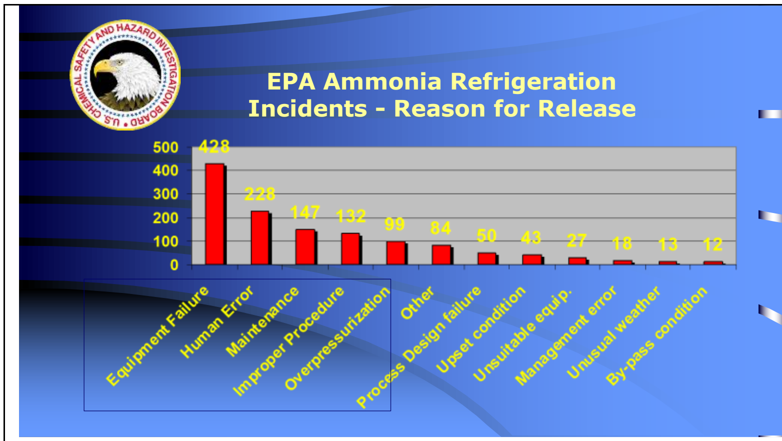
AEGL: Ammonia (NH_3) is Less threatening than Chlorine, Sulfur Dioxide, and Methyl Chloride.

Flammability: NH_3 is a low order flammable gas; Chlorine is an oxidizer that intensifies the fire threat. **Sulfur Dioxide** has no fire threat, and **Methyl Chloride** has the highest flammability threat

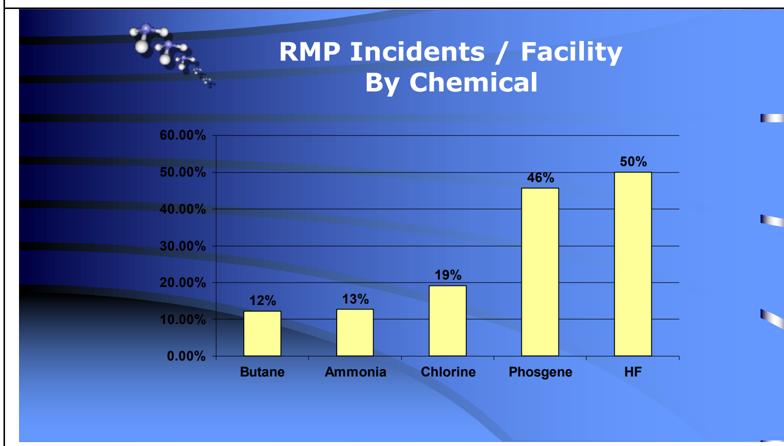
Special Hazards: NH_3 (alkaline) and chlorine (acidic) when mixed with water. Corrosive and cold on the skin at 10,000 ppm.

Industrial Refrigeration is vital to the health and safety of food and other perishables such as medical supplies. Ammonia is a natural refrigerant and is effective and efficient, requiring less energy to cool large volumes of food and other perishables.

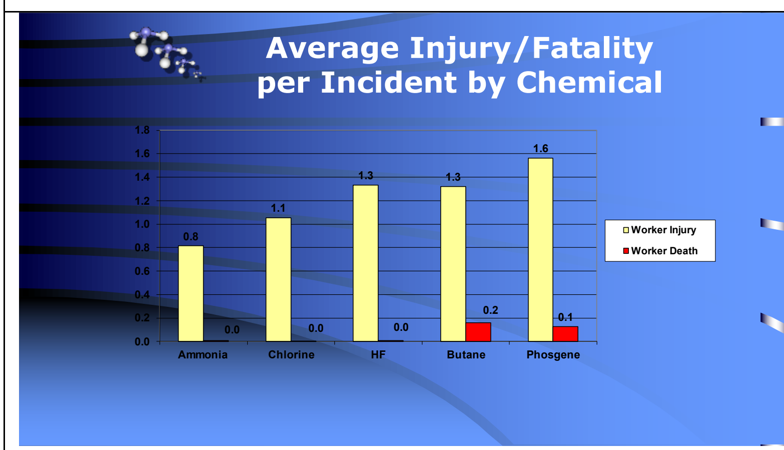
The ammonia system cycles ammonia gas carrying heat from the evaporator to compressors the low pressure gas becomes high pressure that moves to roof top condensers where it is releases heat as the dense hot gas condenses liquid that moves to receiver tanks that supplies the liquid to a metering device into an evaporator cooler unit where the liquid evaporates as it absorbs warehouse warm



air and discharges the gas to the compressors where the refrigeration cycle begins again (removing heat from the warehouse and releasing it at the rooftop condenser).

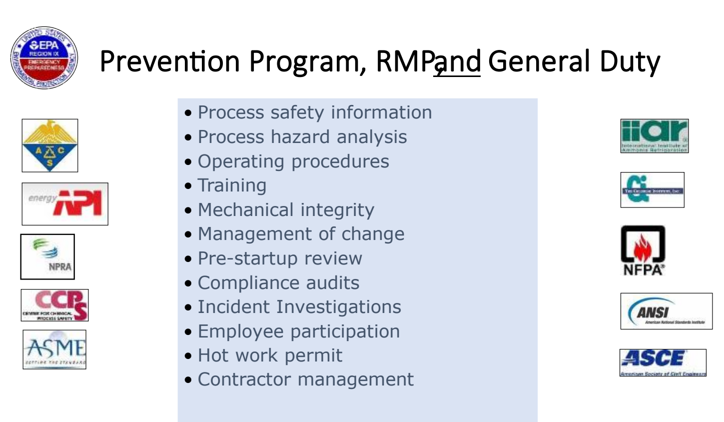


Ammonia refrigeration systems create a continuous cycle of high and low pressure and phase changes from liquid to gas. A potential catastrophic system failure is a possibility but is very rare (as statics show).



The refrigeration industry is much safer than most people recognize.

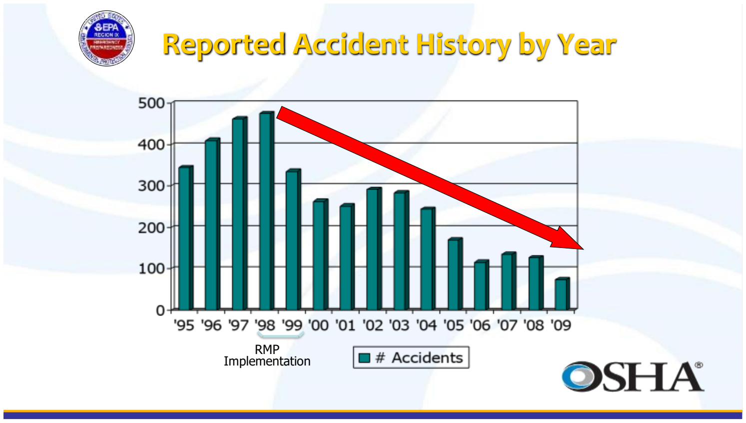
The industry, government, and public safety work as a" Tripod" team to prevent, mitigate, and prepare for any loss of hazard containment.



The emphasis on community life and environmental safety centers around the U.S. Environmental Protection Agency. The EPA risk management plans focus on a federal, state, and local framework for preventing or stopping emergency events when they are small.

The Occupational Safety and Health Agency is focused on worker and process safety.

The 10 year steadily decreaing level of accidents is proof of the value of Safety and Emergency Response Readiness!



The reason is that ammonia industrial standards for worker safety, process controls, and emergency readiness are working well!

Our goal is to prevent emergency events or stop them small!

To find out more see:

IIAR: https://www.iiar.org/ RETA: https://reta.com/ ASTI: https://ammonia-safety.com/

GCCA: https://www.gcca.org/ Emergency Response and Right to Know: https://www.epa.gov/epcra

Process safety: https://www.osha.gov/process-safety-management

October 31, 2022 the EPA clarifies the need for an Emergency Response Plan:

https://www.epa.gov/rmp/who-must-develop-emergency-response-program

29 CFR 1910.38 Emergency action plans

https://www.osha.gov/sites/default/files/publications/osha3122.pdf

1. Procedural, Program, and/or Equipment Requirements Identify possible emergency scenarios based on the nature of the workplace and its surroundings.
2. Prepare a written **emergency action plan. At a minimum, the plan must include:**
3. The fire and emergency reporting procedures;
4. Procedures for emergency evacuation, including the type of evacuation and exit routes;
5. **Procedures for those who remain to operate critical operations prior to evacuation;**
6. Procedures to account for employees after evacuation;
7. **Procedures for employees performing rescue and medical duties; and** Names of those to contact for further information or an explanation about the plan.

Summary Conclusion Regarding the "Prevent them all or stop them small strategy" that ammonia production and use require the collective support of the coalition that exist between industry, government and public safety. The ASTI mission is to make ammonia the safest managed hazmat in the world. Why? Because ammonia is a natural chemical that human life depends upon for food supply, cold storage, and water quality control. Ammonia is the most effective and efficient transporter of hydrogen (as a carbon free fuel source) that can now be substituted for chemicals that create carbon and higher levels of chemical threat than ammonia.

Figure 4-21: Facts About Improving Safety and the reduction of Injury and Deaths

CHAPTER 5: Gaps Requiring Further Study.

General Topic Concerns from this Report that require more scientific analysis

Please include a review of the Green Box Concerns located on page 58, 59, and 79 to 81.

- The boil-off energy from cold ammonia entering warmer water impact on a plume model.
- Most catastrophic ammonia events occur from the impact of explosions from neighboring locations e.g., ammonium nitrate fertilizer plants (Port Neal, West Texas, Lithuania) or from Hydraulic shock damage due to high-impact crashes of MC331 ammonia trailer accidents

Green Box Concern #3-1: There are inconsistencies with the current use of ammonia advisory information mainly because the characteristics of anhydrous and aqueous ammonia are deemed similar...yet evidence shows that high concentrations of aqueous ammonia create a higher threat level than for anhydrous, except for the fact that a high volume of ammonia liquid is transported as high pressure.

We suggest that the following topics be investigated and addressed for the long-term needs of those who manufacture, use, and store/dispense ammonia.

- Explain the difference between the chemical and physical characteristics of anhydrous ammonia and industrial commercial grade aqueous ammonia.
- Reconsider the chemical reactive forces between anhydrous ammonia as it enters or spreads across a body of water. Develop a clear understanding of the energy created when ammonia transitions from a cold (stable) liquid to a boil-off gas. Explain how the aqueous ammonia vapor impacts the plume model differently than for anhydrous ammonia released in dry environments.
- Develop an advisory for judging the alkaline, toxic, and respiratory injury impact of aqueous ammonia at all environmentally available levels of pH above 7.
- Develop an advisory about the flammability potential for an outside ammonia puff cloud (fast spreading dense gas cloud)

Green Box Concern #3-2: Create a higher level of command team, emergency management, and community evacuation and SIP communications for escape to rally points, and SIP locations. The first responder command team must integrate with the industrial team to ensure that the facility personnel accountability is correct and completely accomplished. The local emergency manager coordinates with the emergency broadcast system and the 9-1-1 communications team to ensure that critical information emergency broadcast system within the community. This is why the local Emergency Manager is a critical and immediate contact for initiating the Incident Commander's advisory for SIP or escaping the Isolation Zone and a Protective Action Zone when conditions are safe to do so.

Conclusion: More work is needed to secure a command team CONOPS for effective evacuation and SIP for chemical emergency response rather than to rely on the traditional fire evacuation protocol.

Green Box Concern #3-4: A detailed evaluation of puff cloud fire threat and toxic gas spread characteristics (timing and spread plume dynamics) and methods of managing vapor pressure prior to recovery actions, up righting damaged tank vehicles, pump down transfer of liquid from the damaged tank to a recovery tank. The earlier recommendation for addressing the evacuation, movement to safe refuge, and shelter-in-place dynamics is further validated by this puff cloud analysis.

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Green Box Concern 3-5: The threat levels of aqueous ammonia vapor dispersion threat require more technical assessment. The toxic exposure levels e.g., the comparison of plume movement, reactivity with skin, eye, and respiratory tissue, and the threats to the environment (water table, surface water, and atmosphere) needs to be compared to anhydrous. Tripod (industry, government, and public safety) knowledge that is needed to judge how to select the least threatening comparisons of use of anhydrous and/or aqueous solutions of ammonia

Green Box Concern #3-6: The early use of pre-planned fixed facility and transportation plume models to support emergency responders and emergency planners' ability to address the emergency events during the first 30 minutes, when life threat is the highest concern.

The most urgent plume modeling improvement needed involves water proximate ammonia releases. The chemical and physical characteristics are not given enough value within the current water proximate plume models.

Green Box Concern 3-7: The purposeful use of water to attain specific tactical needs such as a temporary clearing of a dense gas, or a water curtain to absorb the odor of ammonia must be weighed against the pitfalls of adding water. It's critical to analyze the amount of aqueous vapor production that will result from the vaporization of aqueous ammonia. The concern for using water will expand exponentially when water is placed on liquid aerosol and even higher threat when water is applied to liquid ammonia.

We recommend that high powered fans be considered as a better (more effective and efficient) way to divert, diffuse, and/or dilute the ammonia vapor. The fans are also very helpful to support the safe rescue of the rescue team and victims caught in a vapor cloud.

Green Box Concern #4-3: The dynamics of an ammonia release vary, based upon the ammonia release pressure, size of the opening, volume of release and interaction with the surrounding atmospheric conditions, terrain, and the temperature differential between the body of water and the ammonia liquid and/or aerosol dense gas plume that would ride along the surface of the body of water.

It is imperative that the chemical and physical analysis of ammonia absorption and flash gas production from solutions mixing within water need further technical support from a team of ammonia experienced technicians and educators who understand chemistry, physics, chemical vapor, and gas dispersion, on tech-level emergency responders. The team of professionals need to analyze the following three scenarios:

Ammonia cloud traveling across water – the volume of ammonia liquid, aerosol and vapor impacts (absorption and flash gas escape) as it relates to the water temperature, and the continuation of the driving forces that move the aerosol e.g. the continued pressure exerted from the source of the aerosol plume…stop or contain the aerosol source and the vapor cloud becomes less of an absorption impact as the warmer water temperature would drive vapor upward when NOT in a concentrated on-going pressure driven aerosol release.

Ammonia leaking directly into water will generate an underwater plume that would change the state of the anhydrous ammonia to aqueous ammonia. The molecular polar strength of an aqueous ammonia solution would reduce the movement of ammonia gas to the surface of the water to evaporate.

Ammonia released from a submerged pipeline or storage tank – how the liquid and/or aerosol of ammonia released underwater would form a a plume that would stay together for the time, distance, and temperature differentials that the water would impact on ammonia dilution and evaporation.

Green Box Concern #4-4: More technical evaluation of high impact lagging and leading indicators is recommended. The results would improve the depth and technical data needed to create better lagging and leading indicator use by planners, safety managers, and emergency responders.

Product Temperature: A variance of ammonia liquid temperature when delivering ammonia liquid into a tank that already has ammonia must be equalized as per the SOP.

Off-Load Rate: Ambient temperature and/or other sources of heat or volume of liquid adds risks and threats that require early detection and readily available mitigation.

Hydrostatic Over-Pressure: Trapped liquid between two valves that are shut down can build at a rate of 150 psi per minute. The system for off-loading into a pipeline that delivers 1,500 tons per hour is a top-level threat.

Green Box Concern #4-6 and 4-7: There is a high need for a hazard assessment of the contributing factors that cause high impact situations like ammonium nitrate explosions that could damage ammonia tank storage e.g., Terra and West Texas explosions. The same concern exists for a mixture of ammonia and chlorine liquified gases have on the overall community, environmental and property loss potential. The initial hazard analysis of high impact challenges of initiating and sustaining factors that come from contributing release factors e.g., domino – impact of an explosion causing damage to ammonia storage and/or a mixed release of highly hazard chemicals should be evaluated and published for emergency planners to use when planning for new or expanding chemical users.

The concerns extend to the fact that emergency **first responders** are not in sync with adequate standards of operation for the first 30 minutes of an emergency event (before trained and equipped technician trained command and response teams arrive on the scene. First Responders need more knowledge and access to proper personal protective equipment to support the immediate life threats and opportunities to support a joint response with the facility responders and/or operators to engage system controls that would reduce the immediate and growing live threats associated with the loss of ammonia containment.

Green Box Concern #5-2: The use of debriefing sessions and feedback from experienced emergency responders and ammonia system operators is essential for accurate and properly targeted need for information that reveals the unknown or miss-understood factors associated with ammonia releases that can help improve future need for prevention, mitigation, and preparation for ammonia emergencies.

The following is a short list of incidents that should be thoroughly investigated.

1. **All incidents** within this report that call out Green Box Concerns need further assessment to ensure that we have proper levels of clarity and reliability in the recommendations that spin off the debriefing information.
2. **The Beach Park investigation** of the factors that led to the rescue of the victim trapped in her car and the status of the man down and his wife as he attempted to get into his car to drive out of the ammonia vapor to go to work...his wife was seriously injured as she helped him get up and back into the home. https://www.cbsnews.com/chicago/news/ammonia-spill-beach-park/
3. **Full review of three Tampa Pipeline releases across water** - Hundreds of Riverview residents were forced to evacuate their homes in 2008 after a 16-year-old boy drilled into an anhydrous ammonia pipe, lured by an urban legend that it contained money. Three years ago, some railcars carrying anhydrous ammonia derailed at the Port of Tampa, but no ammonia leaked. One worker was injured jumping off a moving railcar.

   Gary Albarelli, director of information programs at the Florida Industrial and Phosphate Research Institute, cited a key distinction between what happens at central Florida's fertilizer plants and at the facility that exploded in Texas. https://www.tampabay.com/news/texas-explosion-puts-tampa-bay-companies-using-anhydrous-ammonia-on/2115983/

Continued on the next page.

4. **Port Neal -** Terra (CF Industries) release and application of water in a containment area full of ammonia liquid from damage from one of Two 15,000-ton refrigerated ammonia storage tanks were ruptured, releasing liquid ammonia and ammonia vapors which forced the evacuation of 1,700 residents from the surrounding area.

   https://en.wikipedia.org/wiki/Port_Neal_fertilizer_plant_explosion

5. **Tampa Electric Company -** Tampa Electric Company ammonia release in Florida occurred when the Selective Catalytic Reduction (SCR) system vented gas from the overpressure of a pressure relief valve (PRV) opened during a very hot day with power production at peak demand. The vented gas was piped into water in the vapor absorption sump (water tank used to vent high pressure gas into water). The alert system failed, and the venting of ammonia continued until the vapor recovery tank over-pressured and released aqueous ammonia vapor that traveled about 500 yards to a guard gate station. Three guards were hospitalized, one had serious long term respiratory damage.

   This release needs to be closely and scientifically analyzed to determine the timing and impact of aqueous ammonia vapor traveling downwind.

   SCR description: https://en.wikipedia.org/wiki/Selective_catalytic_reduction

Generally Realized Critical Tasks and Methods of Response Mitigation Concerns for further investigation and reporting:

1. The comparison of using high pressure air movement from portable fans or fire streams used by the fire service to disperse/dilute or divert (turn an aerosol dense gas jet stream) ammonia vapor.
2. Ability to use high powered high air movement fans (also used to propel flat-bottom boats in the everglades) to disperse/dilute or divert vapor so that it breaks up and moves to atmosphere before creating a need for an isolation zone or protective action zone in downwind communities.
3. Consideration of the Liquid-Dat-R to reduce the pressure and a potential aerosol puff cloud by safely venting system pressure at the first indication of the need for a relief valve release.
4. More research on the efficacy of using water curtains to contain ammonia life safety and environmental safety. Consider the purposeful use of ammonia on the long nose of the dense gas cloud rather than on the beginning of the high volume and/or jet stream of an ammonia release.
5. More evaluation of the best location on the nose of the moving ammonia plume to divert (block) the moving aerosol jet stream to ball it upward rather than allow the plume to track downwind/downstream to higher levels of public safety impact.
6. Comparative analysis between the hazards, risks, and threats, of anhydrous ammonia as compared to high concentration (over 20%), aqueous ammonia.
7. More analysis on the storage and use of ammonia as an energy source that is cracked and reformed to hydrogen fuel.

APPENDIX A - CHAPTER 1: Wolter Skluwer Bowtie and AIChE Leading/Lagging Indicators

https://www.wolterskluwer.com/en/solutions/enablon/bowtie/expert-insights/barrier-based-risk-management-knowledge-base/the-bowtie-method#Hazard

A 'bowtie' is a diagram that visualizes the risk you are dealing with in just one, easy-to-understand picture. The diagram is shaped like a bow-tie, creating a clear differentiation between proactive and reactive risk management. The power of a Bow Tie diagram is that it gives you an overview of multiple plausible scenarios, in a single picture. In short, it provides a simple, visual explanation of a risk that would be much more difficult to explain otherwise.

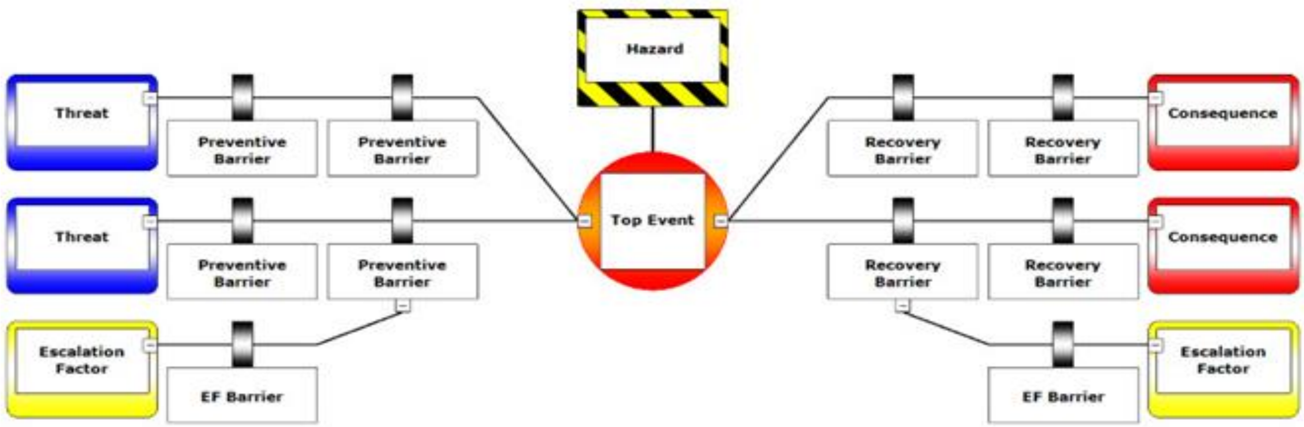


Figure 0-1 Bowtie

Contents

1. Hazard
2. Top event
3. Threats
4. Consequences
5. The picture so far
6. Barriers: controlling unwanted scenarios
7. Control and Recovery Barriers
8. Escalation factors & Escalation factor barrier

Hazard

The start of any bowtie is the 'hazard'. A hazard is something in, around, or part of the organization which has the potential to cause damage. Working with hazardous substances, driving a car, or storing sensitive data are for instance hazardous aspects of an organization while reading this article on your computer is not. The idea of a hazard is to find the things that are part of your organization and could have a negative impact if control over that aspect is lost. They should be formulated as normal aspects of the organization. The rest of the bowtie is devoted to how we keep that normal but hazardous aspect from turning into something unwanted. The first step is always the hardest and this is also the case here. Normally, starting with for instance a HAZID is a good way to get a long list of all possible hazards. Bowties are then done only for those hazards with a high potential to cause extensive harm. Normally, 5 to 10 hazards are a good starting point.

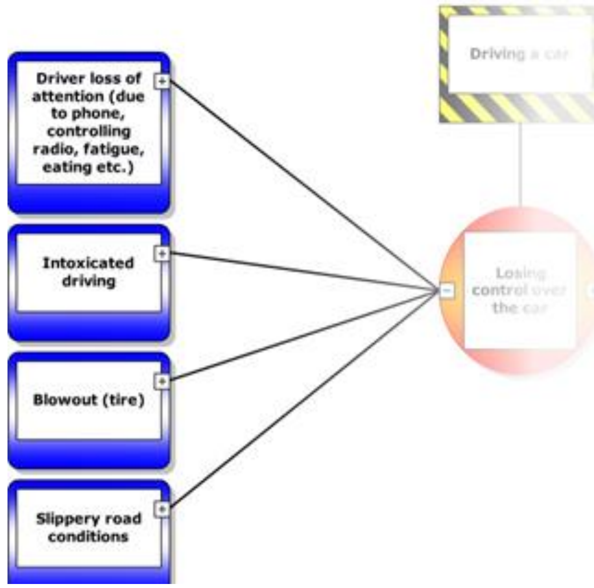


Figure 0-2 Hazards

Top event

Once the hazard is chosen, the next step is to define the 'top event. This is the moment when control is lost over the hazard. There is no damage or negative impact yet, but it is imminent. This means that the top event is chosen just before events start causing actual damage. The top event is a choice though, what is the exact moment that control is lost? This is to a large extent a subjective and pragmatic choice. Often, the top event is reformulated after the rest of the bowtie is finished. Don't worry too much at the beginning about formulation. You can start with a generic 'loss of control' and revisit it a couple of times during the bowtie process to sharpen the formulation.

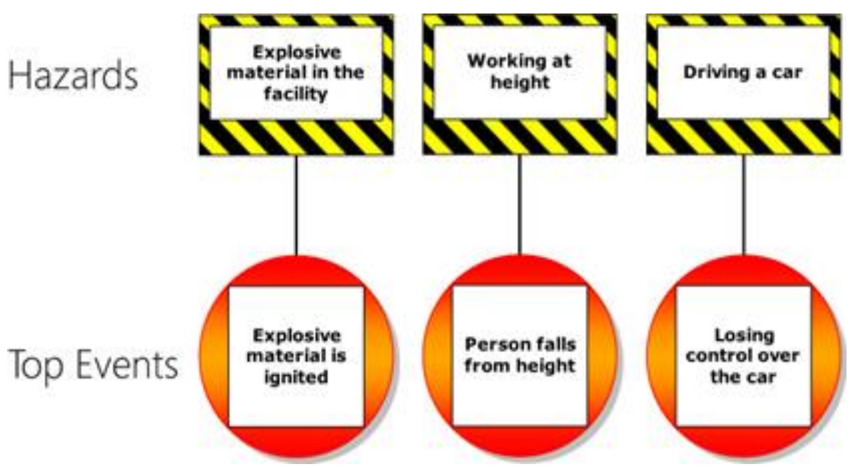


Figure 0-3 Top Event

Threats

'Threats' are whatever will cause your top event. There can be multiple threats. Try to avoid generic formulations like 'human error', 'equipment failure', or 'weather conditions. What does a person actually do to cause the top event? Which piece of equipment? What kind of weather or what does the weather impact? You can be too specific as well, but generally, people tend to be too generic.

Consequences

Consequences' are a result of the top event. There can be more than one consequence for every top event. As with the threats, people tend to focus on generic categories instead of describing specific events. Try not to focus on injury/ fatality, asset damage, environmental damage, reputation damage, or financial damage. Those are broader categories of damage rather than specific consequence event descriptions. Try to describe events like 'car roll over', 'oil spill into the sea', or 'toxic cloud forms'. Besides containing more specific information, you're also helping yourself to think more specifically when coming up with barriers. Think how you want to prevent 'environmental damage' versus 'oil spill into the sea'. The second is an actual scenario which makes it much easier to come up with specific barriers.

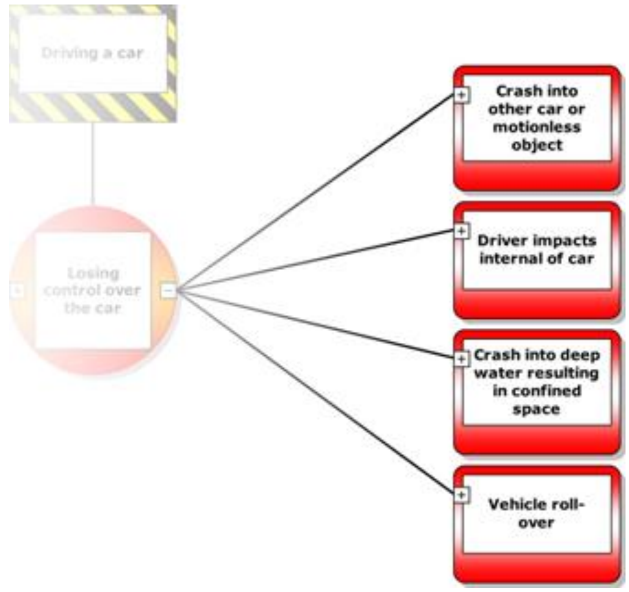


Figure 0-4 Consequences

The picture so far

At this stage we have a clear understanding of the risk and what needs to be controlled. The hazard, top event, threats, and consequences give us an overview of everything we don't want around a certain hazard. Every line through the bowtie represents a different potential incident. Besides containing incident scenarios that might already have occurred, part of the strength of the bowtie is that there is also room for scenarios that have not occurred yet. This makes it a very proactive approach.

Barriers: controlling unwanted scenarios

Now that we have identified and drawn out the unwanted scenarios, it's time to look at how to control these scenarios as an organization. This is done using 'barriers'.

Barrier types

Barriers with additional metadata

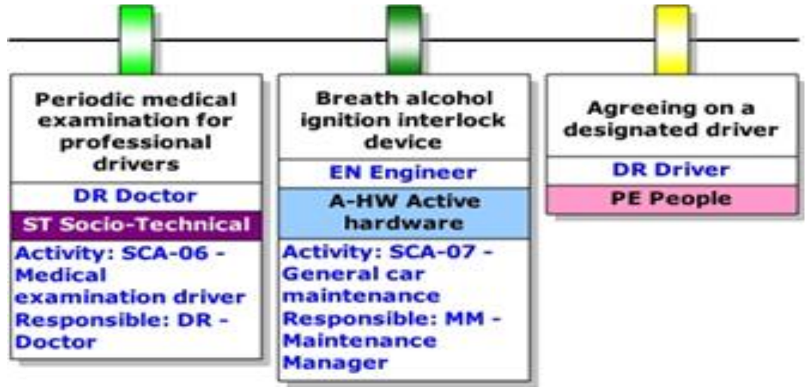


Figure 0-5 Barrier Types

Control and Recovery Barriers

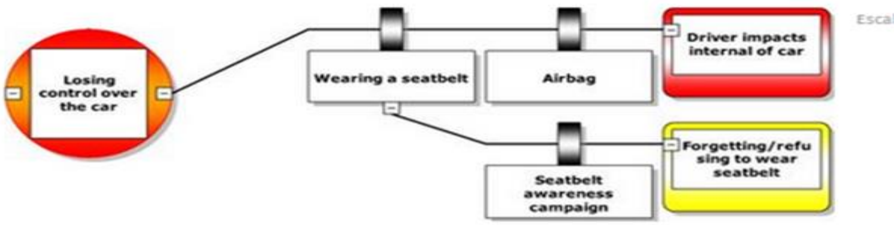
Barriers in the bowtie appear on both sides of the top event. Barriers on the left side interrupt the scenario so that the threats do not occur, and if they do, not result in a loss of control (the top event). Barriers on the right side make sure that if the top event is reached, the scenario does not escalate into an actual impact (the consequences), and/or they mitigate the impact.

There are different types of barriers, which are mainly a combination of human behavior and/or hardware/technology. Once the barriers are identified, you have a basic understanding of how risks are managed. You can build on this basic barrier structure further, to deepen your understanding of where the strengths and weaknesses are. Barriers can be classified and assessed beside barrier types, including for instance barrier effectiveness. This lets you assess how well a barrier performs or is expected to perform, based on available data and/or relying on expert judgment. After that, you can look at the activities you have specified, to implement and maintain your barriers. This essentially means mapping your Safety Management System (SMS) onto the barriers. In addition, you can determine who is responsible for a barrier and assess the criticality of a barrier in the context of all other related information. These are all things you can do to increase your understanding of the barriers. Ultimately, linking and visualizing all this information on a barrier gives you a holistic overview of your safety measures with relevant metadata in the context of your risk scenarios.

Escalation factors & Escalation factor barriers

Barriers are never perfect. Even the best hardware barrier can fail. Given this fact, what you need to know is why a barrier will fail. This is done using the 'escalation factor'. Anything that will make a barrier fail can be described as an escalation factor. For instance, a door that opens and closes automatically using an electrical mechanism might fail if there's a power failure.

Escalation factor with Escalation factor barrier



Warning: be careful with escalation factors. You do not describe all the potential failure modes. Only describe the real weaknesses of your control framework and how you want to manage that.

Figure 0-6 Escalation factor

The logical next step to manage escalation factors is to create barriers for your escalation factors, aptly named ‘escalation factor barriers'. In this case, it could be a backup generator.

To learn more or create bowtie diagrams similar to those on the images on this page, visit the BowTieXP webpage. https://www.wolterskluwer.com/en/solutions/enablon/bowtie/bowtiexp

AIChE Leading/Lagging Indicators Metrics - https://www.aiche.org/ccps/resources/tools/process-safety-metrics

These three types of metrics can be considered as measurements at different levels of the “safety pyramid” illustrated in Figure 1. Although Figure 1 is divided into four separate layers (Process safety incidents, Other incidents, Near miss, and Unsafe behaviors/Insufficient operating discipline), it is easier to describe metrics in terms of the categories shown above. Figure 1 illustrates how each of these four areas is captured under the three sections of this document.

It is strongly recommended that all companies incorporate each of these three types of metrics into their internal process safety management system. Recommended metrics for each of these categories are included in the three primary sections of this document.

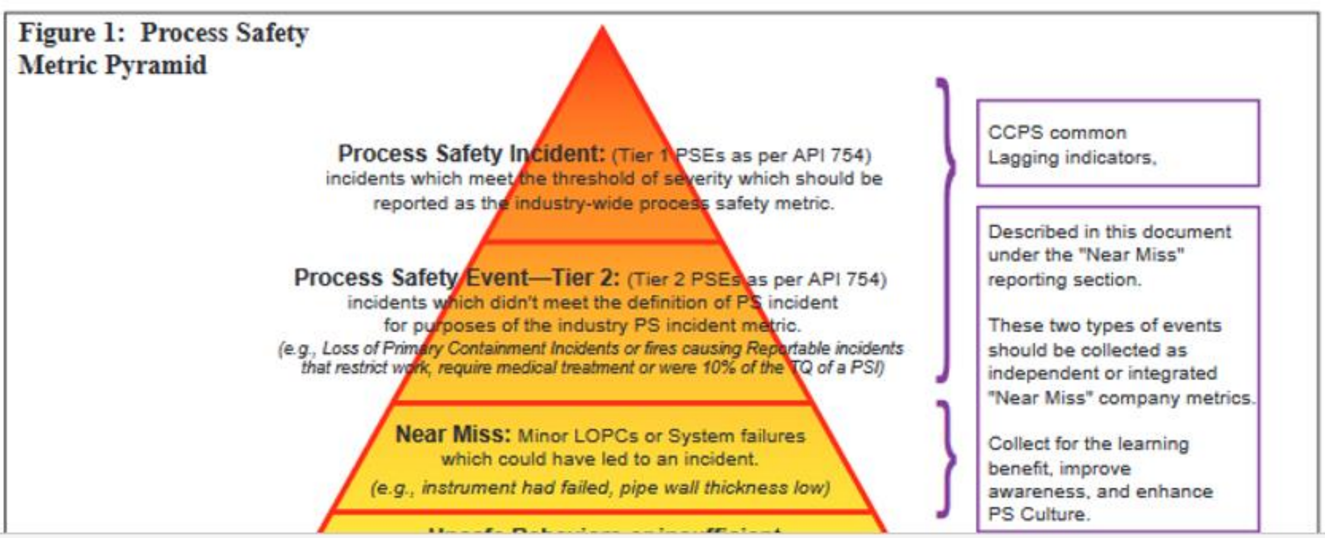


Figure 1: Process Safety Metric Pyramid

Monterey County, California worked with the California Water Quality Control Board to develop a method of analyzing the wastewater disposal of aqueous ammonia wastewater that was drained from an industrial refrigeration operation. The primary concern centered on the analysis of the mixture compressor oil waste (with potential metal contamination) that could be within the ammonia when the system is drained.

The analysis was performed by a licensed Laboratory "Test America Analytic Testing Corporation. The test results are not to be reproduced without the approval of the Testing Corporation.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13 June, 2007

Eileen Woodbury
Monterey County Health Dept.-Env. Health Div.
1270 Natividad Road
Salinas, CA 93906

RE: Ammonia Wastewater
Work Order: MQF0046

Enclosed are the results of analyses for samples received by the laboratory on 05/30/07 13:40. If you have any questions concerning this report, please feel free to contact me.

Sincerely,

Theresa Allen

Theresa Allen For Leticia Reyes
Project Manager

CA ELAP Certificate # 1210

Figure 0-7 approval of the Testing Corporation

The water quality assessment resulted in an increased level of information about the specific impact of the industrial ammonia wastewater that occurs when draining small amounts of ammonia vapor and/or aerosol vents into the water from an isolated part of the ammonia system that needs service and/or repair.

The test results gave Monterey County Health Department the technical support to set guidelines for over a hundred industrial ammonia refrigeration facilities that operate within Monterey County.

The following are the criteria for attaining industrial wastewater disposal to the Monterey County Water Pollution Control District.

Environmental Health Division

Procedures for the proper treatment and disposal of ammonia wastewater generated by ammonia refrigeration operations.

Since the fall of 2007, there have been procedures put together that combine our requirements, what the City of Salinas wants, and, finally, input from the Monterey Regional Water Pollution Control District (sewer agency). The procedures were presented by Bruce Welden during a RETA meeting in October 2007.

Here is a summary:

- It is **illegal** to discharge any ammonia wastewater to the street, gutter, parking lot, landscaping, soil, storm drain, and the like.
- It is **illegal** to discharge ammonia wastewater to the industrial wastewater system maintained by the City of Salinas. They don't want it at all in any amount or any concentration.
- Ammonia wastewater can be disposed of by either 1) contacting a licensed transporter, or 2) properly/safely neutralizing ammonia wastewater and discharging it to the sanitary sewer (again DO NOT discharge into the industrial wastewater system and DO NOT discharge to the environment).

If you choose number 1), then maintain records of disposal.

If you choose number 2), then you need to follow the following:

- **Record** the volume of ammonia wastewater, with an approximate volume or amount of ammonia in the water.
- **Record** the pH of the ammonia wastewater with either Litmus paper or an electronic pH meter.
- Ammonia wastewater must meet a pH range between 6 and 10. To neutralize the slightly basic solution, you may neutralize with a weak acid or you may safely ventilate the container of ammonia wastewater away from the public, and any employees; ventilate until all the vapors have dissipated and the pH is between 6-10.
- Before discharge to the sewer, contact the Monterey Regional Water Pollution Control Agency (sewer agency) and **NOTIFY** them of your intent to discharge the ammonia wastewater.
- **Record** the date you notified MRWPCA, with the final volume of ammonia wastewater and pH, and then, with the **APPROVAL** of the MRWPCA, discharge the ammonia wastewater to the sanitary sewer.

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