# RESEARCH REPORT

## WHAT HAS THE INDUSTRY EXPERIENCE BEEN WITH AMMONIA MANUFACTURING PLANTS? WHAT IS THEIR TRACK RECORD FOR HAVING SERIOUS PROCESS SAFETY INCIDENTS? WHAT ROOT CAUSES HAVE TYPICALLY LED TO THEM?

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## 1. Executive Summary

The production of ammonia involves a complex process of converting hydrogen and nitrogen into ammonia at high temperature and pressure. Because of this adverse operating conditions, accidents are bound to happen in a chemical plant. Ammonia is used in different industries, as a refrigerant, as a precursor to make fertilizer, in waste water treatment. It is explosive and extremely hazardous in case of physical contact. Therefore, preventive measures should be taken while handling it. There are a number of causes that can lead to an accident.

The team analysed 7 accidents from around the world to identify the root causes, degree of seriousness and actions taken by the facilities to prevent dire consequences. The most common causes were found to be, human error, valve or pipe failure and hydraulic shock (in case of Millar Refrigerated Services). Other common causes of ammonia related accidents include control system failure, lack of preventive maintenance, deviation from operating procedures, harsh operating environment, lack of training, component failure. Out of all the reported accidents by Occupational Safety and Health Administration (OSHA), most of the fatalities or injuries is caused by minor leaks leading to inhalation, burns, or even death. Even a short term exposure is hazardous to health.

After studying the accidents thoroughly, loopholes in preventive and mitigative safeguards were found which can be acted upon to prevent future accidents. The facilities can implement the following safeguards:

- An emergency isolation system should be used to isolate machinery and electrical equipment and activate the ventilation system.
- All ammonia detecting and alarm systems should be regularly tested and calibrated in accordance with standards.
- A continuous ceiling level exhaust ventilation should be installed for ammonia plant area.
- In case of a leak, a respiratory protective equipment should be available in the area to use. Any hot work like welding, soldering should not be conducted near ammonia plant area.

With inherently safer design of the plant, the identification of all possible deviations and its hazards are vital. Hazard and Operability Studies or What-if Analysis can be conducted to identify possible hazards and implement safeguards to avoid accidents and mitigate them in an effective manner.

## 2. Introduction

Ammonia is produced in large quantities by chemical industries with more than 80% being produced for fertilizing agricultural crops. The capacity of ammonia being produced has increased from 2000 to 3300 tpd [1]. It is used as an ingredient in household cleaning products, as a refrigerant gas, in waste water treatment, as a stabilizer and neutralizer in food and beverage industry.

Ammonia when released forms denser than air mixtures on release to the atmosphere, despite low molecular weight. TLV of ammonia is 25 ppm (TWA) and STEL is 35 ppm. Ammonia gas is extremely corrosive to the skin, eyes, nose and respiratory tract. Ammonia is corrosive to many metals and alloys specially zinc and copper. Iron and steel are used for ammonia storage, piping and fittings. Under certain conditions anhydrous ammonia produces embrittlement with steel, hence it is very important to follow strict guidelines of metallurgy. Ammonia vapors disperse quickly when released and forms dense ammonia/air clouds by flashing in the surrounding air [1].

Ammonia can be safely vented to atmosphere during emergency situations in the gaseous form and the discharge point must be sufficiently high to prevent downwind plume hitting the ground at high concentrations.

There have been several accidents where ammonia was spilled and had a serious environmental impact. A road tanker released 19 tons of ammonia in Houston in 1976 resulting in 6 fatalities and more than 100 injuries. In 1973 in South Africa, an ammonia tank suffered brittle fracture which released 38 tons of ammonia and led to 18 deaths. It has been stated as the worst accident involving ammonia as there was no overpressure or rise in temperature. The fracture occurred in dish end which was made of carbon steel and had not been stress relieved after manufacture. This failure formed a cloud of approximately 150 m diameter and 20 m deep. With slight breeze, the cloud moved to the township leading to the disaster [1].

The most important aspect for prevention of major accidents in an ammonia plant is by taking prompt action to shut down the compressor. In an ammonia plant, hazardous waste disposal and disposal of spent catalyst is a problem. Excessive vibrations/shaking of the flare and its structure due to mixing of ammonia and carbon dioxide in the presence of water has been observed by plant

personnel. The partial blockage increased the pressure at the flare stack and the sudden release of the gases gave vibration.

Ammonia explosions are rare as the LEL of ammonia is high (LEL – 16% and HEL – 25%). The auto ignition temperature is 650 deg C, therefore ammonia is difficult to ignite [2].

Ammonia production involves various equipment at high temperature and pressure, hence, implementation of safety principles becomes crucial. Some of the causes of accidents are catalyst degradation, catalyst tube rupture, temperature runaway reactions, corrosion in reformers, ammonia refrigeration and other release scenarios of pipe leakage, cracks. Failures can occur in process equipmemt, machines, control systems that can lead to an accident. Human error is a root cause in many accidents and even if it is taken care of, with such range of equipment, large pipelines, valves and connections, some kind of accident is bound to happen if the plant has inherently safer design.

A total of 71 accidents related to anhydrous ammonia have been reported since 1985, with 19 being in the last decade. The main cause of fatalities and injuries was found to be inhalation or burns [3]. The near miss accidents or minor leaks and spills occur more frequently than fire and explosion but have dire consequences and adequate training and knowledge about health hazards should be known to all employees.

## 3. Objective

The primary objective of the team is to study different ammonia related accidents around the world and find the root cause of the accidents. The team researched about 7 accidents listed below,

a) Anhydrous ammonia release at Millard Refrigerated Services
b) Ammonia leak in Shanghai
c) Elk Grove Plant Explosion
d) CF Industries ammonia fire and explosion
e) Pilgrim's Pride Plant Explosion
f) Petronas Plant ammonia leak
g) Medicine Hat Nitrogen Complex ammonia leak

The team aims to determine the most common root causes for incidents in ammonia plants by conducting thorough research and analyzing different probable root causes. Because of adverse operating conditions, the likelihood of accidents is high and requires proper training and emergency preparation to avoid serious consequences. After analysis, recommendations can be suggested to prevent future accidents.

# 4. Analysis

## 4.1. Accidents

### a) Anhydrous ammonia release at Millard Refrigerated Services

On 23rd August 2010, a catastrophically failure of a 12-inch suction pipe on roof lead to a release of more than 32000 pounds of anhydrous ammonia in Millard Refrigerated Services in Theodore, Alabama Additionally, the pressure developed due to hydraulic shock ruptured the evaporator coil inside the facility (Figure 1) [4].

The ammonia cloud was released and traveled 0.25 miles across the river near the plant. In the downwind direction of the release, crew members on the ships docked at Millard and about 800 contractors were working on clean up of Deepwater Horizon oil spill. One Millard employee lost consciousness and got injured. Nine crew members and 143 offsite contractors reported exposure.


Figure 1. Ruptured low temperature suction line (left), Evaporator coil weld failure (right) [4]

Hydraulic shock is an abnormal condition that results in sharp pressure ride which causes catastrophic failure of pipes, valves and other components. In refrigeration systems, the combination of high-pressure hot gas and cold liquid ammonia can result in hydraulic shock.

Three Millard employees closed the valves after 4 hours of incident and secured the release. The ammonia released from evaporator coil contaminated 8 million pounds of poultry and packaging material. Ammonia concentrations as high as 7275 ppm were recorded in the contaminated blast freezer later that day. The emergency response was notified 15 minutes later the incident. Mobile Fire Department conducted air monitoring and reported 500 to 600 ppm of ammonia concentration inside the facility [4].

Before the incident, the facility experienced a loss of power that lasted more than 7 hours. While attempting to troubleshoot equipment issue after the system regained power, the operator manually cleared an alarm in the system. This resulted in interruption of a defrost cycle in progress for a blast freezer evaporator. The evaporator switched directly from defrost mode into refrigeration mode without bleeding hot gas from evaporator coil. The bleed phase is necessary to prevent rapid reduction of pressure. Because of manual intervention by operator and reset of control system, the control system did not recognize that the blast furnace evaporator contained high pressure hot gas. This allowed the low temperature liquid and hot gas to mix in the same pipe, causing the hot gas void to collapse as it rapidly condensed to liquid. This created pressure shock and ruptured the piping and evaporator coil.

Some of the important lessons learnt are as follows [4]:

- For refrigeration system design, avoid grouping multiple evaporators to a single set of control valves. The equipment control systems should be password protected so that only trained and authorized personnel can manually override the system.
- In event of ammonia release, activate the emergency shut down system to de-energize pumps, compressors and valves instead of attempting to isolate leaking equipment while the refrigeration system is running.
- Defrost control systems should be equipped with interlocks to have low temperature feed and isolate hot gas in a hot gas defrost cycle in case of power outage or any other deviation. The system should automatically depressurize or bleed the coils upon restart before opening the suction valve at the evaporator.

**b) Ammonia leak in Shanghai**

On August 31, 2013, a leak of liquid ammonia at a refrigeration unit of plant in Weng's cold storage Industrial Company killed 15 people and 25 injured [5]. The food company involved is engaged in import, export, storage and processing of seafood. It had capacity to freeze 150 tons of products per day. Residents 15 kilometers downwind in Zhabei district could smell ammonia. Initial investigation says that a cap on a pipe carrying liquid ammonia had fallen off. The cause of the accident might be a pipe or valve failure. The serious consequences should have been prevented if proper ventilation was provided and the workers had known the evacuation routes [6].

### c) Elk Grove Plant Explosion

On July 7, 2017, a faulty quarter inch valve caused an ammonia leak at Grecian Delight food processing plant in Elk Grove Village which led to an explosion. Ammonia under 150 psi pressure leaked into an 80 x 40-feet room with 20-feet ceiling [7]. Something sparked the ignition of ammonia leading into a blast which ruptured the aluminum facade on the building (Figure 2). Around 100 employees were working onsite during the incident and were evacuated, and two people were hospitalized [8].

Figure 2. Damaged building due to explosion [9]

### d) CF Industries ammonia fire and explosion

On June 14, 2013, an accident happened at an ammonia plant located at Donaldsonville, Louisiana owned by CF Industries. The plant has ammonia production capacity of 8 million metric tons per year with other urea and urea ammonium nitrate facilities [10]. The accident involved fire and explosion (Figure 3) in one of the four ammonia production units, resulting in one fatality and injuring at least ten people. The fire was brought down in under half an hour and the plant was immediately shutdown [11]. Upon investigation it was found that the unit was shut down for maintenance and the workers were pumping nitrogen into a storage vessel. The accident occurred when they pumped too much nitrogen causing the vessel to rupture [12]. The root cause for this accident can be said to be human error or lack of preventive safeguards. The accident could have been avoided if the vessel was equipped with a safety relief device and a pressure sensor. At this facility, the last accident of such severity occurred in 2000 in the ammonia unit, which killed three people in a fire and explosion [13].

Figure 3. Fire and explosion at the facility [14]

### e) Pilgrim's Pride Plant Explosion

On August 16, 2011, ammonia leak at the Pilgrim's Pride Plant in Guntersville, caused fire and explosion (Figure 4) [15]. The fire was out within 45 minutes and there were no reported fatalities but the explosion damaged the plant. The plant uses anhydrous ammonia for processing chicken and refrigeration [16]. Emergency services were called immediately and as a safety precaution, nearby residents and employees had been evacuated. This company is a good example of a having a great safety culture and adequate emergency response training. Though, installing preventive safeguards like air monitoring devices can prevent large releases and serious consequences and the leak can be contained in time.

Figure 4. The fire caused by the leak [15]

### f) Petronas Plant ammonia leak

Petronas chemicals manufactures petrochemical products such as olefins, polymers and fertilizers [17]. On August 16, 2016, ammonia leak at Petronas chemical facility in Malaysia resulted in two fatalities and three injuries. The leak happened when workers were doing maintenance and got exposed to ammonia [18]. The cause of the accident was a nearby leaking pipeline where the workers were conducting maintenance. The leak was contained immediately by the emergency services [19]. The cause of accident might be pipeline failure but the root cause can be said to be poor regulatory check that could have prevented the accident. Also, the workers should have known the hazard of ammonia and used protective equipment.

### g) Medicine Hat Nitrogen Complex ammonia leak

The Medicine Hat facility at Alberta is the largest nitrogen manufacturing complex in Canada. It produces ammonia and urea with a capacity of 1.5 million tons. This facility is owned by CF Industries [20]. On December 7, 2015, an accidental ammonia leak caused a fatality and a few injuries to the personnel. Two contractors were working to weather-proof a large ammonia storage tank and leak happened when a piece of equipment accidentally struck the tank's valve, releasing ammonia. Both the workers were taken to the hospital but unfortunately one of them died [21]. The cause of the accident is obviously, human error. The workers should have handled the equipment carefully and informed about what was stored in the tank. Also, ammonia poses an inhalation hazard, hence protective equipment must be provided.

## 4.2 Observations

From these incidents it can be seen that the interest of ammonia in industry as a refrigerant is very high as it does not contribute to ozone depletion and global warming. Ammonia is also widely used in fertilizer industry. It has a sharp and distinct odor detectable at low concentrations. Since, it is lighter than air it can be removed easily from buildings by ventilation.

Ammonia gas can decompose at high temperatures to flammable hydrogen and toxic nitrogen dioxide. However, Ammonia is classified as a hazardous chemical since it is explosive when mixed with air in 15-28%. The TLV of ammonia is 25 ppm for 8-hour work day and STEL is 35 ppm for 15 minutes period. Industries using ammonia should conduct risk assessment to highlight potential hazards and prevent catastrophic incidents.

## 5. Conclusions

The biggest risk in ammonia using plant is leakage as can be seen from the incidents which can be harmful to employees and become explosive if it encounters an ignition source.

The leakage can be caused due to:

- Valve plugging or valve malfunction
- Defects in shaft seal, pipe flanges and valve stems
- Pipe failure due to corrosion, mechanical damage or vibration
- Tank material failure

Ammonia is used as a compressed gas and can be toxic and confined space hazard. Hence, engineering controls, training, protective equipment requirements are essential.

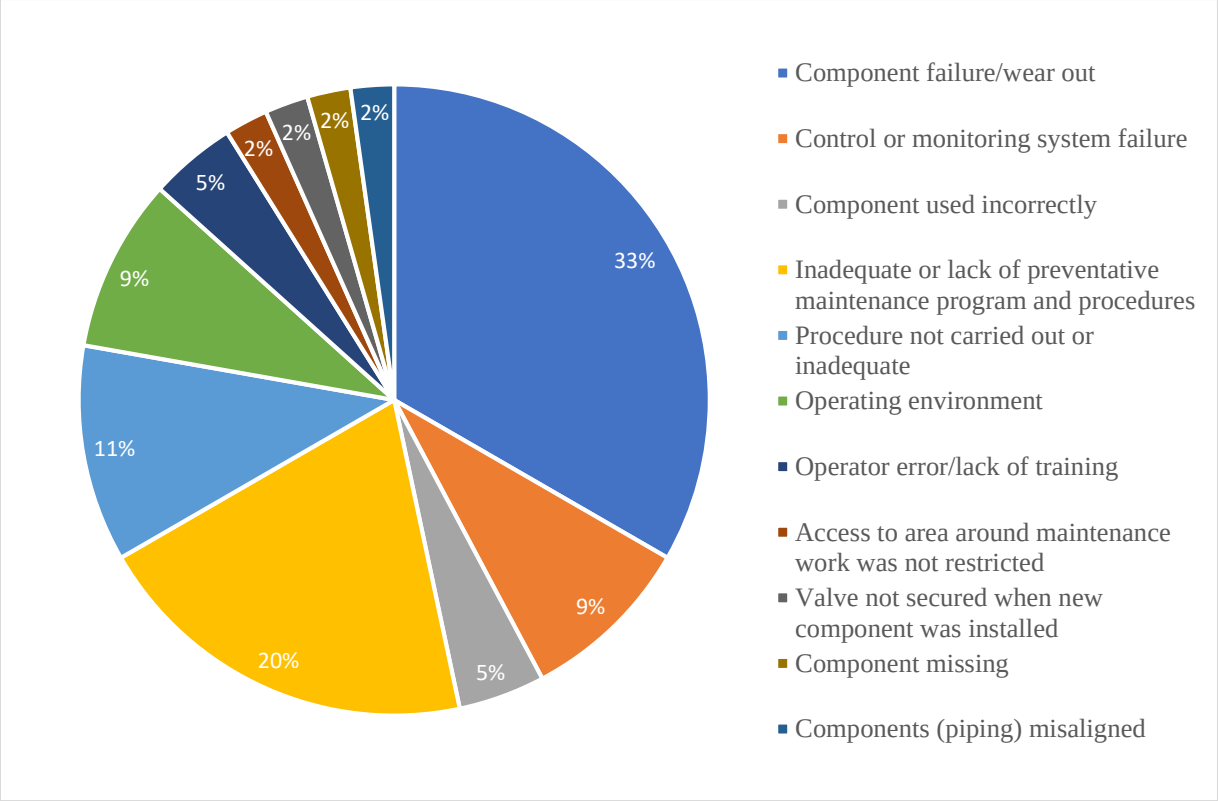


Figure 5. Causes of ammonia related accidents [22]

## 6. Recommendations

Risk Mitigation Measures [23]:

- The ammonia plant rooms should be isolated from rest of the plant.
- No combustible material should be used inside ammonia plant area.
- The room should be well ventilated.
- An emergency isolation system should be used to isolate machinery and electrical equipment and activate the ventilation system.
- The plant room should be built with explosion proofing.

Detection System:

- The plant should be equipped with two stage ammonia detection system, one to activate the emergency ventilation system at 25% of LEL and the other to isolate the equipment and close all valves at 50% LEL.
- All ammonia detecting and alarm systems should be regularly tested and calibrated in accordance with standards.

Ventilation System:

- The emergency ventilation system should activate at 25% of LEL.
- A continuous ceiling level exhaust ventilation should be installed for ammonia plant area.
- Non-sparking ventilation system should be used.

Electrical:

- All electrical equipment should be designed as explosive and fire proof.
- The emergency and ventilation system power source should be in separate area of the plant, not near to ammonia plant.

In case of a leak, a respiratory protective equipment should be available in the area to use. An oxidizing agent and halogen chemical should not be used in the same area. Any hot work like welding, soldering should not be conducted near ammonia plant area [24].

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