Ammonia leakage in a fertiliser production plant

1st December 1994

Ribecourt-Dreslincourt (60)

France

Chemistry
Ammonia /fertiliser
Leak of dangerous material
Inspection / Organisation
Manual operation
Piping / valve
Victim
Operations / shut down

FACILITIES CONCERNED

The facility

The plant manufactures both liquid and solid NPK type compound fertilisers. The facility has been authorised by a prefectoral order under the classified facilities for environmental protection dated 16 May 1991.

Photo DRIRE

The site that comes under the public utility easement is classified as an upper tier Seveso facility. It mainly operates three liquid ammonia (NH_3) tanks with an individual capacity of 150 m³ and a total capacity of 225 tonnes, as well as several ammonium nitrate depots with a capacity over 200 tonnes.

The plant used various raw materials that mainly comprise:

- Ammonium nitrate in granular or hot solution form
- Liquefied NH_3 gas
- Potassium chloride

The production of solid fertilisers is close to 200,000 tonnes/year for a production capacity estimated at 300,000 tonnes/year. The production of liquid fertilisers is around 500,000 tonnes/year.

All production methods of the granulated three element fertiliser use the same procedure:

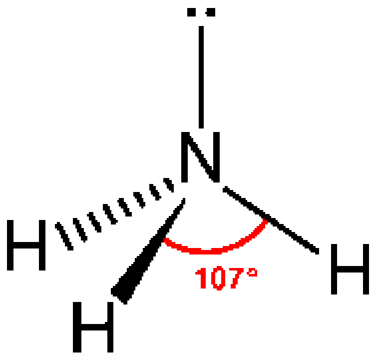
a) Weighing of solid raw material
b) Measuring of liquid raw material
c) Granulation
d) Drying
e) Screening and crushing
f) Coating and cooling
g) Gas scrubbing

The facility concerned

The accident involves a dryer comprising a drum with a 2.50 m diameter and 26 m in length and driven at a speed of 4 rpm by a crown gear. The product from the granulator is transferred to the drum where it is powdered along with phosphoric acid and ammonia (4 kg/s maximum).

Hot air from a natural gas generator is used in the drying process. The combustion gases and the ones used for drying are sent to a scrubbing tower by a 75,000 m³/h fan for dedusting that was carried out by four cyclone type dust collectors. The facility could neutralise 1 tonne/h of NH_3.

The substance involved



NH_3 in its gas state is used to produce fertilisers, explosives and polymers.

The gas is inflammable (R10), toxic if inhaled (R23) and causes burns (R34). It is very toxic for all aquatic organisms (R50).

Ammonia gas is extremely irritating to the respiratory tract and its odour can be detected at concentrations ranging from 0.6 to 53 ppm. At 500 ppm, it causes immediate irritation to the nose and throat. Brief exposure at concentrations greater than 1,500 ppm can result in pulmonary oedema. If the victim survives, complete recovery is possible only if the lesions are not too severe. However, long-terms problems of the breathing system and lungs have been observed after brief exposure to high concentrations of ammonia.

Contact with liquefied ammonia gas causes frostbites and burns due to chemical corrosion. These may leave behind permanent burn marks on the skin.

THE ACCIDENT, ITS CHRONOLOGY, EFFECTS AND CONSEQUENCES

The accident

The cleaning of the dryer was scheduled for 1 December 1994. For this purpose, the tubular reactor of the dryer was shut down at 6.25 am. The reactor was cooled down and drained at 7.00 am. At 9.30 am, the fan of the dryer was stopped and at 9.45 am, the electricity department replaced the inverter protecting the production robots from voltage upsurges, an operation carried out every six months. This involves shutting down programs, cutting off the electrical supply to the inverter, connecting the second inverter and restarting the programs.

At 10.00 am, the maintenance team comprising 3 technicians entered the dryer for its weekly cleaning. Under these conditions, all production lines were stopped. Two technicians cleaned the supply blades of the reactor facing the ammonia injection nozzle while the third technician inspected the hot gas inlet before the injection nozzle.

At 10.30 am, the automatic valve controlling the ammonia injection nozzle in the dryer opened suddenly. The gas contained in the pipe of diameter 33 entered the automatic valve and a manual valve in closed position 10 m before was opened.

A technician managed to escape via the dryer's feed chute after passing below the ammonia injection nozzle. The two others facing the injection nozzle tried to reach the access trap of the dryer located at the opposite end, i.e. 25 m from their work station. Only one of the technicians managed to reach the trap and get out of the dryer. After having travelled less than 10 m, the second technician stumbled and was unable to get up. After putting on a chemical cartridge respirator the team leader managed to rescue his colleague in less than 3 min. The three technicians who suffered from face burns and respiratory problems were taken to the Compiègne hospital where the technician who stumbled inside the dryer died after six days after having sustained burns in the lungs.

The consequences

One of the three technicians died from burns caused by inhaling NH_3 vapours. Another one sustained serious burns and the third was burnt to a lesser extent. The quantity of liquid NH_3 contained in the pipes before draining was estimated to be 5 kg. On opening the valve, this quantity was released in form of a spray in the area in the dryer were the dead technician was working. The resulting cloud that formed was then naturally transported by air to the rear door of the dryer.

The following table specifies the lethal and irreversible effects of ammonia on man depending on the concentration and exposure time.

Concentrations (mg/m³)	Toxicity	Exposure time
6 600	LCLo 1 min	1 min: lethal effect
4 600	LCLo 2 min	2 min: lethal effect
3 800	LCLo 3 min	3 min: lethal effect
1 200	LCLo 30 min	30 min: lethal effect
1 900	TCLo 1 min	1 min: irreversible effects
1 300	TCLo 2 min	2 min: irreversible effects
1 100	TCLo 3 min	3 min: irreversible effects
350	IDLH	30 min: irreversible effects

European scale of industrial accidents

By applying the rating rules of the 18 parameters of the scale made official in February 1994 by the Committee of Competent Authorities of the Member States which oversees the application of the 'SEVESO' directive, the accident can be characterised by the following 4 indices, based on the information available:

The parameters that comprise these indices and the corresponding rating method are available at the following address: http://www.aria.ecologie.gouv.fr.

The quantity of liquid NH_3 contained in the pipes and released in the dryer in form of a spray is estimated to be 5 kg. Since the Seveso threshold of this substance is 200 t, the quantity released corresponds to 0.0025% of the threshold. Level 1 is attributed to the dangerous materials released index for this percentage (see Q1 parameter). One of the poisoned victims died in hours following the accident, resulting in level 2 being attributed for the human and social consequences index (see H3 parameter).

ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

The accident occurred when the weekly maintenance of the dryer involving manual cleaning was performed by three technicians working inside the dryer. The maintenance team was instructed to:

- close the manual valve located before the dryer,

- drain the liquefied ammonia pipes (diameter 33, L = 10 m) before the dryer between the injection nozzle and the manual valve before entering the dryer,

- check for pressure drop using a pressure gauge after the manual valve,

- seal the 10 m segment by closing the automatic valve located just before the injection nozzle.

The technicians could only "regulate" draining using a pressure gauge after the manual valve. However, the pressure drop in the pipe could be observed only after the liquid NH_3 had been completely drained. Nevertheless, this reading could be wrong if the pressure gauge malfunctioned. Moreover, leakage in the manual valve cannot be ruled out along with an increase in pressure indicated by the pressure gauge without the knowledge of the technicians in the absence of any further inspection.

At the same time, the electricity department carried out the half-yearly replacement of the protecting the production robots from voltage upsurges. At the end of the operation, resetting the programs of the robots caused the two electropneumatic stop valves to open and the phosphoric acid and ammonia present in the pipes to be released in the dryer.

The half-yearly replacement of the inverters and the weekly maintenance were carried out by two separate teams with the operations as a rule never being carried out parallelly.

The partial draining of the ammonia pipes, as well as a programming error in the robot caused the automatic valve to open when reset. This resulted in the accident following uncoordinated operations carried out by two separate maintenance teams at the same time.

ACTION TAKEN

Further to this accident, several measures were taken:

- An additional valve was installed at the entry of the reactor and after the automatic valve.
- Guidelines prohibiting any operation on programs alongside any other operations on the system were drafted.
- The NH_3 piping between the manual and automatic valves was drained for an hour when the dryer tube was cooled while maintaining the filtration circuit.
- The computer programs were changed so as to avoid any HIV valves from opening when the programs are reset.
- The equipment was removed from service and a flat joint was installed after the manual valve at the entry of the reactor during any operation on the dryer or on the pipes going to the gas filtration station.
- The safety of the ammonia, phosphoric acid and mechanical component installations was reviewed.
- Lastly, a committee comprising several representatives from parent companies carried out a comprehensive review of the safety installations in the plant as of 20 December.

LESSONS LEARNT

This lethal accident that occurred when two parallel operations carried out as part of preventive maintenance and upkeep of production infrastructure highlights the importance of the following points:

- ✓ Prior risk analysis
- ✓ Study of an appropriate removal of equipment from service and prompt action
- ✓ Supervision of conditions while removing equipment from service
- ✓ Supervision of operations carried out and re-commissioning the equipment after action.
- ✓ Importance of efficient communication (including visual and radio contact) and coordination between the teams in the event of parallel operations.
- ✓ Likely problems in working in closed spaces especially when people must be immediately evacuated.
- ✓ Tightness of circuits involved in the operations.
- ✓ The need or at least the advantages in promoting fail-safe equipment

Several lessons can be learnt from this accident:

Organisation and inspections

Especially for safety reasons, two dangerous operations must not be performed at the same time without real coordination even for keeping intervention times to a minimum and reducing the equipment downtime. If several teams are working at the same time, they must preferably be in constant and direct visual contact.

The current valve shutoff devices may not be fully reliable in terms of removing equipment from service and subsequent re-commissioning. Coordination of operations and safety guidelines play a vital role in acting as the ultimate obstacle to accidents.

The required coordination and existing guidelines were unfortunately insufficient in this case.

Change management, identification and evaluation of major accident risks

When operations are performed in closed spaces, measures must be implemented to avoid any possible toxic gas leak or drastic fall in the room oxygen level.

A part of the operations was carried out inside a reactor but the “safety equipment” to avoid any sudden leak of ammonia was scarce, hard to access or not adapted to their original protective function: consecutive sectional devices excessively spaced out creating a significant dead volume, NH_3 “detector” in the pipe (mere pressure gauge), non fail-safe safety valves and poorly adapted programming of robots (program reset ← → valve opening).

Feedback management

After the accident, the operator took into account the various aspects mainly by shutting off this part of the facility (additional valves and flat joints), modifying the programming of robots to avoid the sudden opening of sectional valves, planning operations to avoid parallel running of dangerous operations, carrying out an inspection of all safety systems in place and revising operational and safety procedures.