Ammonia leak in a urea production plant

March 27, 1998

Toulouse (Haute-Garonne)
France

Ammonia
Equipment malfunction
Rupture disc / relief valve
Human error
Organisation / crisis management
Media impact
Incident analysis

THE FACILITIES INVOLVED

The site:

This chemical plant, employing a workforce of 515, was synthesising a series of basic products (ammonia: 1,000 tonnes/day, nitric acid: 750 tonnes/day), fertilisers (ammonium nitrates: 800 tonnes/day, urea: 1,000 tonnes/day, nitrogen solution: 600 tonnes/day, and an industrial ammonium nitrate in either solution or pellets: 2,250 tonnes/day), as well as various other substances (melanin, cyanuric acid, resins, glues, etc.). The facility is *SEVESO-classified for* the use of chlorine and storage of ammonia, ammonium nitrate and miscellaneous chlorine-based products.

The specific unit involved:

The plant's urea production unit came online in 1982. Urea is synthesised by means of a chemical reaction, under a pressure of 150 bar and temperature of 180℃, occur ring between ammonia and carbon dioxide.

THE ACCIDENT, ITS CHRONOLOGY, EFFECTS AND CONSEQUENCES

The accident:

During the morning of March 27, 1998, Toulouse residents woke up to the smell of ammonia across many districts of the city. Fire and police stations recorded complaints as of 7:40 am, while other public organizations were inundated with calls until 9:30 am. Highly unfavourable weather conditions (slight wind and temperature inversion) magnified the effects of the ammonia leak. Fire-fighters measured ammonia concentrations near the olfactory threshold (5 ppm) at several locations throughout the city. The population was requested to remain indoors for a few hours until the foul-smelling cloud had completely dispersed.

Plant management, which only became aware of the seriousness of this accident when emergency teams were dispatched subsequent to a large volume of phone calls, created a crisis handling cell as prescribed in the internal emergency plan at 8 am and began conducting investigations.

The likely hypotheses of this accident were only identified as of 10:30 am: an ammonia leak had occurred between 4:50 and 6:25 am on one of the liquid ammonia pipes running from the medium-pressure storage zone (315 tonnes distributed among 7 tanks pressurised at 12 bar) to the urea synthesis workshop. A press release was issued at 11 am.

The exact origin of the leak, i.e. a safety rupture disc, could not be confirmed until 1:30 pm. The plant estimated having discharged into the environment on that day 1 tonne of ammonia during a 90-minute period via a 100-m tall chimney. The actual quantity output, which amounted to 10 tonnes, would only be known several days later.

Consequences of this accident:

Though many phone calls were received by the plant, fire stations, city hall and the local DRIRE Environmental Agency, no medical impact was reported on any city residents.

Fire-fighters measured ammonia concentration values in Toulouse (north of the plant) at 3 to 5 ppm between 7:30 and 9 am. The local atmospheric pollution monitoring sensors recorded a maximum of 3 mg/m^3.

The European scale of industrial accidents:

By applying the rating rules applicable to the 18 parameters of the scale officially adopted in February 1994 by the Member States' Competent Authority Committee for implementing the '*SEVESO*' Directive on handling hazardous substances, and in light of information available, this accident can be characterised by the four following indices:

The parameters composing these indices and their corresponding rating protocol are available from the following Website: http://www.aria.developpement-durable.gouv.fr.

The overall level of the "Hazardous materials released" index reached a "3", since the quantity of ammonia discharged was estimated at 10 tonnes (parameter Q1 – quantity between 1% and 10% of the *SEVESO* threshold).

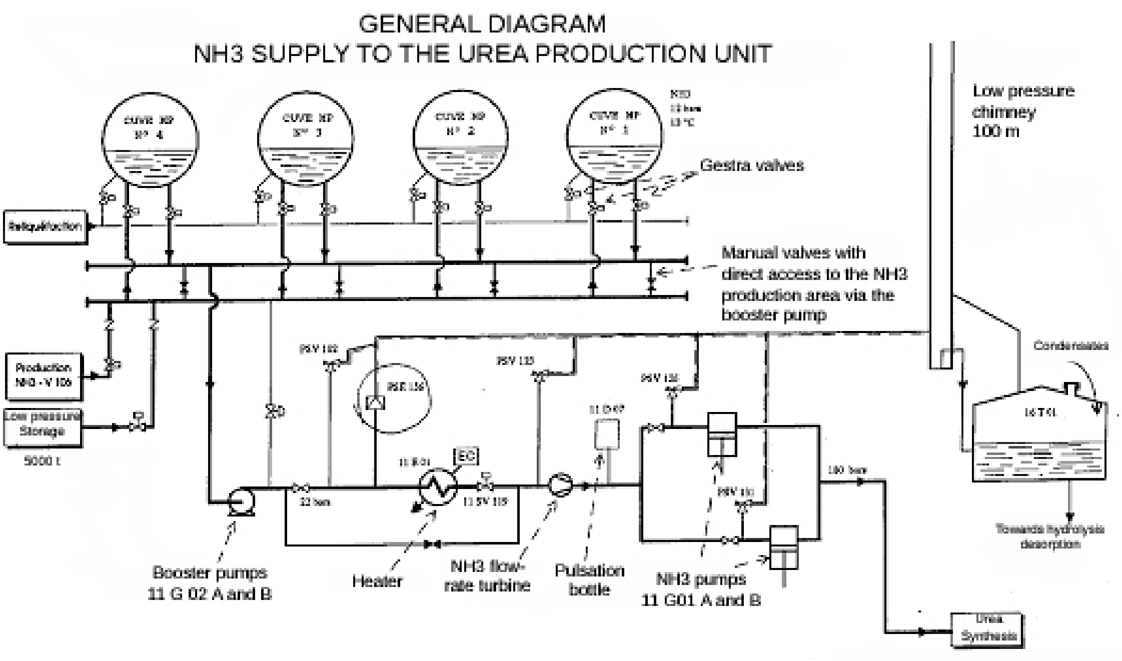
Due to a lack of information, none of the "human and social consequences", "environmental consequences" or "economic consequences" indices could be scored.

THE ORIGIN, CAUSES AND CIRCUMSTANCES SURROUNDING THE ACCIDENT

At 4:50 am, a drop in the ammonia flow rate occurred on the line feeding the urea synthesis unit subsequent to the triggering of an alarm on the closed-circuit contacts of 2 low-pressure valves at the bottom of liquid ammonia tanks. Following a rapid inspection, the supervisor on duty decided to open a manual direct feed valve in order to re-establish the flow rate, which reached a minimum level 1 min later. At 5 am, the supervisor made another round just prior to completing the night shift, and this inspection yielded no observable anomaly.

At 5:03 am, a backlash of the safety barrier cover could be heard on the 16T01 ammonia water tank, which was used to collect condensates at the bottom of the chimney. This noise occurred a total of 4 times until 6:20 am. At 5:13, an ammonia alarm sounded inside the plant for 15 min; this incident was interpreted as the consequence of displacing the safety barrier on the ammonia water tank. The site's other ammonia detectors, including those installed around the plant property line, never indicated that an incident had happened.

At 5:20 am, a night watchman noted a frosting (which indicates the presence of ammonia) downstream of a relief valve (PSV126) at the output of pump 11G01 that supplied NH_3 to the urea production facility. The corresponding equipment was located on the exhaust collector system shared by all relief valves installed in this part of the plant and connected to the chimney base. The leak was considered to be very slight and induced by reactivating the NH_3 circuit after opening direct conduits. A steam reheating unit was set up on the PSV126 relief valve to defrost the circuit.



From 5:50 to 6:25 am, once the assigned plant engineer had arrived on duty and analysed the situation (in drawing the conclusion of inefficient valve heating), the heat exchanger located downstream of the NH_3 pump was isolated along with its relief valve.

The hypothesis of a rupture to safety disc PSE153 was suggested at one point but then rejected since the unit supply intake appeared to be operating correctly; instead, the focus was directed towards a break in the seal of a relief valve after its opening subsequent to disturbances created by malfunctioning check valves.

The accident analysis revealed that this leak occurred at night while the unit was in stable operating mode, following a quarter-turn opening of its cross-section by a PSE156 rupture disc (ref.: P. rupture 33,4 b), which served to protect a tubular exchanger subsequent to a pressure surge on the liquid NH_3 circuit connecting the medium-pressure NH_3 storage zones with a urea production workshop. The exchanger was also protected by a relief valve adjusted to 31 bar (PSV102). The exhaust from this disc and relief valve was collected in the same pipe, which was also hooked up to a duct common to all liquid NH_3 relief valves in the circuit (12-inch duct diameter). Moreover, this duct was connected to the low-pressure chimney in the shop area.

Given weather conditions unpropitious for effective dispersion of the toxic cloud formed as a result of partial NH_3 entrainment towards the top of the plant's degassing chimney, strong odours emanated over several districts of the city, causing Toulouse residents to react. Complaints were first received by authorities at 7:40 and continued to be recorded as late as 9:30 am.

The discharge began seeping into the atmosphere at 4:50 am, unbeknownst to onsite technicians who erroneously interpreted the several alarms that sounded. The leak was isolated at 6:25 am, although the plant operator only became aware of the seriousness of this event past 8 am, meaning it took a full 2½ hours to determine the origin and likely causes of the accident. The quantity of NH_3 lost, initially evaluated at 1 tonne, would only be known with precision several days later, when it was reported that 10 tonnes had actually been released over a 90-min period.

ACTIONS TAKEN

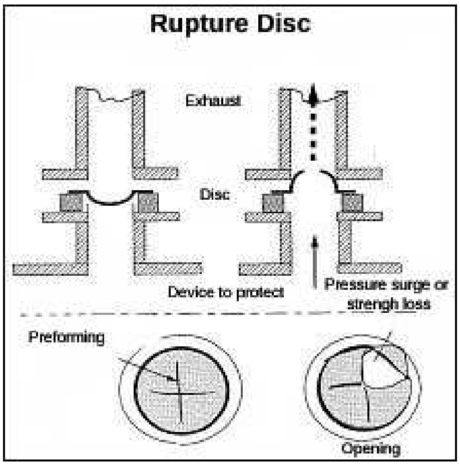
The site operator conducted an in-depth technical analysis of the accident, and plant installations were subsequently modified (by eliminating the rupture disc, installing sensors and automated safety devices). A safety report was also produced for all of the site's ammonia circuits.

The DRIRE Environmental Agency implemented a new internal organisation and emergency response plan. The local Prefecture decided that a crisis management cell was to be activated in the event of an accident receiving heavy media attention.

LESSONS LEARNED

This accident, which prompted strong media response, stemmed from a series of equipment malfunctions, as well as both organisational and human error:

Design of installations and instrumentation / Lack of equipment reliability:



- √ A defective rupture disc supplied from an old batch (1982) and installed in 1995. The accident investigation revealed a smaller thickness (0.05 mm) than that of "identical" discs supplied afterwards, resulting (according to calculations performed) in an actual bursting pressure significantly less than the design pressure, i.e. a value of 22.3 bar, which lies very close to typical pressure levels encountered. This disc needed to be eliminated from the installation.
- √ Inadequate systems for detecting anomalies and automating installation safety features: lack of sensors capable of indicating disc rupture, pressure monitoring on the urea production supply circuit, detectors and alarms in the case of low temperature (frosting), etc.
- √ Poor design of both the circuit and rupture disc (i.e. a shared collector pipe).
- √ Despite the poor dispersion conditions, inoperable NH_3 detectors installed around the plant periphery were detrimental, given that the toxic cloud was discharged by a 100-m tall chimney.
- √ No NH_3 leak detection device had been installed at the chimney flue.

Unit operations / Organisational breakdown:

- √ Insufficient analysis of risks relative to the site's liquid NH_3 distribution circuits.
- √ Decision-making process devoid of adequate analysis or verifications following the poor diagnostic evaluation, even after a number of precursors, including: closure of 2 of the 4 GESTRA tank bottom check valves, thereby isolating the medium-pressure NH_3 tanks; unusual and repeated noises due to backlash of the safety barrier cover on the ammonia water tank; an NH_3 alarm lasting 15 min; observation of the frosting phenomenon downstream of a relief valve, indicating the presence of NH_3 (the hypothesis of a faulty relief valve is to be emphasised); and inefficiency of attempted relief valve heating.
- √ Lack of information relayed to the control room (e.g. disc rupture went unnoticed).
- √ Inadequate or missing safety procedures and written instructions: closure of safety valves, monitoring of detectors and sensors indicating eventual environmental discharges, etc.
- √ Deficient tracking procedures and corresponding inspection guidelines.

Alert / Crisis management:

- √ The poor diagnosis performed explains: the failure to acknowledge variations observed at the ammonia water tank; the delay before isolating the deficient part of the circuit; and the potential impact of NH_3 emissions.
- √ Response time was lengthy from the beginning of the accident until tripping the alarm and activating the internal emergency plan, and then until identifying the origin, causes and circumstances of NH_3 emissions, as well as definitively evaluating the quantity of gas actually released.
- √ No emergency notification procedure was in place between the plant and the local air quality measurement network (ORAMIP).

Lessons for the future:

A rupture disc does not return to the closed position! One of the objectives in the risk analysis was to assess the operating principle of the various safety devices and the consequences likely to ensue. Such an analysis must lead to deriving a pertinent diagram of both fluid circulation and corresponding equipment, which in turn allows establishing measures for effective incident management.

The fact that neighbouring residents noticed the effects of this incident before the site operator could grasp the magnitude attests to a unique difficulty that wound up slowing implementation of appropriate mitigation measures. As a corollary, such an anomaly is likely to exacerbate the seriousness of an event and increase the resources to be deployed; moreover, this ineffectual response could require introducing a special crisis management approach, complete with a rather sophisticated media handling strategy.

The development of instrumentation and detection systems, along with a protocol for managing resultant information, constitute the key element when responding to such incidents.