Rupture of a cryogenic ammonia tank

March 20th 1989

Jonova

Lithuania (USSR)

Fertiliser
Roll-over (?)
Toxic release
Fire
Victims
Organisation
Compressor

INSTALLATIONS CONCERNED

The site :

The chemicals plant for the production of NPK fertiliser was built in 1969; located at 12 km from the town of Jonova which had a population of 40 000 inhabitants. The plant employed 5 000 people and was positioned inside a military zone with controlled access.

The installation :

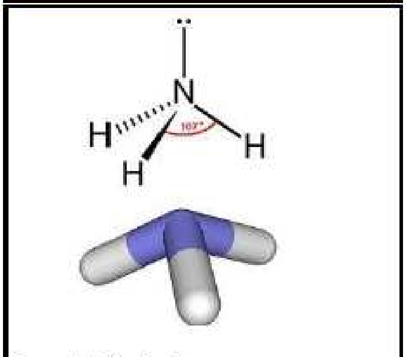
The ammonia tank involved in the accident is a cryogenic storage vessel with a capacity of 10 000 t (inside diameter: 30 m / height : 20 m), of Japanese design but built by the Soviets in 1978. The reservoir had a single wall insulated with perlite held in place by an external skin of steel. The gap between this skin and the reservoir wall was filled with nitrogen under low pressure. This tank, designed to resist an internal pressure of 0,1 bar and a depression of 5 mbar, stored liquid ammonia (density : 0,68) under slight overpressure (between 0,02 and 0,08 bar) at a temperature between – 32° and – 34°C.

Fed by a production factory (1400 t / day) at 600 m distance, the reservoir was close to 3 storage sites containing a total of 55 000 t of fertiliser.

The other equipment comprising the unit was as follows:

- 2 piston compressors with a transfer capacity of 323 m^3/h, one with an electric motor, the other with a diesel engine. These could be used when the 2 turbo-compressors used for the transfer of the ammonia from the production unit to the reservoir were halted.
- A flare-stack with a capacity of 500 kg/h,
- 2 valves each with an evacuation flow rate of 4 200 m^3/h,
- 2 safety valves protecting the reservoir against depressions,
- A monolithic reinforced concrete protective wall 14.1 m high and 400 mm thick, also used as retaining tank and dimensioned to bear the hydrostatic pressure of the liquid.
- Alarm systems relating to the pressure and the liquid level in the reservoir.

Ammonia



Source : http://fr.wikipedia.org

General	
Formula	NH_3
Aspect	Compressed colourless liquid gas, with acrid odour
Properties	
Boiling point	- 33°C
Melting point	- 78°C
Solubility in water at 20°	54 g / 100 ml
Vapour pressure at 26°C	1013 kPa
Relative density of vapour	0,59
Relative density of liquid	0.68 (à -33,5°C)
Temperature of auto-combustion	651 °C
Explosiveness limits in air (volume)	15 % - 28 %
Hazards	
Fire	Inflammable
Explosion	air/gas mixture is explosive
Environment	Highly toxic for aquatic organisms
Professional limits for exposure	
VME (8 h)	7 mg/m^3 / 10 ppm
VLE (15 min)	14 mg/m^3 / 20 ppm

Source : http://www.cdc.gov/niosh

THE ACCIDENT, THE SEQUENCE OF EVENTS, ITS EFFECTS AND CONSEQUENCES

The accident

On March 20th 1989, the pressure in the reservoir climbed abruptly between 11:00 a.m. and 11:15 and it burst at the level of its base. Under the effect of the wave escaping from the gaping breach, the reservoir broke free from its stand, pushed in the opposite direction. It destroyed the reinforced concrete protecting wall and ended up 40 m from its foundations.

The 7,000 t of ammonia contained in the tank spread over the ground forming a layer which was, in places 70 cm deep. With only a light wind (< 2 m/s), it took 12 hours to evaporate.

According to the local authorities, part of the liquid ammonia was propelled, in the form of a jet, towards the phosphonitrate production buildings. A fire then spread to the fertiliser depots. Other sources claim that the ammonia cloud was ignited by the flare-stack, the flames being then propagated to all the buildings on the site. The collapse of a burning conveyor belt onto a store of NPK fertiliser (11-11-11) would then have initiated the decomposition of the fertiliser which continued for 3 days while releasing large quantities of nitrous oxide (NOx) to the atmosphere.

The emergency services arrived 30 minutes after the accident, the means deployed increased progressively: civil defence, emergency commission of the Lithuanian Republic and the military region, civil defence teams from the USSR and from the Soviet ministry of fertilisers.

The consequences :

The official human casualty list cited 7 deaths and 57 wounded (treatment lasting from 2 to 3 weeks) among the operational personnel of the plant and of the construction companies working close to the accident site. The municipal authorities, alerted 25 minutes after the beginning of the accident, decided to evacuate the high risk areas as soon as the concentration of ammonia in the air exceeded 10 mg/m^3 ; 32 000 people were thus displaced.

A toxic cloud composed of ammonia vapour and products of the thermal decomposition of the fertiliser (nitrous oxides, ammonia…) was at the origin of irritation observed as far away as 35 km from the accident site. The contaminated zone extended to 400 km². The estimated height of the cloud at 5, 10 and 20 km from the site appears to have reached respectively 100, 400 et 800 m.

According to the report from the Soviet authorities, the concentration of ammonia along the track of the cloud and within a radius of 3 km did not exceed 200 mg/m^3. The levels found at a distance of 10 to 15 km were between 20 and 40 mg/m^3. These relatively low levels of ammonia could be explained, at least in part, by the ignition of the ammonia vapour in the plant. The maximum distance over which the presence of ammonia could be detected in the air was 23 km.

The concentration of nitrous oxides (NOx) which could have reached 25 mg/m^3 on the site close to the storage zone for the phosphonitrates, did not exceed 2 mg/m^3 in the wake of the cloud that had formed.

To reduce the impact of the cloud on the surrounding areas, water curtains were set up using fire hoses all along the track of the gas cloud. Furthermore, special measures for the protection of water courses were taken to avoid the risk of pollution of the nearby NERIS river. Pumping of the extinction water, positioning of containment basins…

European scale of industrial accidents

Using the scoring rules of the 18 parameters on the scale formalised in February 1994 by the Committee of Competent Authorities of the Member States in the application of the 'SEVESO' directive, the accident can be characterised by the following 4 indices, taking into account the available information.

The parameters comprising these indices and the methods of scoring are available at the following address: http://www.aria.ecologie.gouv.fr

The 7,000 t of ammonia involved in the accident represent 35 times the Seveso threshold associated with this substance (toxic : 200 t) which explains why the index "dangerous substances released" in the scale of accidents reaches level 6 (parameter Q1). The index for "human and social consequences" is at level 5 because at least 57 employees were seriously injured (hospitalisation longer than 24 h – parameter H4). The lack of information concerning the environmental consequences makes it impossible to provide data concerning the corresponding indices in the scale of accidents.

THE ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

The day of the accident, one of the liquefying turbo-compressors used for the transfer of the ammonia from the production unit to the cryogenic reservoir was halted for long term maintenance. Around 10 a.m., the second turbo-compressor was halted for a repair job of short duration.

The operators then put into service the safety piston pump to draw the gaseous ammonia from the production unit but difficulties in starting up the cooling circuit for the compressor delayed this operation. The pressure inside the storage vessel at that moment was at 0.07 bar. The ammonia coming from the production unit was then diverted to the flare stack. Despite these measures, according to the official report, nearly 14 t of warm ammonia (+10°C) were introduced into the lower part of the cryogenic reservoir (corresponding to 15 minutes of transfer).

According to the official information, these 14 t of NH3 injected into the bottom of the reservoir formed a bubble in the lower part of the reservoir under the effect of the hydrostatic pressure. The warm ammonia may then have reached the surface (a phenomenon comparable to roll-over?) causing a sudden increase of the pressure in the reservoir, exceeding the release capacity of the valves and causing the rupture of the reservoir, more than an hour after the introduction of the warm ammonia.

Nonetheless, according to Anderson and al.[1], this hypothesis seems unlikely, taking into account the pressure differential between the liquid ammonia at the base of the reservoir (relative ≈ 1.1 bar) and the ammonia at 10°C that was injected (relative 5-6 bar) ; the hydrostatic pressure was certainly insufficient to prevent the vaporisation of the warm ammonia at the at the bottom of the reservoir and its rise to the surface. The calculation of the mass of vaporised ammonia (2,52 t) and consequently of the volume of gas generated (2919 m^3 à –33°C) shows that the protection valves, capable of evacuating 2016 m^3 of gas in 15 min, were not sufficiently dimensioned to protect the reservoir in this precise case. Internal pressure had thus probably increased, provoking the rupture of the retaining shell.

Enquiries conducted following the accident reveal that:

- the stronger resistance of the roofing of the reservoir as compared with the attachment of the inside walls of the tank to the base, as well as of the gusset plates, caused the rupture of the reservoir at its base. The floor of this remaining solidly attached to its foundations,
- the wave of liquid ammonia released broke the protecting wall, before spreading out over a wide area, thus aggravating the consequences of the accident,
- the resistance of the protection wall was not in conformity with the specifications drawn up in the design of the unit (real breadth inferior to the 400 mm specified) on account of modifications made during construction to reduce the materials and labour costs. During construction, it appears that modifications were also made, for the same reasons to the foundations of the reservoir and its anchoring devices.

Finally, the official report speaks of “unfavourable operating conditions” in particular as regards the liquefying turbo-compressors.

THE MEASURES TAKEN

To deal with the causes at the origin of the accident which occurred on the Jonova site, the report from the Soviet authorities mentions various technical measures relating to the design, construction and operation of cryogenic reservoirs of this type:

- reinforcement of the protecting walls around the storage tanks, so that they can resist the dynamic pressure resulting from a maximum volume released in the event of shattering of the reservoir,
- continuous recording of the major variables involved in cryogenic storage, with duplication and recording in the control room,

[1] B. O. Anderson (Supra AB, Sweden) and J. Lindley (ICI Chemicals and Polymers Ltd, Wilton, UK) - Ammonia Tank Failure in Lithuania by – Loss Prevention Bulletin 107 – October 1992

- automatic taking out of the circuit the ammonia feed at the base of the reservoir as soon as the temperature rises above -30°C and filling of the reservoir from the t op,
- automatic diversion of the gas towards the flare stack when the pressure in the tank exceeds 800 mm column of water, the handling capacity of the flare stack having to be at least equal to 20 000 Nm^3/h,
- storage capacity for ammonia limited to 80 % of the volume of the cylindrical part of the reservoir,
- installation of non-return valves and elimination of certain sections of piping to prevent the arrival of warm ammonia into the cryogenic reservoir,
- remote start-up of the re-capture pumps for ammonia spilt into the retention tank.

THE LESSONS LEARNED

This major accident shows that the ruin of a cryogenic reservoir is possible, as is the ignition of an unconfined cloud of ammonia (without explosion) although this phenomenon has been rarely reported in accident science.

The dramatic consequences of this accident result from the rupture of the reservoir at the level of its base, with release of its entire contents. On the other hand, the rupture of a cryogenic ammonia reservoir in Geismar (USA) in 1984 (ARIA n°5421),at the level of the upper ring die did not lead to the release of liquid ammonia: the only consequences observed were the presence of 150 to 400 ppm of NH_3 downwind from the storage site during the 6 hours following the accident. The adequate dimensioning of the resistance of the reservoir at the level of their base and their summit (the frangible nature of the reservoir) can thus allow for the limitation of the consequences of severe over-pressure. Roll-over phenomena may, furthermore, be avoided by feeding the reservoir from the top or equipping the tank with an internal re-circulation system.

The accident which occurred at Rostock (Germany) in 2005 provides another example of the violence of the thermodynamic phenomena which can occur in cryogenic storage : the formation of two strata (one of ammonia at 20 % and the other of anhydrous ammonia) in a cryogenic reservoir during filling, on account of the presence of oil, caused the rupture of the tank during a sudden mixing ot the two layers (ARIA n°29 517).

These two accidents illustrate the misleading phenomenon of inertia associated with large scale storage and the low level of thermal exchange which can generate a too rapid mixture of ammonia in different phases.

To limit the risk of over-pressure in cryogenic reservoirs, it is essential to maintain a sufficiently low temperature (-33°C) during storage and also during filling even if small quantities are involved relative to the volumes stored (14 t à 10°C in the present case as against an amount stored of 7,000 t). Protective equipment such as such as bursting discs and valves, correctly dimensioned, must also play their role. Nonetheless at La Madeleine (59) in 1989 (ARIA n°733), the rupture, belatedly detected, of a security disc equipping a cryogenic reservoir provoked the release to the atmosphere of 2.4 t of NH_3 and therefore it is useful to examine preventively the evacuation conditions for released materials.

More generally, information of several kinds can be drawn from this accident:

- Maintenance periods are always risky situations which demand increased vigilance, as do exceptional situations or unusual operations. A prior examination of the risks, proportional to the stakes, should be conducted and compensatory measures should be formally taken.
- Even if it considered as passive, the retaining equipment may turn out to be ineffective, as against the dynamic effects of the flow of liquid (submersion) or when it is damaged by the effect of the wave or by domino effects (projectiles).
- Safety measures and equipment, such as emergency controls must be permanently accessible, even in degraded situations.
- The redundancy of the equipment (2 turbo-compressors available + 1 piston pressure pump in the present case) reduces the probability of a major accident but does not exclude it : multiplication of the various types of barrier (alarms, servo-systems, emergency operating procedures, fail-safe security systems…) while avoiding common sources of failure particularly when the stakes are high or the installations are particularly dangerous, are the most effective way of reducing major risks, without claiming to eradicate them. Bearing in mind the quantities stored in cryogenic reservoirs, the potential sources of danger in these installations are numerous; therefore the measures taken on the technical, organisational and human fronts to prevent accidents should be proportionate to these.