

Explosion inside a nitrosyl sulphate production facility

21st September, 1992

Lacq (Atlantic Pyrenees)

France

Ammonium nitrite
Ammonium nitrate
Dust explosion
Modifications
Procedures / guidelines
Degraded mode of operation

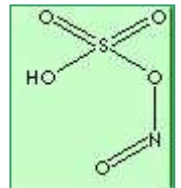
THE FACILITIES INVOLVED

The site:

This site was a major chemical installation located within the Lacq Basin, a zone specialised in "thio chemistry" techniques (involving the chemistry of sulphur originating from the desulphurization of gas extracted onsite). This business was mainly responsible for producing:

- mercaptan (thiol) in order to odourise gases and thereby detect leaks;
- organic sulphides and disulphides (DMDS), used as sulphur carrying agents in steam crackers or else sulphurization agents in certain refinery processes;
- sulphoxides (DMSO), which are solvents used in chemistry and pharmacy applications;
- polysulphides entering into the composition of certain special lubricants;
- sulphuric acid oleum and nitrosyl acid sulphate.

Sulphur-based products are also used in the polymer industry as chain transfer agents, which serve as a raw material in the synthesis of additives and solvents used to synthesise or transform elastomers; another potential application consists of synthesis intermediates for phytosanitary or pharmaceutical products.



Nitrosyl sulphate

The unit involved:

The unit where the accident occurred was built in 1970 and was producing nitrosyl acid sulphate, which is a raw material introduced to manufacture Lactame 12, a basic product found in certain plastic and nylon materials.

The manufacturing process entailed the reaction of nitrogen dioxide (NO₂) with oleum (SO₃ in H₂SO₄) in order to form the nitrosyl acid sulphate compound (NO)HSO₄.

Nitrogen monoxide (NO) was obtained from the catalytic combustion of ammonia in an oven operating at atmospheric pressure, according to the catalysed reaction: $4 \text{NH}_3 + 5 \text{O}_2 \rightarrow 4 \text{NO} + 6 \text{H}_2\text{O}$. Downstream of the oven, nitrous gases were being cooled from 850° to 30°C before processing by a centrifuge compressor to a (blowing) wheel where they underwent final conversion from nitrogen monoxide to nitrogen dioxide, at which point they got absorbed into the oleum.

In the nitrous gas formation step, secondary reactions were responsible for producing both ammonium nitrate and nitrite (stable NH₄NO₃ and unstable NH₄NO₂), which could then form deposits on the installation and require cleaning.

During summer 1991, the unit's production capacity was expanded by replacing the original ovens with larger ones operating in parallel, by means of rearranging the gas cooling circuits (so as to increase the exchange surface areas), the condensation circuits (addition of a separator to avoid secondary nitric acid production) and oxidation circuits (inclusion of a 2nd reactor), as well as by renewing a number of machines. Production output jumped from 40 to 55 tonnes/day. The safety report valid for the unit was updated when submitting the corresponding authorisation request.

Upon start-up in October 1991, the ovens on this "revamped" unit had in fact been oversized, forcing operations to proceed with just a single oven. The other oven was isolated by a series of valves, with its catalytic screen remaining onsite.

During the year 1992, several problems arose on the upstream oleum production unit, causing plant shutdowns. At the beginning of September, vibrations were noticed on the blower; these were due to the presence of white deposits of ammonium nitrate and nitrite on the compressor wheel. Such deposits were characteristic of a poor rate of ammonia conversion coupled with a significant drop in catalyst activity (catalytic screens). The site operator responded by washing all "clogged" equipment (blower and condensers).

On September 14th, subsequent to newly-observed vibrations detected on the blower, the unit was once again shut down, this time in order to proceed with:

- isolation of the operating oven to replace the catalytic screens;
- service start-up of the 2nd oven, which had been idle with its catalytic screens onsite since the beginning of 1992;
- water washing of the blower and condensers so as to dissolve ammonium salts;
- steam cleaning of the absorption column to dissolve the ammonium sulphates.

THE ACCIDENT, ITS CHRONOLOGY, EFFECTS AND CONSEQUENCES

The accident:

The unit was placed back online on 21st September at 6 am, after a series of typical controls conducted in accordance with established guidelines and procedures. Two catalyst re-activations were necessary to trigger the reaction, following which, at 9:15 am, ammonia was slowly input into the oven. A local inspection performed at 9:50 am revealed no anomalies, though 5 minutes later both the nitrous gas blower and its discharge line exploded violently.

Consequences of this accident:

The property damage caused by this accident was noteworthy. The compressor and a portion of its discharge line at the oxidation capacity intake were destroyed. Pipelines located nearby were warped and ripped apart, fragments of machinery were found (along an east-west alignment) up to 100 m away and 20 m off the alignment; also, building cladding was damaged. The shock wave broke window panes in the control room 25 m from the explosion site.

A technician, stationed 8 m from the installation at the time of detonation, was examined for acoustic trauma and barotrauma, but was found to have no impairment. No other victims were reported.

Besides the operating losses sustained (the unit had to be shut down for 40 days), the cost of this accident was assessed at 3 million francs, including diagnostic studies, appraisals and repairs.

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:

Dangerous materials released	 <input checked="" type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/>
Human and social consequences	 <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/>
Environmental consequences	 <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/>
Economic consequences	 <input checked="" type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/>

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

The power of the explosion was evaluated at 2 kg TNT equivalent, hence the hazardous substances released index was ascribed a level "1" score (parameter Q2).

Since no one was injured by the accident, the human and social consequences index was rated a "0".

With no information available on potential environmental impacts, the environmental consequences index was not rated.

Given accident costs amounting to 3 million francs (1992 currency), the economic consequences index received a "1".

THE ORIGIN, CAUSES AND CIRCUMSTANCES SURROUNDING THIS ACCIDENT

The site operator, assisted by third-party experts specialised in explosions, analysed the accident and offered the following observations:

- The bursting of equipment was not caused by a metallurgical problem with the steel, since these materials burst at much higher stress levels than the yield stress of steel; moreover, the fragmentation was considerable.
- The liquid collected in the condensation tank contained nitric acid as well as ammonium nitrate and nitrite. A deposit sampled at the level of the oxidation reactor intake valve showed a 95% ammonium nitrate composition and contained 350 ppm of nitrite.
- Instrumentation controlling the various process parameters revealed no anomalies. The NH_3 / air ratio was in an appropriate range (i.e. < explosibility limit).
- Nickel was polluting the catalytic screens.

These observations served to reject the hypothesis of a gas explosion in favour of a dust explosion due to the presence of ammonium nitrate / nitrite in a confined medium, with a TNT equivalent evaluated at 2 kg.

The event would have taken place as follows:

- During the phase of ignition and temperature rise, the conversion rate of ammonia at the level of the catalytic screens (with pollution causing less activity) suddenly dropped; ammonia escaped from the ovens and was only partially absorbed in ammonia solution as condensates at the time of gas cooling.
- With improved conversion efficiency, the partial nitrogen oxide pressure increased relative to the ammonia pressure, which in turn triggered the formation of ammonium nitrites and nitrates.
- At the end of the cooling circuit, the partial water pressure was minimal and both condensation and water drift had ceased. The ammonium nitrite thus settled on the sides and was capable of spontaneously decomposing in the presence of acid vapours as of 60°C.
- The thermal effect of the conversion from nitrogen monoxide to nitrogen dioxide, combined with gas compression and friction inside the blower (the pumping phenomenon was tied to a flow rate below the nominal rate), led to a temperature rise at the level of the blower or oxidation reactor intake, and this rise caused the nitrites to self-decompose.
- The explosion of these nitrites triggered an explosion of the nitrates, which released much greater energy.

The onsite catalytic screens were new (only 24 hours of use), yet they had remained assembled for a whole year inside the stainless steel oven left idle. Upon analysis, these screens proved to be polluted by nickel (as their central region had been entirely covered by a nickel oxide deposit). Their activity was therefore reduced (or even nonexistent in the central zone), leading to an incomplete oxidation of ammonia, which was at the origin of the accident. Moreover, both the screen activation and oven temperature rise had taken longer than normal.

ACTIONS TAKEN

The explosion occurred due to fulfilling three conditions simultaneously, namely: the presence of ammonia in the nitrous gases (formation of nitrates / nitrites), absence of water (preventing salt dissolution) combined with a high enough temperature, and a shock or the presence of impurities to initiate the explosion.

Operating conditions appeared to be satisfactory, though the implementation of new catalytic screens with partial activity loss induced the presence of ammonia in the nitrous gases.

During onsite works, the operator had placed a separator upstream of the blower in order to avoid the formation of nitric acid and/or improve production efficiency, which had the effect of lowering the quantity of water circulating in the unit and thus decreasing the possibility of ammonium nitrite dissolution and decomposition.

To restore the process to a safe operating regime, the operator resumed demineralised water injections so as to wash the gases, absorb the ammonia and prevent nitrites from forming. Process control and operations were improved through: high temperature alarms in the condensation liquid phases and low temperature alarms on the ovens, redundancy of sensors on key process parameters (i.e. air and ammonia flow rates, screen and condensate temperature). Also, a protective wall and metal structure were installed around the blower so as to limit projections.

From an organisational standpoint, the operator revised the entire set of procedures and operating guidelines to avoid a precipitous degradation of the catalytic screens and to better test measurement and alarm instrumentation. More specifically, the screens were to be disassembled if the oven had to be stopped for more than 2 weeks, and an acid wash would be performed as a preliminary step to installing new screens. The protocol was completed by a series of actions to be taken in the event of fire or degraded operations.

Lastly, a more rigorous methodology was adopted to ensure unit documentation remained up-to-date, in addition to drafting guidelines and analysing risks prior to introducing any modifications in the units.

LESSONS LEARNT

In the corresponding safety reports, the operator had taken into account the instantaneous process-related risks (toxic gas leak, danger of forming an explosive air/ammonia mix, etc.). On the other hand, the slow drift towards unit degradation had not been anticipated or, at the least, was underestimated; the formation of ammonium nitrate and nitrite had been considered "inevitable" and had not caused any major operating problem for over 20 years.

This accident highlights the importance of managing modifications and focuses in particular on the need for rigorous preliminary analysis. A modification considered "minor" on a "routine" process in fact exerted a sizeable impact on operational safety. Another highlight is the essential step of incorporating transient phases and degraded modes of operation into safety reports and organisational set-ups.

In conclusion, this accident has revealed two key aspects: first, the importance ascribed to appropriate design for all operating equipment (especially compressors) and to maintaining the use conditions stipulated from the outset (variation in residence time for the present case); and second, the consequences of a pollution incident, hence the loss of activity in catalytic screens kept in an unsuitable location (i.e. unused stainless steel reactor).