Explosion of a sulphuric acid tank

4 August 2009

Gonfreville-l'Orcher (Seine-Maritime) France

Chemistry
Sulphuric acid
Hydrogen
Explosion
Tank
Maintenance
Equipment defect
Organisation / controls

THE FACILITIES INVOLVED

The site :

This plant, rated upper-tier SEVESO, was using naphtha and butane as inputs to produce the most widespread intermediate chemical compounds in the petrochemical industry (i.e. ethylene, propylene, butadiene and benzene), for subsequent input into plastics manufacturing processes.

The unit involved :

The accident occurred on a 100-m^3 capacity tank (built in 1974) containing sulphuric acid concentrated to 96%. Installed outdoors on piles above a retention basin lined with epoxy resin and part of the unit for treating sodium-bearing water, this tank was used to supply :

- the neutralisation reactor for sodium water stemming from the absorption of hydrogen sulphide on the vapour cracking unit ;
- demineralisation chains of water for boilers and cooling towers with sulphuric acid when the dedicated tank was undergoing maintenance.

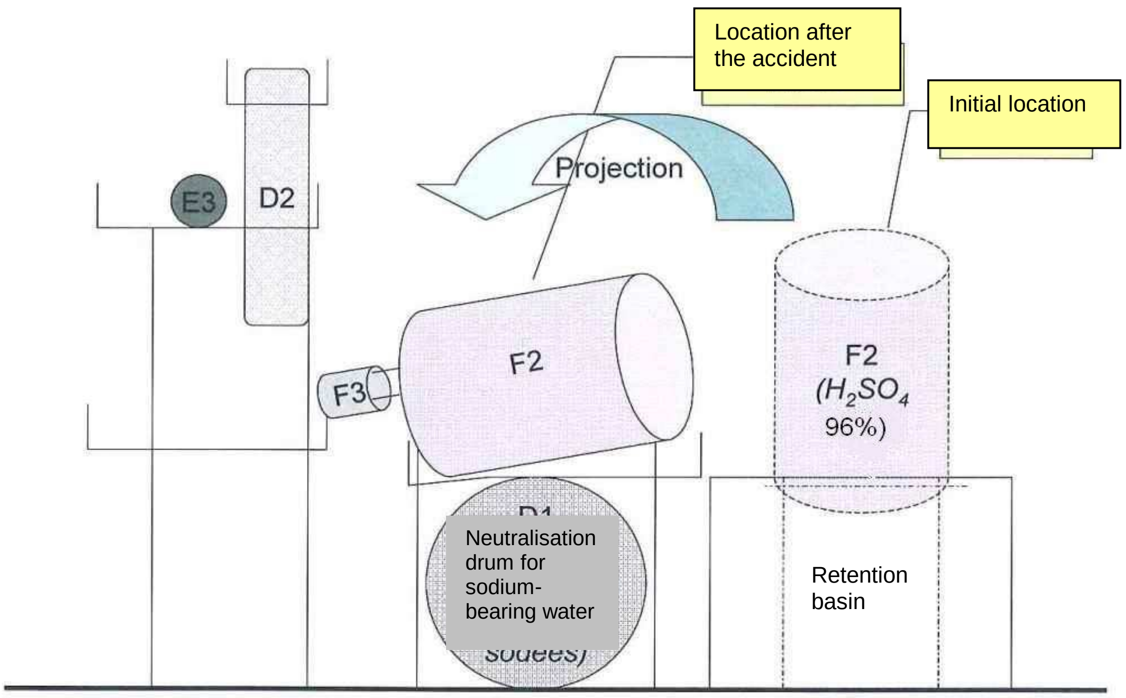

Diagram of the accident scene

This tank had already been repaired in 1989 following an incident that caused its delamination, yet without breaking any fastenings, due to a release of carbonic gas during the sulphuric acid neutralisation step (ARIA 23705). A support bracket had been added in response to this initial accident, and the cleaning procedure was also revised.

THE ACCIDENT, ITS CHRONOLOGY, EFFECTS AND CONSEQUENCES

The accident :

On 17 July 2009, a leak was detected on the F2 tank containing 70 m³ of concentrated sulphuric acid (caused by a 1-mm hole). This leak was plugged on 18 July using a temporary sealant system following approvals delivered by the onsite inspection department.

On Friday 31 July, the tank was emptied to a point of inducing pump cavitation. The remaining product was drained into the retention basin and the tank was rinsed with water over the weekend. A scaffolding was set up to accomplish the rest of the works programme.

On Monday 3 August, the rinsing water collected in the retention basin was conveyed to the water treatment plant.

On Tuesday 4 August, the task of chemical consignment (platinum plating) of the inventory was undertaken in order to isolate the storage capacity. A member of the plant staff, accompanied by 2 subcontractor employees, climbed onto the tank to open the manhole. An explosion occurred around 9:15 am when the plant technician used a grinder to shear the seized bolts.

The F2 tank, empty at the time of the accident, was suddenly lifted 2 or 3 m high and then fell back to the ground on top of a nearby drum. As it was falling, the tank brought down the scaffolding that had been installed for upcoming maintenance.

The Internal Emergency Plan was activated. The site operator notified the local Prefecture, town halls and the general public.

Consequences of this accident :

Three individuals were hurt, with two of the injuries serious.

Two subcontracted employees and a site technician were on the scaffolding at the top of the tank at the time of the explosion. One subcontractor was ejected towards a neighbouring structure 5 metres aboveground when the tank suddenly thrust upward. He landed back on the ground away from the scaffolding. The other subcontractor was pinned in the scaffolding. The third victim (plant technician) took a hard fall and was found on the ground unconscious. Ten other people were seen by the psychological response team at a treatment office opened onsite.

No environmental impact was reported and no hazardous substances released.

The damages were limited to destruction of the tank and all connecting piping; the unit was shut down. The tank was torn apart over half the shell/bottom junction circumference. Its anchorages were also ripped out.

Photos courtesy of DREAL:
Concrete base where the tank was positioned

Damaged tank

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:

As the accident unfolded, an explosion occurred that revealed the presence of a Seveso-listed substance, namely hydrogen. Since the quantity was estimated at 200 g, the index relative to hazardous substances released was set equal to 1 (see parameter Q1). Three injuries were reported, two of them serious, assigning the index relative to human and social consequences a "2" score (parameter H4). No environmental consequence was identified, resulting in a "0" rating for the environmental consequences index. Lastly, the cost due to property damage and operating losses was estimated at €6 M, yielding a score of "3" for the index relative to economic consequences (parameters €15 and €16).

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

THE ORIGIN, CAUSES AND CIRCUMSTANCES SURROUNDING THIS ACCIDENT

Insufficient rinsing of the tank (just a single rinsing cycle was performed) combined with the presence of a low concentration of sulphuric acid caused an acid attack of the metal, leading to the formation and accumulation of hydrogen at the top of the tank (dome-shaped tank roof). The explosion occurred by means of igniting the flammable mix created with air at the time of splitting the corroded bolts on the dome manhole with a grinder.

The metallurgical assessment performed on this tank indicated the presence of extensive internal corrosion over the lower part of the structure. This observation confirmed the sudden onset of corrosion at the tank sidewall due to diluted acid, thus generating a source of hydrogen production.

Photo courtesy of DREAL: The damaged tank

ACTIONS TAKEN

A lawsuit was filed against the site operator; a safety perimeter was set up around the installation on the day of the accident.

On the day following the accident, an extraordinary session of the Committee for Hygiene, Safety and Working Conditions (CHSCT) launched an investigation commission that held its first meeting on 13 August. An executive summary of the accident analysis, accompanied by a set of guidelines (see below under "Lessons learnt"), was presented at a second meeting of the full CHSCT body. This report stated the findings of a 200-g release of hydrogen and the formation of a 4 to 6-m³ flammable gas cloud, in accordance with simulations run in-house when reproducing the effects observed due to the presence of sulphuric acid at low concentrations inside the tank after failing to bleed the tank.

The sodium water treatment facility remained idle for several weeks. Following its temporary storage (which entailed a temporary authorisation, with renewal) within a bulk chemicals warehouse immediately adjacent to the site, the sodium water was conveyed as waste to authorised treatment centres.

A temporary sulphuric acid storage unit was set up to allow restarting the sodium water treatment unit.

LESSONS LEARNT

Regarding risk identification and evaluation

Iron, like the primary common metals (zinc, aluminium), is attacked by diluted acids with hydrogen release, according to the following reaction:

$$Fe + 2H^+ \leftrightarrow Fe^{2+} + H_2$$

Hydrogen is a highly flammable gas (4%-75% in air) at very low levels of ignition energy (0.02 mJ, vs. 0.29 mJ for methane). The risk of a hydrogen explosion is present whenever an acid corrosion of metal has extended to a point of being observable. In certain cases, the flow of fluid against a wall (through friction) or a shock can be of sufficient magnitude to ignite.

A locally high hydrogen concentration (above 4% in air), e.g. in a dead air pocket or at the upper level of an enclosed capacity, can engender an explosion risk when undertaking works on a tank. Such an event occurred in Saint Fons (69), on 9 August, 1989 (ARIA 169), where preliminary flammability measurements conducted prior to the works phase had not enabled detecting the presence of hydrogen at the top of the tank.

The feedback available included reports of several H_2 explosions following an attack of diluted acid on steel tanks in a number of facilities: ARIA 169, 22278, 31082 (detailed accident report).

Regarding feedback management, organisation and controls

A series of recommendations were issued before placing the installation back into operation:

- Design : The new tank would be fitted with a bleed valve that was both accessible and manoeuvrable.
- Tank availability (through steps of drainage and rinsing) was improved. The completed drainage step, facilitated by tank design, was to be visually inspected by opening a manhole at a high point. This improved accessibility will serve to minimise the quantity of residual acid to just drippings at the tank bottom and on its sidewalls, in addition to enhancing not only acid neutralisation to return to a neutral pH but also tank rinsing. Moreover, this operation avoids producing diluted acid and attacking the tank.
- The method for awarding hot-work permits was improved. Feedback mainly focused on building awareness among onsite personnel of both the risks incurred and the atmospheric measurement methods to be implemented (as regards positioning of the explosimeter probe).
- The tank was to be rebuilt using carbon steel; this solution was preferred over a composite so as to streamline inspections.
- During the normal operations phase, a very minor hydrogen release into the tank remains a possibility. Measures were taken to minimise hydrogen production and prevent its accumulation by means of :
    - a vent positioned at a high point, with no internal tank structure causing evacuation of the hydrogen eventually produced during operations and preparation;
    - continuous flushing with dry air to allow hydrogen to evacuate and the tank to breathe; this feature serves to prevent moist air from entering the tank (one possible cause of corrosion).
- The classified facilities inspectorate requested that the tank be made breakable at the shell-roof junction, so that in case of an incident, the tank would remain in place and its contents not ejected.

Following this accident and several others during the same period within the chemical and petroleum industries as well as in the transport of hazardous substances via pipeline, a meeting was organised in September 2009 between the Secretary of State for Ecology and leading figures in these sectors to review the key challenges inherent in industrial safety and environmental protection. Industry leaders forwarded a series of proposals intended to improve the safety of their installations, with emphasis on strengthening controls dedicated to facility ageing and maintenance, while agreeing to pay special attention to ecologically-sensitive zones with the aim of enhancing species protection or protecting designated habitat. As part of the action plan intended to limit the risks tied to equipment ageing, launched on 13 January 2010, this resulted in the issuance of two administrative orders on 4-5 October 2010 relative to structural ageing and technological risk, making it possible to incorporate ageing concerns into the site's safety management system (SMS).