H_2S leakage during the transfer of effluents

7 July 1993

Grasse (06)

France

Chemistry
Hydrogen sulphide
Tanks
Tanker trucks
Effluent transfer
Organisation / procedure / supervision
Victim

FACILITIES CONCERNED

The facility:

Since 1972, the plant has been manufacturing active ingredients for the pharmaceutical sector. The plant was taken over in 1987 by another company. Under the new management, fine chemistry gained significant ground as of 1988. At the time of the accident, the company was producing basic substances for cosmetics and perfumery while continuing to manufacture active pharmaceutical ingredients.

The company had 80 employees and had been authorised to operate under the prefectoral order dated 11 October 1991. The plant was issued a formal legal notice on 26 June 1992 for several violations. The operator was also ordered by an additional notice served on 29 September 1992 to carry out a new danger study subsequent to the incident dated May 1992 (ARIA 3725).

The facility concerned:

The accident involved the storage facilities of concentrated effluents located south of the plant. The facility concerned has several storage tanks including the 20 m³ tank in question. A specialised company collects the concentrated aqueous effluents 3 to 6 times a week.

The effluents are transferred using a vacuum pump of a tanker truck. Since the pump is driven by a hydraulic motor on the truck, it must be left running.

Two technicians systematically oversee the transfer: the truck driver and a security guard of the company. After the tanker truck has been filled, an alarm alerts the driver to perform the following operations:

- turn off the horn (right side of the truck) and close the outlet gate to cut off the tanks.

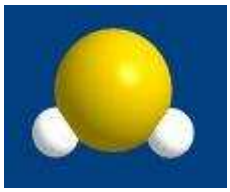
- close the suction circuit of the pump while letting the pump rotate (left side of the truck).

- action the control panel to stop the vacuum pump (right side of the truck).

A flexible cargo hose is used for the transfer that requires one person near the tank to completely empty the hose.

Tank 11, the object of the transfer dated 7 July was emptied on 5 July. On the day of the accident, the tank only contained effluents that were collected over the last 24 hours, making the composition of the mixture known.

The substance involved:



Hydrogen sulphide has the smell of rotten eggs and occurs naturally in crude oil, volcanic gases and hot springs. It is produced during the bacterial decomposition of organic matter (plant or animal waste) and from certain industrial activities.

The gas is acidic, very corrosive, extremely inflammable (R12), very toxic if inhaled (R26) and toxic to marine life (R50).

When inhaled in concentrations greater than 1,000 ppm, H_2S causes death in a few minutes. As of 500 ppm, loss of consciousness followed by a coma sometimes convulsive along with respiratory problems (breathing difficulties and cyanosis), fluid in the lungs, cardiac rhythm disorders and changes in blood pressure. If exposure is not stopped, death follows quickly. However, if the victim is removed from the polluted area and properly treated, he may recover quickly. As of 100 ppm, irritation of the eye and nose mucous membrane is seen resulting in conjunctivitis, rhinitis, breathing difficulty or even late accumulation of fluid in the lungs. These manifestations may be accompanied by headache, nausea, sialorrhea (excessive secretion of saliva) and loss of consciousness for a short duration.

Repeated exposure to H_2S may be the cause of the reactive airways dysfunction syndrome and skin irritation that often leads to painful and itchy rashes.

The French ministry of labour has set the short term exposure limit (TLV-STEL) for H_2S at 10 ppm (14 mg/m³) and a time weighted average (TLV-TWA) at 5 ppm (7 mg/m³). The extremely low recognition threshold (0.00066 mg/m³) alerts the presence of H_2S before the toxicity threshold can be reached. However beyond a certain concentration that is very quickly reached, the olfactory nerve is paralysed and the sense of smell disappears.

THE ACCIDENT, ITS CHRONOLOGY, EFFECTS AND CONSEQUENCES

The accident:

On Wednesday the 7 July around 9.30 am, the truck driver of the sub-contracting company in charge of transporting the liquid industrial waste to an incineration centre arrived at the reception area of the plant. His badge gave him access to the storage site of the concentrated effluents. This was the second time that his company worked in this facility as back-up to the company that usually collects the concentrated effluents.

In compliance with the « concentrated effluents » guidelines, the security guard of the plant comes to the driver while the truck was already parked. The driver was wearing a coverall along with gloves and safety glasses.

The operation started and involved the transfer of concentrated effluents contained in tank 11 to two of the four 10 m³ compartments of the tanker truck. At the end of the transfer (~ 20 m³), the alarm was sounded. The driver who was with the security guard for 45 min got down from the tank. He stopped the alarm near the control panel of the vacuum pump at the right of the vehicle. While the security guard drained the cargo hose used for the transfer, the driver closed the outlet gate to seal the compartments of the tanker truck. He then walked over to the left of the truck, passing by the driver's cab to cut off the vacuum pump and make it rotate. He then returned to the other side

to carry on with the remaining operations (stop the pump) and fell unconscious near the driver's cam without before completing them.

The security guard still near the tank 11 saw this and rushed to help the driver. When he arrived near the driver, he felt uneasy as well. He left the spot before loosing consciousness for a short duration. He then came to and returned to rescue the driver while holding his breath and move him about 15 metres away from the spot. He then asked a technician driving a power lift truck to call an ambulance and bring oxygen and prohibited other employees from entering the dangerous zone. He then put on a self-contained breathing apparatus to stop the truck's motor that was still running. When he returned, the paramedics had arrived who called a second ambulance on seeing his condition. The first ambulance transported the driver who died soon after.

The consequences:

The autopsy performed on the driver ruled out all conditions such as heart attack as the cause of death. It was shown that he died by inhaling H_2S. The security guard hospitalised following the accident had no sequela.

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*.

H_2S was released from the effluent tank The SEVESO threshold for this substance is 20 tonnes. Due to the non-availability of information on the quantity of gas released, level 1 has been assigned by default to the dangerous materials released index (see Q1 parameter). The social and human consequences index (see H3 parameter) has been assigned level 2 due to the death of one person.

ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

The initial analysis carried out by the forensics department in Marseille revealed the presence of a H_2S saturated solution in the tanker truck as well as in storage tank 11.

In fact, the H_2S involved in the accident had been generated in the production workshops where an active ingredient that is part of a pharmaceutical product (antihistamine) was manufactured. The H_2S obtained had to be neutralised in compliance with a specific and stringent procedure since significant quantities of the gas were released (12 % in weight compared to the substance manufactured). The procedure sheet stipulates treatment of H_2S by adding sodium hydroxide and hydrogen peroxide. Liquid bleach must then be added until the sulphur ions completely disappear. The hydrogen peroxide that was initially planned was replaced with liquid bleach.

The following chemical reactions come into play in the treatment of H_2S:

1 – Neutralisation and formation of sulphur: $H_2S + 2\,NaOH \rightarrow Na_2S + 2\,H_2O$

2 - Oxidation with hydrogen peroxide: $Na_2S + 4\,H_2O_2 \rightarrow Na_2SO_4 + 4\,H_2O$

or with liquid bleach: $Na_2S + 4\,ClONa \rightarrow Na_2SO_4 + 4\,NaCl$

The reaction resulting in the formation of H_2S was performed in several stages on 22, 24 and 28 June and yielded 250 kg of active substance each time.

At the end of production, on 22 June, the H_2S produced was sent to a neutralising column with 720 kg of caustic soda, 1,000 litres of water and 72 kg of liquid bleach. However this treatment has not been mentioned by the operator in the procedure sheet of 22 June. The analysis of the solution revealed the presence of sulphur ions.

Production on 24 June: The operator added 260 kg of caustic soda to the neutralising column already containing the solution of 22 June.

Production on 28 June: The operator again added 250 kg of caustic soda and 36 kg of liquid bleach to the neutralising column already containing the solution of 22 and 24 June (oxidation re-trial).

Since there was no H_2S measuring device, the technician had to rely on his sense of smell to supervise the reaction. The treatment was carried out by the successive addition of compounds without constant surveillance of the reactions taking place. The procedure sheet that stipulated the addition of hydrogen peroxide and not liquid bleach was not respected as well.

The addition of liquid bleach in the neutralising column did not prove to be useful. It was then decided to transfer the concentrated effluents from the neutralising column to a 12 m³ tank using a flexible cargo hose to complete the oxidation of H_2S which was supposed to have already been completed as per the reaction procedure sheet. At this stage, it was likely that H_2S was in the form of sodium sulphide (Na_2S).

The operations continue with:

- addition of water in the tank to reach a sufficient level to allow mixing of the effluents (2,500 litres of effluents + 3,500 litres of water, i.e. 6,000 litres of total volume).

- addition of liquid bleach (36 kg and then 108 kg).

- agitation of the entire mixture for 24 h.

The oxidation reaction is not based on any written procedure. When the effluents were transferred to this 12 m³ tank and as per the operator's calculations, 15% of the H_2S would have been treated. After adding more liquid bleach in the 12 m³ tank, theoretically only 36% of the H_2S would have been treated. The various technicians involved in the operation did not consult each other while calculating the amount of liquid bleach that was progressively added and at no time did ensure that the sulphur ions were completely eliminated. A thorough examination of the reaction procedure sheet highlighted several malfunctions:

- The procedure sheets have too much of unwanted details and lack necessary information
- During treatment, it was planned to oxidise the Na_2S solution by adding hydrogen peroxide that was replaced with liquid bleach.
- Liquid bleach must be added till the sulphur ions are completely eliminated. This was not checked.
- pH readings were not recorded in the procedure sheet.
- H_2S treatment carried out after the transfer does not appear on the procedure sheet not on any other document. The quantity of liquid bleach used is stated to be 240 kg, which was not titrated beforehand. Moreover, the theoretical quantity calculated to treat the effluents resulting from the 3 reactions is 700 kg of liquid bleach and 1,230 kg of 30% diluted sodium hydroxide.

Effluents

At the end of these successive treatment reactions that are definitely not complete, the effluents contained in the 12 m³ tank are disposed of in two stages: one disposal operation on Monday 5 July of 3,000 litres of effluents to fill tank 11 to 20 m³ before collection and a second one on Tuesday 6 July in the evening (3,000 litres as well). The effluents were not analysed at all.

Lastly, to evacuate waste to storage tanks 11, 12 and 13, the operator uses a flexible cargo hose to connect to the reactor containing the product to be evacuated to a polypropylene pipeline that empties the effluents into the storage tanks by pull of gravity.

The Classified Facilities Authority during their visit on 9th July observed that:

- the valves cutting off the three storage tanks from one another and the valve regulating the flow of new effluents from other production facilities were blocked in open position,

- the effluent inlet valve was leaking.

The operator stated that

- network overhaul was planned during the shutdown of the plant for technical reasons in August. This was reported on 28/04/93 by the security guard

- no special procedure relating to the product compatibility or chemical composition was drafted before disposal into the concentrated effluent storage tank.

A variety of reasons are responsible for the accident on the 7 July.

- The H_2S treatment conditions were not stringent, liquid bleach replaced the hydrogen peroxide that was initially planned without proper assessment of the quantity required and the treatment procedure which later on proved to be incomplete was not supervised at any stage.
- The procedure sheet on the production of the product in question, contained unnecessary details and overlooked operations that were not carried out systematically.
- Effluents rich in H_2S were not analysed before disposal.
- The concentrated effluent network was faulty and mainly the valves cutting off the three storage tanks were blocked in open position.
- Guidelines and procedures were not followed (start of operations report not signed, readings on the tank after homogenisation not taken, etc.).

These factors lead to the death of the driver, a victim of H_2S poisoning. While transferring effluents from tank 11 to the tanker truck, the vacuum pumping of the partially neutralised effluents saturated with H_2S lead to the release of the gas at the pump exhaust.

ACTION TAKEN

Further to this accident, the operator sent several documents taking into account the technical and organisational feedback to the Classified Facilities Authority:

- Procedure relating to H_2S production reviewed and corrected by working group and the development and production department.
- Sulphur elimination and special storage procedure.
- Concentrated effluent loading and unloading procedure.
- Prevention plan signed on 29/07/93 with the company specialised in collecting factory waste.
- Various internal memos on the immediate measures taken subsequent to the accident.
- Root cause analysis and action plans prepared with a consultancy firm.
- Concentrated effluent transfer procedure from site to transfer tanks.
- Report prepared by the consultancy firm on the validation of the action plan adopted by the operator.

LESSONS LEARNT

Several organisational pitfalls have contributed to the 7 July accident. The procedures were either poorly defined or not respected. The situation is further compounded by the production of a very toxic substance whose treatment was not supervised and turned out to be incomplete.

Organisation and supervision.

Since the start of operations report was not signed, the loading-unloading procedure was not respected. The driver was thus unable to check the compatibility of the product to be loaded with the ones previously transported or with the construction material of the tanker truck.

Further to this accident, the drafting of strict guidelines, written procedures and detailed procedure sheets by the operator will now help technicians better target their operations, and tighten post-production supervisory procedures and analysis.

The guidelines to follow-up the management of concentrated effluents from the various workshops in the plant (wastewater from chemical reactions) were not followed. A representative sample from the concentrated effluent tanks was not taken before transfer to tanks 11, 12 and 13 after the homogenization device was commissioned in the tank. This sample would have enabled the detection of H_2S. Similarly, on the eve of waste collection by the specialised firm, the upper portion of the three tanks should have been sampled for analysis. This instruction, vital to security was not respected.

The non-compliance of guidelines and procedures described previously masked the defects that were uncovered later during the production stage.

Training

The supervisory staff has a crucial role in informing technicians on the various risks inherent to the operations performed, as well as the precautions to be taken against these risks. The written guidelines and procedures play an important role in making each person realise his responsibility.

The operating procedures especially the ones involving external service providers are vital in informing and raising awareness on the risks inherent to site's activity and products.

Identification and assessment of risks, process control and change management

The main reaction released significant quantities of H_2S, a very toxic substance that must be treated before being transferred to the effluents tank. The technician proceeded by adding ingredients without ensuring if the reaction equilibrium had been attained. Furthermore, no specific procedure sheet was drafted to neutralise the sulphur ions, and the treatment was not supervised (no H_2S measurement device). The treatment that was initially planned with hydrogen peroxide was carried out with liquid bleach instead.

These facts clearly show a lack of rigour right from the absence of supervision at the end of production to effluent management leading to the presence of highly toxic H_2S in the tank. At each stage, analysis of a sample would have helped detect the presence of the gas and avoid the accident.

A prior analysis of risks inherent to this treatment operation was an efficient way of ensuring proper functioning. Rigorous management of changes (use of liquid bleach instead of hydrogen peroxide) in a process ensures smooth operations.

Contingency management

Rigorous management of contingencies including specific guidelines on risks inherent to a process and action to be taken (e.g. in the event of discomfort due to high concentrations of H_2S in the air) is vital in an accident situation (always carry out this type of operation in pairs, do not loose sight of technicians involved, etc.)

Other cases:

ARIA 19 967. Lethal asphyxia due to H_2S – Baupte (France) – IMPEL 2002

ARIA 31000. Emission of H_2S in a waste treatment facility – Rhadereistedt (Germany) – IMPEL 2007