Leaks on a phosphorus trichloride iso-container

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Fos sur Mer – [Bouches du Rhône] France

Chemistry
Loading
Degassing
Human factor
Communication
Internal Contingency Plan

THE INSTALLATIONS IN QUESTION

The site:

In 2003, the chlorine fabrication plant and auxiliary buildings, including a phosphorus trichloride (PCl_3) manufacturing facility equipped with a loading station for shipments, were operated by a single company. In 2004, an international company specialised in the manufacture of phosphorus and its derivatives bought the PCl_3 unit and became the registered operator. The former operator, however, remained to run the unit under a partnership agreement. The site is classified as AS ("High Threshold" Seveso).

The unit concerned:

The production capacity of the PCl_3 manufacturing unit is 16,000 t/year, 550 tons of PCl3 (unit and storage) and 200 tons of phosphorus are stored and implemented on the site that also produces chlorine.

The manufacturing reaction employed is very exothermic: $3\ Cl_2 + ½\ P_4 \rightarrow 2\ PCl_3$. Phosphorus trichloride is a liquid (Tm = -93°C, Boiling point = 76 °C), is heavier than wate r (d = 1.6) and its vapours are heavier than air (d = 4.8). Classified as being highly toxic (by inhalation and ingestion), it hydrolyses spontaneously in contact with humidity, producing suffocating fumes (hydrogen chloride). Being a corrosive and non-flammable product, its very exothermic hydrolysis and its decomposition can be related to an "explosion".

THE ACCIDENTS, THEIR BEHAVIOUR AND CONSEQUENCES

Accidents:

Accident on the morning of 08/25/03 – Loading:

At around 10 am, the operator at the PCl_3 loading station began filling a new type of iso-container with 14.6 m^3 (23.5 t) of product. The container was being used for the first time in the establishment. The driver of the vehicle combination on which the tank was secured was assisting him.

Following the preliminary tests on the automatic valves, the operator connected the iso-container according to the colour coding and the indications on the 2 couplings: one green (the colour used for nitrogen which can be used to accelerate the drainage), and the other marked by 2 red lines (the usual marking for the eduction tube). He removed the plugs on the automatic valves, connected the fill hose to the valve marked with the eduction tube, connected the capacitive overfill probe and the flexible fumes evacuation tube toward the stack to the valve marked with the green colour coding. He then began transferring the PCl_3 by releasing the pneumatic automatic valves by the manual valves, connecting them to the tractor's compressed air system and then starting the loading pump. These manual valves are marked "gaspendel" and "steigrohr", which mean nothing to the operators.

After 3 minutes, the capacitive overfill probe was triggered causing the loading pump to stop and the automatic valves to shut. As there was no obvious anomaly, the operator cleaned the probe and repeated the loading procedure twice, the alarm was triggered again after 2 minutes.

During the 4th attempt, the operator first spread the probe's contacts then started the loading sequence again. The PCl_3 overflowed from the degassing pipe (a flexible, non-hermetic hose).

Accident in the afternoon of 08/25/03 – Degassing:

After having analysed and understood the causes of the incident that same morning (confusion between the eduction and vent pipes), the iso-container's degassing operation was undertaken. The latter has a slight overpressure due to exposure to the sun. After the driver had operated a valve, the internal pressure caused liquid to be sprayed onto the operator.

The consequences:

Accident on the morning of 08/25/03 – Loading:

According to the operator, roughly one hundred litres of phosphorus trichloride released into the atmosphere hydrolysed to form a compact and dense cloud of hydrogen chloride, which is extremely difficult to dissipate.

Upon seeing the white cloud, the operators in the control room put the establishment's Internal Contingency Plan into action. A "peacock tail" type water curtain was set up. Problems were encountered in triggering the fire fighting pumps: 3 calls were necessary. The Internal Contingency Plan was lifted 20 minutes after it had been initiated.

Pushed by a slight northerly wind (4 to 5 m/s), the cloud moved several hundred metres without dissipating. Five employees in a neighbouring chemical site (High Threshold Seveso) were affected. That site also initiated its Internal Contingency Plan and 10 employees from an industrial waste treatment company ordered its personnel to confine themselves. No one was injured (including the operator or the driver) on the site that was directly involved.

Accident in the afternoon of 08/25/03 – Degassing:

The legs of the operator sprayed by the PCl_3 were burned (1st degree burns). The driver, standing to the side, was affected and received slight burns on the forearms.

The volume of PCl_3 released was evaluated to be at less than one hundred litres, although the size of the resulting hydrogen chloride cloud lead the operator to trigger his Internal Contingency Plan once again. As a result of a wind change (westerly – 10 m/sec), the neighbouring sites were not concerned by the cloud, but the neighbouring chemical site nevertheless put its Internal Contingency Plan into motion as a precautionary measure.

During these 2 incidents, the tank contained only 4.65 t (2.9 m^3) of PCl_3, approximately 200 l (300 to 350 kg) of which was probably vapourised.

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 indicated in the appendix hereto and are available at the following address: http://www.aria.ecologie.gouv.fr

The 350 kg of phosphorus trichloride released represents 1.75 % of the corresponding Seveso threshold (20 t – highly toxic), which equals level 3 of the "quantities of dangerous materials" index according to parameter Q1. Level 3 of the "human and social consequences" index is associated with paragraph H5: 15 individuals in the surrounding population and 2 site employees received care at the site for slight burns.

ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENTS

Accident on the morning of 08/25/03 – Loading

The inversion of the filling and degassing line connections caused the PCl_3 to leak via the eduction pipe connected to the degassing pipe. The coloured couplings (removable) differentiating the valve connected to the eduction pipe from the one connected to the iso-container's vent and the indications in German on the manual valves were not understood by the operators ("gaspendel" and "steigrohr" mean "vent" and "eduction pipe" respectively).

Accident in the afternoon of 08/25/03 – Degassing

During the degassing operation, the 2 blind flanges were removed but only the degassing pipe and the probe were installed on the vent. The eduction tube was thus not protected. By erroneously actuating the eduction tube's manual opening valve instead of the vent's opening valve, the driver opened the eduction tube through which the liquid sprayed due to the slight overpressure in the container.

Degassing is not habitual at the site. Although it had been analysed, this operation did not follow the normal process with regard to "process control"; the prior examination was conducted without regard for safety and analysis instructions that notably specify lists of elements to be examined, which was omitted in this case.

ACTION TAKEN

Immediate technical action:

The next day, degassing was continued prior to taking the container to the German contractor site. To do this, the operators intervened wearing hermetic suits and breathing apparatus. An emergency response team stood by during the operation (Marseilles public services). In addition, in order to better manage the degassing operation, 2 manual valves were added in addition to the automatic valves.

Short and medium-term technical and organisational actions:

The loading station was modified with a rigid arm on the loading line and with a hermetic collection pipe for connecting it to the stack.

Personnel protection was improved. Plastic gloves and overalls are maintained, although new hardhats with protective visors will be supplied.

In addition to the measures taken to ensure that firefighting means are deployed faster (water pumps), the procedures of the Internal Contingency Plan were modified to include information about the surrounding sites should an alert be sounded.

The approval procedure for new packaging was reviewed: all new container models can be admitted only following a validation procedure with the material's technical manuals and drawings in French.

Following the changes made by the operator, the site personnel (operator) went to the contractor's main site in Germany (the group became operator in 2004) to exchange good practices with the German operators.

A working group, internal to the Group's European units (The Netherlands, Germany, France), was set up to more closely examine the specificities and the risks associated with the loading stations and the chemical products, in terms of both 'hygiene and safety' and the environment.

LESSONS LEARNED

Several elements of feedback can be retained:

- ✓ The loading and unloading phases are particularly accident-risk operations which require enhanced awareness in this respect.

- ✓ Despite the term "iso-container", there are no European standards regarding these tanks or the colour-coding associated with their openings. At each industrial site, it is also important to define clear and standardised signage for connecting elements, valves, and conduits…and ensure that the operating instructions are written in French.

- ✓ The use of new equipment and materials is a risk factor: a validation procedure for this equipment associated with personnel training should improve safety.

- ✓ An inhabitual or exceptional operation – which could lead to an accidental situation as described above – must be subjected to a complete risk analysis beforehand in order to avoid creating an accident.