Release of sulphur dichloride and hydrogen chloride

26 April, 2006

Catenoy – [Oise]

France

Fine chemicals
Distillation
Pressure sensor
Control valve
Design / dimensioning
Lock-out/lock-out removal

THE INSTALLATIONS IN QUESTION

The site:

The chemical plant manufactures intermediate chemical products used in the synthesis of antioxidants that in turn are used to manufacture industrial and general consumption products in order to improve their performance characteristics (plastic materials, electric cables, and foodstuffs, etc.).

The site, which employs roughly 100 people, runs reactions in which phenol compounds are alkylated by isobutene, and then the resultant molecules are cross-linked by sulphidation using sulphur dichloride. The distillation columns used in these workshops, which include 20 to 40 theoretical platforms, can operate in vacuum up to 250 °C. The production equipment mainly includes around ten reactors ranging from 6 to 26 m^3.

The plant is subject to authorisation with public easement (AS) particularly for the storage of sulphur dichloride; the last prefectoral order governing the operation dates back to August 30, 1996.

The unit concerned:

The sulphur dichloride (SCl_2) distillation unit involved in the accident comprises the following elements:

- a boiler with a 150 kg capacity
- a ∅ 300 mm distillation column comprising two layers each measuring 1.5 m high
- control equipment (steam supply valve, SCl_2 supply valve, etc.)
- safety equipment (process PLC, pressure and temperature sensors, pressure switch, …).

The sulphur monochloride and dichloride mixture delivered to the site is enriched with dichloride through continuous distillation; it is then stabilised with phosphorous trichloride (PCl3) before being transferred to the TBM6 [2,2'-thiobis (3-methyl 6-tertiobutyl phenol) or 2,2'-thiobis(6-tertiobutyl metacresol)] synthesis or sulphidation installations.

The operator monitoring the distillation of the crude dichloride is also in charge of:

- regularly inspecting the installation,
- recording production parameters
- adjusting the opening of the distilled dichloride filling valve to maintain the stability of the column's sensitive temperatures and to ensure a regular flow of distilled dichloride.

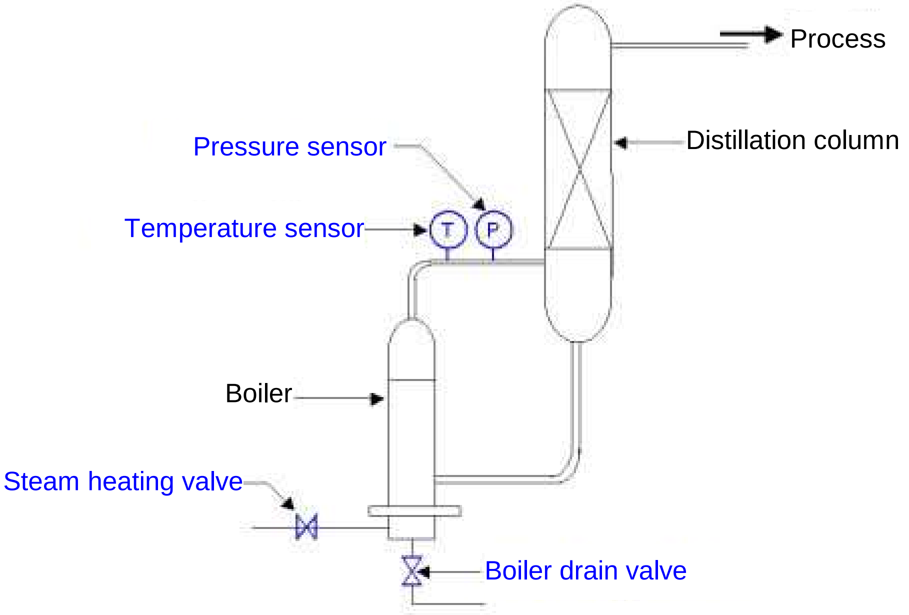
Distillation column

Sources: DRIRE Picardie

THE ACCIDENT, ITS BEHAVIOUR, EFFECTS AND CONSEQUENCES

The accident:

On April 26, 2006, the sulphur dichloride installation was operating normally.



Boiler
Sources: DRIRE Picardie

At 7.50 am, an excess pressure of 108 mbar was recorded at the outlet of the boiler containing sulphur dichloride. The installation then automatically switched to standby mode owing the high-pressure safety system (threshold = 100 mbar). The sulphur dichloride supply and heating steam control valves closed and the sulphur monochloride circulating pump shut down.

In the absence of heating, the installation began to cool down (boiler outlet temperature 28℃ at 9 am) although the pressure sensor on the boiler's junction pipe and the distillation column still indicated a high pressure. The investigations showed that this sensor was faulty; a work order stipulating its replacement with an identical sensor was thus drawn up by the workshop supervisor.

At 11.30 am, with the installation still shut down (heating setpoint at 0%, valves closed), the maintenance technician observed that it was impossible to drain the boiler when attempting to remove the pressure sensor in place.

Branch connection exiting the boiler (*Sources: DRIRE Picardie)*

1 : temperature sensor
2 : pressure sensor

He also noted that the pressure sensor could not be dismantled from its shut-off valve as the connecting bolts had seized. As he was unable to forcibly remove this part of the installation without risking a rupture of the metal/glass interface, the technician removed the entire assembly, thus allowing air to enter the installation via the sensor's branch connection (ND 25).

At 11.50 am, a release of hydrogen chloride (HCl) was observed in the distillation workshop.

At 12.05 pm, the alarm was sounded after 3 alarm triggering points were actuated. Two water curtains were set up around the column.

At 12.20 pm, the establishment's internal contingency plan was put into action and the decision to evacuate the site and implement a third water curtain was taken.

At 12.25 pm, two individuals from a second team, assisted by a third, were able to shut off the steam supply.

The external emergency services arrived at the site at 12.40 pm.

The internal contingency plan was stepped down at 1.30 pm, after the situation had returned to normal and a series of atmospheric measurements had been taken.

Consequences:

- Environmental consequences

No direct environmental consequences were recorded. The atmospheric hydrogen chloride measurements taken outside the site did not indicate any accidental pollution; only 50 ppm was recorded in the distillation column.

The 150 m^3 of water used by the water curtains deployed to neutralise the acid cloud was recovered (pH = 7), distilled and recycled in the process.

- Human consequences

The three employees who had entered the building during the operation had suffered from irritations and were thus hospitalised less than 24 hours.

- Activity and economic consequences

The activity downstream from the sulphur dichloride distillation operation, namely the synthesis of TBM6, was shut down for 18 days. Operating losses were evaluated at 270 k€.

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 that oversees the application of the ‘SEVESO’ directive, and considering the available information, the accident can be characterised by the following 4 indices.

The parameters that comprise these indices and the corresponding rating method are available at the following address: http://aria.ecologie.gouv.fr.

As the materials sulphur dichloride and hydrogen chloride are designated in the Seveso directive with thresholds of 1 t and 250 t respectively, the "dangerous materials released" index is at least equal to 1 (parameter Q1).

As three employees were hospitalised less than 24 h, the "human and social consequences" index is equal to 1 (parameter H5).

As the internal operating losses associated with the accident are less than 0.5 M€, the "economic consequences" index is equal to 1 (parameter €16).

ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

Various investigations were conducted on the process, products and intervention procedures to determine the cause of the accident.

The tests conducted on the electrical portion of the faulty sensor showed that it had operated normally during the accident. The faulty pressure measurement most likely resulted from solid deposits of impurities on the sensor membrane (PCl_5, sulphur, etc.).

The fault tree compiled by the operator, and subject to critical examination by a third-party expert, shows a combination of several undesirable initiating events:

- **the presence of 150 kg of sulphur dichloride in the boiler during the maintenance operation (lock-out defects)**: the potential hazard subsists as it was not possible to drain the boiler due to the clogged bottom valve. The analysis highlighted the presence of glass debris (failure of the mounting of the packing support disk) mixed with product deposits (low-quality sulphur dichloride) was the reason for the clogging;

- **boiler reheating** : when the high-pressure level was detected (> 100 mbar), the steam control valve heating the contents of the boiler was shut by the process control PLC. Disconnection of the sensor during its replacement triggers a –25 mbar signal to be transmitted that controls the re-opening of the steam control valve and reheating of the boiler;

- **pressure sensor branch connection open** : as the corrosion of the threaded fasteners of the pressure sensor's shut-off valve had essentially welded it to the mounting piping, the operators disassembled the entire valve/sensor assembly so as not to risk rupturing the metal/glass interface. This operation was not compliant with the initial work order.

An accident fault tree is provided in the appendix hereto.

ACTIONS TAKEN

Technical action:

The operator took several measures immediately to secure the sulphur dichloride distillation unit:

- **reinforcement of the lock-out/lock-out removal procedure** on critical installations, reminder of rules and responsibilities and definition of a checklist for "routine" operations***;***
- **replacement of a pressure sensor** by a sensor using the same technology;
- **complete cleaning of the installations*:*** neutralisation of acid traces on the outside of equipment and cleaning of clogging residues inside the installation;
- **operational control of the installation and interlocks;**
- **modification of the shutter / pressure sensor assembly.**

In the medium term, the operator shall implement the following safety measures:

- creation of a **pre-completed chemical lock-out form** in case of intervention on the distillation column, in order to outline the installation's lock-out problems;

- **retightening of the liner support platform fixtures** on the distillation column and **shut-down**, after exchange with the supplier, **stabilisation of the sulphur dichloride with PCl_5** in order to reduce or halt the generation of glass debris and product deposits;

- installation of a **fail safe loop** (pressure switch at top of column, safety relays and On/Off valve upstream from the steam control valve) **independent of the control** restricting automatic restart after the high pressure threshold has been attained (manual reset mandatory);

- **formalisation of the test procedure** of alarm triggering points;

- **definition of sulphur dichloride distillation procedures, in normal and downgraded situations**: description of actions to be taken in case the sulphur dichloride storage tank is overfilled, and restart of the installation after a shutdown and/or an intervention;

- **study of possible deviations and inherent risks in each stage of the dichloride transfer and distillation**.

In the longer term, complementary actions are planned, including:

- **overhaul of the work request procedure** to clarify the roles and responsibilities of the staff involved;
- including the retightening of platform fixtures of the column in the **maintenance programme**;
- implementation of a **fail-safe configuration in the safety system** capable of securing the installation when the high pressure threshold is reached;
- **modification in the assembly of pressure sensors installed** on pipes without shut-off valves.

Finally, the manufacturer intends to improve the distillation column's overall safety level through the implementation of the following measures:

- a SIL2 type **second fail safe safety system**; (SIL: Safety Integrity Level – characterises the quality of the safety chain);
- **pressure sensor and pressure switch assembled "directly"** on the ND50 glass tubes to prevent all risk of clogging. This system will trigger the installation's safety system from a new safety PLC and **4 new dedicated automatic valves**, including a steam valve;
- a **valve calibrated at 300 mbar** installed at the top of the column and dimensioned to address the supposedly radical phenomenon (maximum opening of the boiler's steam valve);
- **pressure testing** of the column conducted at 300 mbar;
- an **alarm reported** on the workstation of the operator dedicated to the sulphur dichloride.

The cost of all these measures was evaluated at 93 k€.

LESSONS LEARNT

The accident, which occurred in an installation that had not been examined during the danger study, brought the following points to light:

- the importance of detecting, controlling and assessing the consequences of changes in the nature of stabilisers and other additives added to dangerous raw materials (sulphur dichloride) by suppliers. These modifications may be a source of triggering events (crystallisation and clogging in this case) and increased risk;
- Even if events that seem insignificant in the smooth running of the process such as the presence of glass debris from the lining of the distillation column coupled with the lack of a maintenance program on the production equipment (cleaning of the boiler) or safety equipment (clogging of the pressure sensor) do not directly lead to accidents, can have a considerable impact on the safety in downgraded modes;
- a routine, unusual or exceptional maintenance operation (replacement of a pressure sensor) must be subject to a complete prior risk analysis, in order to avoid creating conditions which could lead to an accident or aggravate the initial consequences. In case of dangerous substances, these operations must be monitored and re-evaluated according to the hazards of the intervention;
- the relative efficiency and the reliability of the procedures and more generally, organisational barriers (lock-out/lock-out removal);
- a control system (steam valve) for a process can in no way be considered a safety system and cannot be retained as such. In particular, the production PLCs follow logic and criteria which the intervention teams are not fully aware of and which do not necessarily take the downgraded modes and lock-out situations into account.
- the importance of installation design as early as the design phase (glass/metal interface);
- the importance of risk analysis and failure modes, as well as technical and organisational barriers, with maximum details, for the various "operating" modes.

APPENDIX: fault tree of the accident which occurred on April 26, 2006