Release of a chlorinated organic chemical
2 June 2017
Mazingarbe (Pas-de-Calais)
France

Chemicals
PVC
Polymerisation
Runaway of an exothermic reaction

THE ACCIDENT AND ITS CONSEQUENCES

At around 3:15 p.m., vinyl chloride monomer (VCM ; which is carcinogenic, mutagenic, and toxic to reproduction) was released following the thermic runaway of a reactor at a polymerisation facility of a basic-plastics (PVC) manufacturing plant.

At around 2:50 p.m., the emergency diesel generators started up to power the safety and monitoring-control systems after the plant's main power supply shut off and the 20 kV emergency electrical supply failed to take over. The plant's units automatically placed in the safe position.

Without electricity, the polymerisation reactors were no longer being stirred. As a result, substances known as 'polymerisation stoppers' or 'reaction killers' were automatically fed into them. However, this did not occur in one of the facility's 22 reactors because its inhibition system failed. The uncontrolled polymerisation that ensued in this reactor caused its internal pressure to rise. When this pressure reached 16 bar, one of the two pneumatic relief valves (automatic safety) failed to open, allowing the reactor pressure to continue to increase. The site's technicians manually opened the second valve by turning on an emergency air compressor, but the reactor pressure continued to rise, ultimately causing the 20 bar safety valve to open and release VCM into the atmosphere.

At around 3:30 p.m., the 20 kV supply was restored and stirring in the reactor restarted. This cooled down the reactor and decreased the pressure. The situation was brought under control at around 3:50 p.m. when the valve closed after the pressure returned to 13.9 bar.

The amount of VCM released into the air was continuously measured using a fibre-optic infrared analyser. The operator estimated that 90 kg of VCM was emitted from the site's 40 m-high stack (referred to as a 'cold flare').

The emission limit value of the chemical oxygen demand (COD) for waste water was exceeded for several days due to the reaction killers (which contained DEHA [N,N-Diethylhydroxylamine]), being injected into the reactors that were operating when the electrical power supply was lost. Internal treatment of the effluent did not completely compensate for the high COD concentration.

THE ORIGIN AND THE CAUSES

The accident was caused by a series of technical failures on various components that work together to ensure the facilities remain safe:

- loss of the main power electric supply:

The significant rise in temperature inside the 45 kV transformer room, which occurred when the main network's fans shut off, is what caused the main power supply to shut off. The electrical panel powering the network's fans had a faulty electrical outlet that caused the panel to trip when a device was plugged into it. A high-temperature alarm on the 45 kV electrical network tripped during the technicians' rotation. However, they did not deem it a priority;

- secondary-network switchover failure:

A programming fault in managing the alarms of the 45 kV network prevented the switchover to the 20 kV secondary network;

- failure of the reaction inhibition system on a reactor:

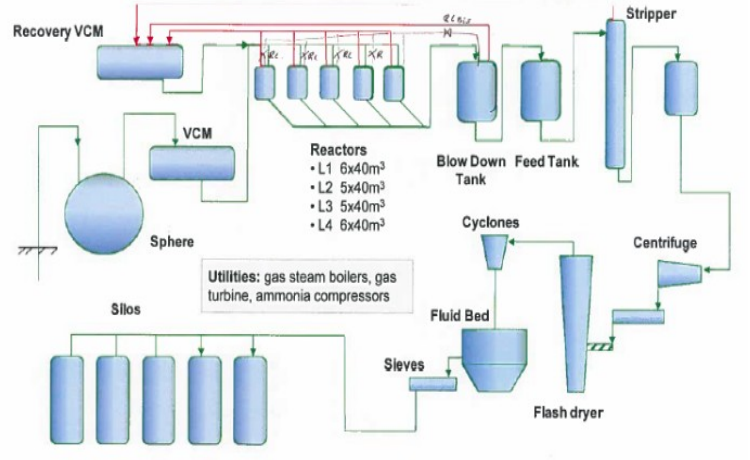
The reaction inhibition system is an active safety function that trips when the pressure in the reactor is high (15 bar) or when stirring is lost. When the accident occurred, the 'reaction killer' was injected due to the second situation. This injection, carried out using nitrogen as a driving gas, failed for one of the 22 reactors due to a loss of pressure in the nitrogen line that made it impossible to achieve the pressure difference needed to break the rupture disc between the tank and the reactor ;

- lack of pressure in the compressed air network:

When the reactor pressure reaches 16 bar, two reactors relief valves (actuated using compressed air) automatically open to the 120 m^3 blowdown tank (BDT). One of the two relief valves upstream of the BDT and fitted on the relief line shared by the reactors did not open due to the lack of pressure in the compressed air network. The compressor supplying the network is backed by a diesel generator but requires that a technician be physically present to restart it. This operation took some time and, all the while, the reactor pressure was increasing ;

- the reactor valve, the last line of defence:

Each reactor has a relief valve (setting of them 20 bar). Each valve is connected to the gas discharge network, which leads to a 40 m-high stack fitted with a continuous measurement system.



Simplified diagram of the PVC manufacturing process

FOLLOW-UP ACTIONS TAKEN

Following the accident, the inspection authorities for classified facilities arrived at the site to hear the operator's initial analysis and ask it to look for the root causes. Corrective actions were quickly taken, in particular:

- correction of the programming fault that prevented the 45 kV from automatically switching over to the 20 kV network;
- update of the list of equipment that automatically starts back up or must be started and writing of the associated operating instructions;
- check of the inventory of outlets in the facility and creation of a dedicated electrical supply for the 5 kV transformer's fan;
- check of the relief valves at the reactor outlets leading to the BDT.

After performing a causal tree analysis, the following actions were taken:

- creation of an overall supervision view of the reactors and creation of an alarm that appears when there are problems with injecting reaction killers into the reactor;
- leak detection by means of loss of nitrogen pressure (with alarm);
- closer follow-up of electrical check reports and main-to-backup power supply switchover tests.

The inspection authorities requested that the action be implemented. This implementation is being monitored closely.

LESSONS LEARNT

This sequence of technical failures prompted the operator to look into equipment and processes that would prevent this type of accident from recurring.

The operator made two changes to the electrical network's supervision alarms. It added an audible and visual alert that activates when a problem is detected on the 45 kV network and characterised their management priority based on the required response time. A clearer message allows technicians to take the right decisions based on the various alarms to be managed.

The operator also analysed the electrical vulnerability of its facilities. This analysis confirmed that risk management measures will operate properly in the event of a major accident and that the organisation currently in place was relevant. Avenues for improvement were nevertheless identified.

The reliability of the three safety levels currently in place to avoid the risk of runaway reactions is increased by the use of diesel generators associated with a supervision system. That ensures that the reactors are stirred at rated power if the main power supply is lost and planned replacement of the compressor with automatic restart along with the display of information on the control room panel (air network pressure, compressor states, alarms).

The operator is also considering whether to create a second reaction killer injection channel.