Release of ethylene to the atmosphere

21 July, 2005 and 21 September, 2005

Saint-Avold – [Moselle]

France

Petrochemistry
Polyethylene
Ethylene
Rupture disc
Clogging / Fouling
Equipment failure
Organisation / maintenance fault

THE INSTALLATIONS IN QUESTION

The site:

The establishment, located in Saint-Avold in the county of Moselle, is part of a vast industrial platform spread over 340 hectares, and created in 1954. The platform includes a variety of activities associated with the chemistry and petrochemistry sectors. The petrochemical activity of the establishment was developed during the 1960s with an initial steam cracker and a polyethylene manufacturing unit commissioned in 1969.

With 900 employees in 2006, its activities today range from basis petrochemical products (ethylene, propylene, benzene, and styrene) to consumer plastics (polyethylene and polystyrene).

This establishment includes a number of installations subject to authorisation with public utility easement. It is classified high-level "SEVESO" owing to the quantities of dangerous substances manufactured and implemented (flammable and/or toxic substances).

The unit concerned:

The unit involved is a continuous low-density polyethylene manufacturing unit (LDPE). It consists of 3 production lines with a total capacity of 765 tons of LDPE/day. The process implemented involves the high-pressure radical polymerisation of the ethylene:

$$n\ CH_2{=}CH_2 \xrightarrow[\text{Peroxydes (initiators)}]{\substack{P>1000\ b \\ T \approx 150 \text{ to } 300\ ^\circ C}} (-CH_2\text{-}CH_2\text{-})_n$$

Considering the exothermal character of this reaction and due to the extreme flammability of ethylene, this unit represents a particularly dangerous hazard.

A simplified description of the reaction is as follows (see figure 1): the ethylene undergoes polymerisation in a reactor pressurised between 1,000 and 2,200 bar and at temperatures ranging from 150 to 300 °C. The pressure is controlled by a valve located at the outlet of the reactor; this valve also is used to extract the reagent / polyethylene mixture. The mixture is then directed to the separator of the Medium Pressure Return line where it is separated into two phases (approximately 20% polymers and 80% ethylene as the conversion rate of the reaction is in the order of 20%). The polyethylene drawn from the lower part is then conveyed to the high then low pressure hopper. The ethylene is also conveyed with the polymer phase.

The largest fraction, the ethylene which exits the upper portion, is cooled then recycled by the MPR line to the intake of the secondary compressor.

The low polymers (greases) are extracted during the cooling of the recycled ethylene in the medium pressure return lines. These polymers are trapped in the tanks (grease cylinders) which are purged to the grease hoppers one after the other. The greases can then be drawn or reinjected to the low-pressure hopper.

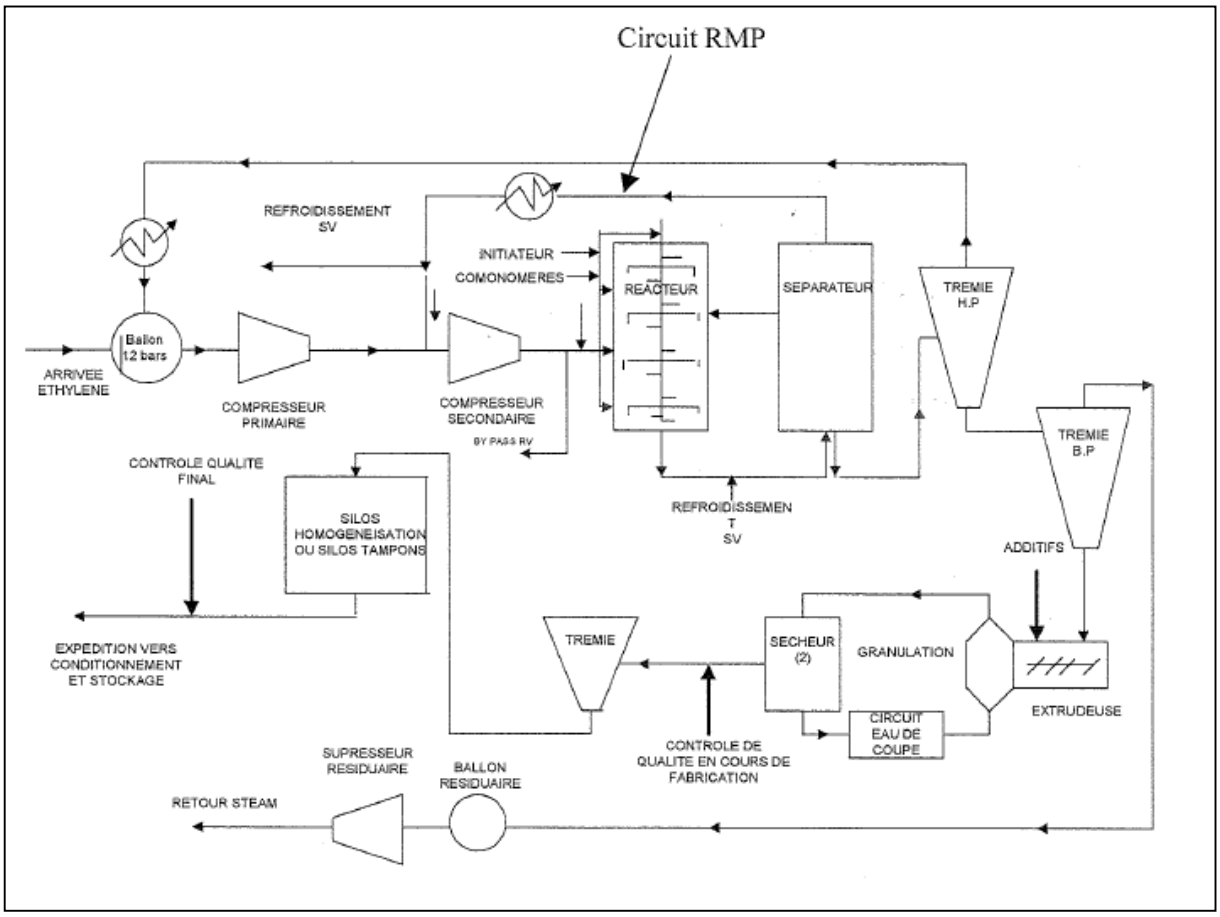

Figure 1: Simplified diagram of the process

THE ACCIDENTS, THEIR BEHAVIOUR, EFFECTS AND CONSEQUENCES

July 21, 2005: rupture of disc resulting in the release of 3.2 t of ethylene to the atmosphere

The accident:

On July 10, 2005, a leak was detected on the filling valve of a grease cylinder (MPR) on line 42 in the workshop; the cylinder was cooled down and was not in use pending servicing by the operating and maintenance crews. The repair took place July 20: the line was shut down for 4 hours for servicing, then restarted the same day at around 6 pm.

On July 21st, the primary compressor tripped two times due to a fault detected on the lubrication system of the compressor. Shortly after the line was restarted after the compressor tripped the second time, the pressure measurement on the inlet of the secondary compressor indicated a value in excess of 300 bar while the valve at the outlet of the primary compressor should have opened at 284 bar. In addition, the primary compressor should have tripped off automatically (standby) at 270 bar. This did not happen. Noting the abnormal increase in pressure, the operator switched to manual mode to reduce the pressure. Too late: the pressure increased rapidly to 310 bar causing the disc protecting this part of the installation (MRP) to rupture and the release of 3.2 tons of ethylene into the atmosphere.

The consequences:

The event did not have an impact on people or the environment. The conduit of the rupture disc is directed toward a 20-meter high stack. The cloud thus dispersed rapidly. Dispersion models conducted by the operator showed that the cloud did not fall to the ground and that its flammability limits were a few limits from the stack; concerning the risks of cloud exploding, simulations showed that the explosive mass in the ethylene cloud was too small (6 to 7 kg) to generate an explosion in an unconfined space.

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 .

The quantity of ethylene released into the atmosphere was evaluated at 3.2 tons. The upper classification threshold associated with extremely flammable gases is set at 50 tons. Parameter Q1 is thus rated as 3 (3.2 x 100/50=6.4%).

The incident had no human, social or environmental consequences. The economic consequences were well below the classification threshold.

September 21, 2005: rupture of disc resulting in the release of 1.4 t of ethylene to the atmosphere

The accident:

On September 21, 2005 at 6.15, line 41 of the polyethylene unit was shut down for programmed maintenance to be performed during the day. According to the established shut-down procedure, the reactor is rinsed automatically, and purged three times. Each purge (or flushing operation) is conducted in two phases:

- the ethylene reactor is pressurised to 600 bar with the secondary compressor,
- depressurisation to the MRP line.

During depressurisation of the first flushing operation, a rupture disc opened on the grease cylinder of the MRP line, resulting in the release of 1.4 tons of ethylene to the atmosphere.

The consequences:

As with the event which took place July 21st, this accident had no human or environmental impact (rapid dispersion at altitude and a quantity released less than that of 07/21).

European scale of industrial accidents:

The accident can be characterised by the following 4 indexes:

The quantity of ethylene released into the atmosphere was evaluated at 1.4 tons. The upper classification threshold associated with extremely flammable gases is set at 50 tons. Parameter Q1 is thus rated as 3 (1.4 x 100/50=2.8%).

The incident had no human, social or environmental consequences. The economic consequences were well below the classification threshold.

ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENTS

July 21, 2005: rupture of disc resulting in the release of 3.2 t of ethylene to the atmosphere

The various investigations conducted following the accidents showed that two malfunctions were necessary in order for the pressure on the discharge side of the primary compressor to exceed 310 bar and lead to the rupture of the disc protecting this section:

- The primary compressor did not trip off at 270 bar as designed. The pressure control gauge was partially plugged, thus leading to a measurement taken into account by the controller that was actually lower than the actual pressure. The operator, having noted an abnormal pressure increase in the unit, switched the primary compressor control to manual to reduce the pressure. Switching to manual inactivated the automatic tripping mechanism of the compressor.

- The valve, theoretically calibrated at 284 bar, did not open at this pressure. This malfunction resulted from a maintenance operation during which the valve replacement procedure was not respected (calibration pressure > 310 bar).

The increase in pressure was thus an aggravating factor to these two malfunctions. The analyses following the incident tend to show that the increase in pressure was aggravated by an abnormally high level of clogging in the MPR section due to several days of operation without purging the grease.

It should be noted that the rupture disc was efficient in performing its role in protecting the equipment.

September 21, 2005: rupture of disc resulting in the release of 1.4 t of ethylene to the atmosphere

The release of the disc occurred following an increase in pressure in the MPR line during the reactor rinsing phase after the programmed maintenance shut-down. The dismantling of the equipment in order to replace the failed rupture disc revealed that the check valves on the MPR line were clogged with grease. In fact, during the production shut-down and subsequent rinsing operation, variations in pressure and output in the MPR line moved the accumulated grease onto the check valves to the point that they became plugged.

For line 41, a larger quantity of grease than normal is associated with the introduction of co-monomers, required to obtain certain quantities of polyethylene manufactured.

ACTIONS TAKEN

July 21, 2005: rupture of disc resulting in the release of 3.2 t of ethylene to the atmosphere

The operator was required to apply several provisions as stipulated by an additional prefectoral order:

- modification of the tripping conditions of the primary compressor so that this operation is active both in automatic and manual mode,

- fail-safe operation of the pressure measurement triggering the tripping sequence,

- Integration of the valve replacement procedure in the training and certification process,

- formalisation of grease cylinder operating rules to prevent clogging of the lines. Furthermore, the operator was requested to further complete its danger study with an analysis of the causes and consequences of the clogging in the MPR sections.

September 21, 2005: rupture of disc resulting in the release of 1.4 t of ethylene to the atmosphere

Reflective thinking regarding the technology of the check valves used was required to reduce the accumulation of grease in this equipment. This study lead to the removal of this equipment following risk analyses showing that their removal would not downgrade the unit's level of safety. These check valves were initially installed to ensure safety.

In addition, as proper cleaning of the installation has an impact on safety, formal procedures were drawn up outlining the type and frequency of the cleaning operations to be performed. These operations are now checked and recorded. Performance indicators were defined to determine the efficiency of these cleaning operations.

These provisions were registered by an additional prefectoral order.

LESSONS LEARNT

The first incident was an advance warning signal of the risk associated with the lines clogging with grease. The second incident only confirmed this risk by underlining that the equipment initially installed to provide a safety function, can also be responsible for causing incidents. These two events show the need to conduct risk analysis, including for the installation of "safety" equipment so that they do not add additional risks that are greater than those that they are intended to prevent.

The installation of safety devices must thus be prepared and be subject to safety analyses as any modification made to a dangerous installation, notably those classified as high-level SEVESO.

Furthermore, these two incidents illustrate:

- that switching an automated action to manual may inactivate an automatic safety feature.
- that replacing "ultimate" safety devices such as a safety valve or rupture disc must be governed by the strict application of clear and pragmatic instructions.