Overpressure in a reactor in an organic synthesis workshop

March 23, 2004

Montluçon – [Allier]

France

Gaseous release
Chemistry
Cyanide
Pressurised equipment
Burst disc
Valve
Field of safety
Organisation / human factor

THE INSTALLATIONS AND OPERATIONS CONCERNED

The chemical plant belongs to an industrial group that federates small independent structures, including 7 production sites in France. The Montluçon site, located in an urban zone, has a workforce of 56 people. It is dedicated to products for the pharmaceutical and electronics industry, which little by little are being substituted for agrochemical products. The plant has two synthesis shops called "organic synthesis shop I and II" equipped with multi-purpose equipment representing a total reactor volume of approximately 115 m^3, a finishing workshop (drying and crystallisation) and various storage facilities.

The accident took place in organic synthesis shop I. While relatively old and small (420 m², roof peak height 13 m), this multi-purpose shop houses 8 reactors and all the utilities (steam, cooling plant, neutralisation tower, fire detection and automatic extinguishing system) and conducts a large number of traditional organic chemical operations in aqueous environments or in solvents as well as physical-chemical operations.

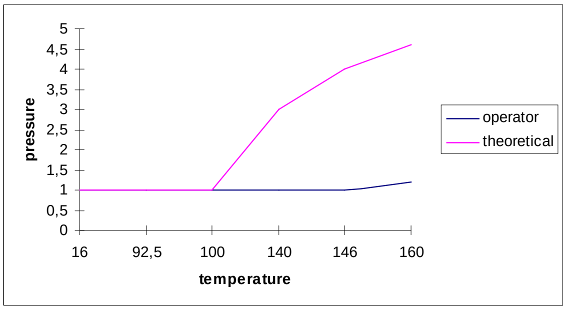
THE ACCIDENT, ITS BEHAVIOUR AND CONSEQUENCES

The accident:

On March 23, 2004 at 2 pm, the R201 reactor was loaded with the effluents from the neutralisation tower contained in the 3 tanks, for total of 4.4 m^3. A cyanide concentration of 6 ppm is analysed on one of the tanks.

At 3.40 pm, when the load was finished, the operators opened the steam circulation in the double walled reactor to heat up the environment. The operators' readings on the increased temperature of the reaction environment and the pressure indicated on the pressure gauge were as follows:

- 3.40 pm T= 16°C P = P atmospheric
- 5.00 pm T= 95.2°C P = P atmospheric
- 6.30 pm T= 146°C P = 1 bar
- 7.30 pm T= 160°C P = 1.2 bar



As the pressure setpoint had not yet been reached, the operators did not stop the steam heating of the reaction environment. As shown on the graph, they did not react to the inconsistency of the values between pressure and temperature.

During the 7.30 pm reading, just prior to the accident, an operator noted a leak on the reactor's manhole and tightened its bolts without giving any thought to this indirect alarm signal. The burst disc ruptured 3 minutes later, releasing steam into the workshop; part of the fibrocement roof was blown away.

The 3 operators present, standing about 20 metres from the reactor, evacuated the workshop after a short lapse of approximately 10 seconds due to the surprise.

It appears that the noise of the steam exiting via the ruptured disc could be heard for 2 to 3 minutes. After this period, the operators entered the workshop, secured the reactor (heating and insulation shut off) and ventilated the area (extractor).

The volume of water transformed into steam and lost in the accident was 1,350 litres (1680 m3 of water vapour).

The consequences:

The direct consequences are uniquely equipment:

✓ one rupture disc destroyed,

✓ some pipe jacketing was destroyed,

✓ a few m² of fibrocement roofing blown out (see photo).

The damage was evaluated at 8 k€.

The environmental consequences were low: the cyanides were completely destroyed (not detected in the reaction environment residue) and the measurements conducted on the gaseous atmosphere and in the environment showed no trace of hydrocyanic acid. Note: the concentration in the effluents to be treated were already low (6 ppm).

The human consequences were also low. The operators, surprised by the explosion, were shocked, but decided not to go to the hospital as the public emergency services had suggested. Retightening the manhole could have lead to much worse consequences for the operator. Despite the shop's relatively small surface area, the operators were located a distance from reactor R201 at the time of the explosion. This distance explains why they were only slightly affected.

Roof damage

As the explosion was perceived outside the site, the public authorities were initially alerted by calls from residents. The Montluçon firemen arrived in 11 minutes (from the time of the explosion to their arrival at the site) with considerable means: two fire trucks, a ladder truck and a chemical hazards vehicle. The Montluçon municipal police blocked the access road to the site and evacuated the neighbouring sports facility for 30 minutes, the time required for the atmospheric measurements to determine that no pollution was present. An assistant Mayor and the Montluçon Deputy-Prefect arrived at the site.

The management of the post-accident crisis aimed at controlling the media and social consequences which would have damaged the acceptance of the activity by the residents.

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.

Dangerous materials released	☐	☐	☐	☐	☐	☐
Human and social consequences	☐	☐	☐	☐	☐	☐
Environemental consequences	☐	☐	☐	☐	☐	☐
Economic consequences	☐	☐	☐	☐	☐	☐

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 chemical substances at cause are not classified under terms of the SEVESO directive and the accident had no sufficiently significant consequences to be rated on the European scale for industrial accidents. The evacuation of the zone and the nearby sports facility for less than 2 hours has no impact on the 'human and social consequences' indices (criterion H7). Furthermore, the evaluation of internal property damage was less than 100 K€ (criteria €15).

ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

Circumstances:

The damaged reactor is the R201. It was new at the time and had been installed in the workshop since the summer of 2003. In compliance with the operator's specifications and according to regulations, the equipment was delivered without equipment or safety devices.

The operator is thus responsible for choosing and installing accessories.

When installed, the following safety equipment was installed on the R201 reactor:

- a valve (6.3 bar) (at this pressure, the saturated steam output is 1,800 kg/h, or approximately 30 kg/min).
- a rupture disc (6 bar, ND 150 mm) (at an operating temperature of 20℃).

They correspond to overall consideration of the protection of the reactors throughout the site against overpressures and represent a standardised technical solution.

At the time of the accident, the piping downstream from the R201's rupture disc had not yet been connected to the "crash tank" network of organic synthesis shop I. Only a tubular element measuring approximately one metre in length extended the branch connection vertically.

The establishment was granted prefectorial authorisation (AP No. 2168/93 dated May 11, 1993) which sets a daily release limit for the cyanides, in terms of concentration at 0.001 mg/l and flow at 14 g.

Before releasing wastewater that could contain cyanides into the community network, the operator analyses the concentration, and processes the water by a process that lowers the cyanide content, as required.

To do this, the effluents undergo thermal treatment for a few hours in a soda environment (NaOH) in order to downgrade the cyanide radical C⁝N. The water from the neutralisation towers is introduced into a reactor with the soda, then maintained at a certain temperature for 2 hours under a pressure kept at 3 bar. This operation (required only 4 to 5 times per year) was not considered to be dangerous and no special instructions were issued.

Three operators were at their workstations in the shop at the time of the accident. The operations in progress on reactor R201 showed normal operation of the workshop, without no special aspects. However, this relatively basic operation (increase in temperature of the environment and hold for 2 hours) is not frequently performed.

Causes:

The fault tree established by the operator indicates two main causes and aggravating events:

- As the pressure gauge used by the operators to control reactor steam heating was plugged in an elbow, they did not have correct pressure information. As reactor heating was controlled from this information, the operators didn't stop the heating, letting the pressure increase in the reactor.
- As the valve was calibrated at a value greater than the burst pressure of the rupture disc, the reactor was not decompressed by the value prior to the burst disc rupturing.
- The lack of a collection pipe from the burst disc aggravated the situation.

On March 30, 2004, the Classified Installations Inspectorate and the labour inspectorate noted two question points:

1st point (technical): Reason why the valve didn't work? Possible design errors?

2nd point (organisational): why didn't the operators detect the alert signals? An hour before the accident, an operator recorded the temperature and the pressure without realizing that the two parameters were incoherent. When faced with a manhole leak, the first reflex was to tighten the screws on the lugs without checking if the manhole had been correctly closed and to determine if this leak was logical in relation to the observed low pressure of 1.2 bar.

This operator's reflex demonstrates a lack of knowledge of the hazards of pressurised equipment. By retightening the nuts, force is put on the lugs which are already under stress from the pressure inside the reactor. When a lug ruptures, the stress spreads to the remaining lugs, the entire manhole is weakened successively and may break. The risk of injury is high for the operator doing the operation. In addition, the increase in pressure was not stopped; on the contrary, as the leak output was eliminated, the pressure in the chamber continued to increase.

The safety equipment installed during the installation of reactor R 201 in late August / early September 2003 in workshop S1, included:

- a valve (6.5 bar)
- a rupture disc, 6 bar (20°C).

As the two triggering threshold values are very close, it is difficult to predict, in the case of a pressure increase, which equipment will operate first, considering the precision of the calibrations and the variations of the rupture disc thresholds with the temperature.

The design of the overpressure protection and the choice of safety devices comply with regulation requirements in terms of performance characteristics. The operator set up standard protection for its reactors without looking any further. A more detailed study and in-depth reflective thinking would have discovered this design fault.

The causal tree submitted by the manufacturer emphases only the technical problem. The joint report (drafted by the Classified Installations Inspectorate and the Technical Inspections Division), and Labour Inspectorate, which goes further in the analysis, underlines the design problem (dimensioning of overpressure safety features) and inappropriate reaction by the operators who should have reported the warning signs of the danger:

✓ A design anomaly of the safety features:

The design of the overpressure safety devices for all of the site's reactors is based on the choice of standard protection of -1/+6 bar founded on the service pressure requested by the pressurised equipment manufacturer. Generally, the syntheses are conducted at atmospheric pressure; on all the manufacturing operations listed, only 6 phases are conducted under pressure.

× The trip thresholds of both devices are close and no preventive reflective thinking about their operation was carried out, thus no clearly established defensive strategy was established.

× The trip thresholds of both devices are near 6 bar, although the nominal pressure of the reaction is two time less (3 bar).

× The rupture disc's discharge pipe must be connected to the workshop's discharge network.

✓ Faulty operational control:

× The operators controlled the rise in temperature from a faulty pressure indicator. They regularly record the temperatures and pressures in the reactor, without analysing them, and did not notice the inconsistency between the two parameters.

× The operators did not react to the alarm signals, nor to the abnormal duration of the pressure increase and the manhole leak.

ACTION TAKEN

A report from the Classified Installations Inspectorate, the Technical Inspections Division (DRIRE) and the Labour Inspectorate, dated June 21, 2004, was forwarded to the District Attorney.

The causes of the accident were clearly established, the Classified Installations Inspectorate and the Technical Inspections Division also sent the report to the operator including a letter stipulating that several actions be performed:

✓ Personnel information:

× the report was sent to members of the CHSCT (the committee for hygiene, safety and working conditions), and the Inspectorate requested that the document be presented at a CHSCT meeting so that the entity could give its opinion.

× the Inspectorate also requested that the personnel training programmes and the reminders designed to improve the behaviour and knowledge of the operators as a result of the feedback about this accident also be presented to the CHSCT.

✓ Reminder of pressurised equipment regulations (ministerial decree of March 15, 2000):

× the Technical Inspection Division requested that the operator correct the lack of thoroughness in the application of the regulations concerning pressurised equipment, revealed by the accident. Article 8 establishes strict obligations: "the personnel in charge of operating pressurised equipment must be informed and competent to monitor and take all initiative required for their safe operation" and "the personnel must be deemed fit to operate pressurised equipment and periodically tested in this position".

× the Technical Inspections Division also requested that the operator provide the Inspectorate a schedule to meet the obligations of Article 6, paragraph 5 "required measures must be taken so that the release of fluid possibly caused by their operation (Editor's note : in this case, it concerns the operation of the rupture disc) is not hazardous".

Following the incident and the meeting to establish the causal tree, the operator immediately implemented an action plan. This plan called for verification of the valve opening pressure calibration on all reactors and their verification during preventive maintenance operations, as well as an inspection of all rupture discs. This action, conducted in the following days, did not highlight any anomalies. Other actions were subsequently conducted.

× A procedural modification introduced the monitoring of reactor operation based on two pieces of available information (pressure and temperature) and not just one (pressure). The procedures were also modified to include fail-safe verification of the reactor's pressure gauge with that of the supply line during the nitrogen leak tests prior to loading.

× At the request of the Classified Installations Inspectorate, the operator listed all of the reaction phases performed under pressure. The operator decided to implement a fail-safe configuration to measure the pressure on all reactions identified.

× The work enabling any fluids released by the rupture discs to be collected in a crash tank was scheduled for the summer of 2004.

Following the report by the Classified Installations Inspectorate in late June and the work performed, the operator completed its action plan by providing its operators basic training to enhance their skill levels. 30 operators should benefit from this training in 2005.

Finally, the operator undertook in-depth reflective thinking on the defensive strategy against overpressure in the reactors. As such, for reactor R201, after having analysed the operating conditions under pressure and temperature through laboratory work, the operator defined the rupture disc [bursting pressure: 6 bar at 120 ℃] as the reactor's ultimate protective barrier. The valve calibration, defined at 5.3 bar, is used to discriminate the trip thresholds. The valve must thus operate first and limit the internal pressure thereby giving the operators enough time to intervene. The design work of the safety accessories thus had to be performed *a posteriori*.

Lastly, the company changed its effluent treatment method; it no longer uses the pressurised phase to destroy traces of cyanide.

LESSONS LEARNED

Although very basic, the elements of feedback to be retained should be indicated:

✓ **Design safety devices according to the safety objectives:** this means having a defined strategy, subordinate to the safety objectives. Just respecting the regulations (for the pressurised equipment in our case) is not enough. The good strategy consists in defining the equipment's field of operational safety and the objectives to be reached for the safety barriers, then and only afterwards, select and design the components of these barriers in order to reach these objectives.

✓ **The control of all dangerous operations must not rely on a single system:** systematising the fail-safe configuration on all control-related parameters or promoting the breaking down of safety barriers for defence in depth, but always consolidating its operational safety without encumbering it or putting it off balance, remains a real permanent challenge for all players.

✓ **The place of the human factor in industrial safety, from design to operation:** this incident once again shows how important the human factor can be. From the selection of safety equipment used on the reactor to the skill level and availability in the manner to run it, man is at the core of the essential decisions.