Explosion and fire of a reactor in a chemical plant

April 17, 2003

Oudalle – [Seine-Maritime]

France

Esterification
Mineral oils
Heating
Operations
Temperature
Control room
Organisation

THE INSTALLATIONS IN QUESTION

The plant, specialised in the manufacture of additives for lubricants, is classified as high-level Seveso II. It is located in the Havre industrial estate.

The site is equipped with various manufacturing and product mixing units. The damaged unit was used to synthesize dispersing agents. It features two identical production lines. The equipment mainly consists of synthesis reactors and filtration installations.

THE ACCIDENT, ITS BEHAVIOUR AND CONSEQUENCES

The accident:

On April 17, 2003 at approximately 3 am, an explosion occurred in a dispersing agent manufacturing unit that uses oils.

Overall view of the reactor

The consequences:

The explosion resulted in very localised property damage. The effects were observed up to twenty metres from the accident (projectiles and broken glass). The reactor had opened up (see photo) despite the overpressure protection device installed.

The personnel was not affected as the accident happened at night. One person was shocked however.

View of the damaged reactor from above

The firefighting water was routed to a buffer tank to avoid it being released into the natural environment. Atmospheric releases were mainly associated with the emission of products during the fire.

The operator estimated the costs generated by the incident (including the replacement of equipment, operating losses…) at 11 million euros (direct costs: 6.5 M€ - indirect costs: 4.5 M€).

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

As the effects of the explosion had not been characterised and windows were broken at distances less than 330 m, parameter Q2 (explosive substances) was given a rating of 1.

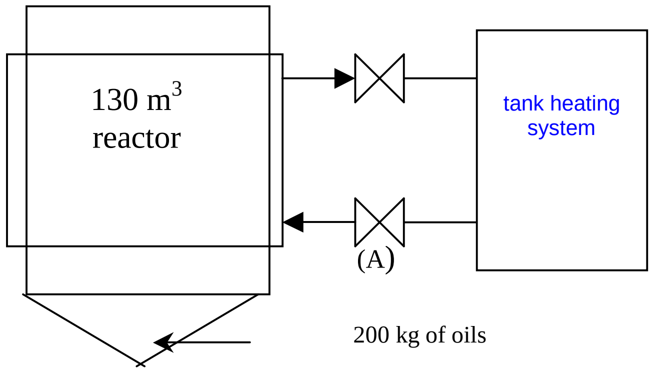
Level 3 of the "economic consequences" index results from parameters 15 (6.5 M€ of property damage in the establishment) and 16 (4.5 M€ of production losses).

ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

The operator and the French "Welding Institute" (which specialises in materials testing), an external laboratory (for the tests) and an engineering firm (for the a posteriori estimate of the energy potential released when the reactor exploded) lead to detailed investigations during the inquiry that followed the accident.

Circumstances:

Just prior to the accident:



- the unit concerned directly was completely shut down,
- the 130 m³ esterification reactor (with a capacity of 90 t) was empties after the last batch and rinsed with mineral oils (estimate: there was approximately 200 kg of oil with 5% additive in the reactor's drainage cone – which corresponds to level "0"),
- temperature rise tests were being conducted on the reactor's heating system,
- the reactor was not disconnected from the heating system. The inlet valve (A) on the reactor's heating coil remained open,
- the atmospheric temperature of the reactor thus increased and caused the mineral oils in the bottom of the reactor to evaporate and decompose,
- the unit's monitoring parameters were reported in the control room although no specific action was taken by the operators as the unit was shut down and the production personnel did not consider that the unit presented any danger, a priori.

Subsequent analysis of the unit's parameters reported to the control room showed that:

- the temperature of the thermal fluid had reached 250 °C,
- the atmospheric temperature remained around 200°C for many hours with a sudden increase in temperature just prior to the explosion. This was not noticed in the control room as the temperature alarm was set above 300°C only for "product quality"-related questions (handling of non-flammable products).

- The valve of the heating coil had opened when the boiler was made available (according to the procedure) but had to be closed when the heating system of the tanks was restarted.

Causes:

The fault tree showed:

- operating conditions prior to the accident which caused the mineral oil vapours to exceed the lower explosivity limit (temperature in the reactor above 180℃, flashpoint of the rinsing oil used, for approximately 20h). The operator assessed that in these conditions, the oil contained in the reactor had reached the boiling point.

- The presence of oxygen in the reactor at the time of the accident may be the result of degassing of a line via the reactor during maintenance work being performed near the unit concerned. According to the operator, the degassing manoeuvre was performed several times in the days prior to the accident.

- The investigations enabled several possible ignition sources to be identified:

    - Self-ignition of decomposition products generated by the reactor heater:

    Specific tests were conducted on the rinsing oils used by the operator in order to reproduce the incident in a laboratory setting.

    According to the supplier's MSDS, the self-ignition temperature of the oil used is greater than 250℃.

    The laboratory analyses on the rinsing oil indicated a self-ignition temperature of 370℃. Analyses conducted on the additive at 5% showed that the product started to decompose above 435℃. The operator also postulated that there may have been an accumulation of reaction products or sub-products in the reactor. However, the self-ignition points of these components are above 350℃. According to the parameter report, these temperatures were not reached in the reactor.

    The operator however referred to the literature, stipulating that the self-ignition temperatures of the products can be lowered by various parameters, such as: surface area of the metal, presence of oxides functioning as a catalyst, and the nature of the materials present.

    In addition, it is possible that maintaining the atmosphere of the tank at different high temperatures may have promoted the decomposition of the oil that would have reached their self-ignition temperature.

    A third-party organisation conducted tests on the oil contained in the bottom of the reactor prior to the accident. These tests did not provide information relative to the cause of the explosion. The mass effect presented by the industrial equipment can produce phenomena that cannot be detected in a laboratory setting.

    The theory of the self-ignition of fumes was neither confirmed nor overruled.

    - Static electricity:

    The non-excluded potential presence of static electricity may have caused the oil vapours to ignite. The presence of boiling oil may have generated a liquid flux on the walls of the reactor against the flow of oil vapour. This phenomenon may be the cause of a potential difference and thus an electric discharge. Nevertheless, the conclusions of the theoretical ignition analysis by an independent organisation showed that the risk was not zero, also it remains extremely low. This point was thus neither confirmed nor overruled.

    - Electric spark:

    This hypothesis was disregarded by the operator since the equipment that could potentially cause a spark is insulated or explosion-proof and there was no impact associated with lightning at the site.

ACTION TAKEN

Technical action:

Although the exact cause of the accident was not clearly determined, the operator implemented various corrective measures prior to restarting the unit in order to prevent an accident of this type from happening again, considering the two probable causes of the ignition of the vapours. Firstly, these measures were designed to limit the heating of empty equipment during shutdowns and to limit the presence or the formation of static electricity in the installations. Several measures were taken:

✓ Limitation of oil vaporization.

The operator undertook the following actions:

- installation of a temperature control system on the coolant system to limit it at 210℃. In addition, the literature indicates coolant fluids for which the flashpoint may sometimes be lowered to 60℃ depending on its water content and the ageing of the fluid. It must thus be renewed regularly, which the operator does.
- review of the operating instructions to include checks to be performed during shut down, transitory operation of installations, particularly to stop the heating of tanks in the product transfer phases and when the mixer is not operating,
- modification of the high temperature alarm on the reactor to set it at 210℃,
- increase of the sampling frequency of the IPS (several times per minute) to obtain more precise information about parameter changes.

Furthermore:

- the shut-down and maintenance procedure integrates the disconnection of the heating system equipment,
- the monitoring of shut-down installations and the maintenance procedure relative to the heating systems of the industrial capacities were applied through the site,
- the personnel received training in the new procedures,
- the inspection parameters of the installations while shut down are monitored from the control room,
- the monitoring equipment (temperature, for example) were doubled at the reactor level.

✓ Limitation of the presence of air in the reactors:

- the restarting procedure for the unit's procedure was reviewed to integrate the inerting of the nitrogen tanks.

✓ Limitation of the risk associated with the static electricity in the reactor:

- the operator installed equipment to limit the formation of static electricity. The products are introduced by a dip tube to limit the formation of static electricity.

Administrative actions:

Within the scope of actions taken following the accident, four inspections were conducted jointly by the "environment" and "pressurised equipment" agents of the DRIRE regarding the on-site reports (April 2003), and the verification of the provisions for the partial, then total restart of the unit (June and July 2003).

The actions proposed during the second quarter of 2003 by the classified installations inspectorate:
The accident was not considered a major accident in terms of Article 2 of the Ministerial Order of May 10, 2000 and did not have significant consequences for the environment.
The operator met the provisions of the Prefectorial order of March 31, 2003 – title III which governs the unit in question.
The classified installations inspectorate did not note any violation meriting a fine, nor any element requiring formal notification. The only administrative actions consisted in a Prefectorial emergency measures order outlining the conditions required for placing the installations back into service.
This Prefectorial order was issued April 25, 2003 and the operator satisfactorily complied with the provisions of this order, prior to the last start-up phase of the units in July 2003.

LESSONS LEARNED

The major feedback elements retained:

- Avoid heating tanks considered to be "empty".
- Include this restriction in the shut-down and start-up procedures of the units and the heating systems.
- Reinforce the monitoring of process parameters of the units shut down.