Release of nitrous vapours in a pectin extraction unit

December 10, 1993

Redon – [Ille-et-Vilaine] France

Food industry
Nitric acid
Nitrogen dioxide
Burst disc
Automatic control systems
Modification
Human factor

THE INSTALLATIONS IN QUESTION

The site:

The establishment is the only facility in France that extracts pectin from apple marc or lemon rind. This natural pectin can then be treated in a basic environment to reduce its esterification rate. Pectins are used in the pharmaceutical industry or as dietary gelling agents.

The pectin treatment unit, commissioned in 1991, is entirely automated. However, the operator may take over manual control of the installation at any time, particularly when an anomaly occurs. Direct operator control is even mandatory to restart an operation that was stopped following an inerting problem. A rupture disc calibrated at 3.7 bar protects the production installation. A vent channels the release to the atmosphere when the disc bursts.

THE ACCIDENT, ITS BEHAVIOUR, EFFECTS AND CONSEQUENCES

The accident

On December 10, 1993, the operator began his shift at 5 am. He had many years of experience and had worked in this shop since it was created. When the reaction was completed, the mixture in the reactor was then neutralised with a nitric acid solution. It was then transferred to a pectin separation device. Once empty, the reactor was rinsed with alcohol.

When the neutralisation process was completed, beginning at 9.57 pm, and although the PLCs could do it for him, the operator elected to manually control the addition of nitric acid by forcing a valve open. With the neutralisation phase completed, the system automatically continued to the following phases until the transfer pump started at 10.40 am.

As the transfer pump had been replaced recently, its output was greater than that of the previous model. This difference regularly results in an excessive drop in the inerting nitrogen pressure in the reactor and the safe shut-down of the installation. When the nitrogen pressure is once again satisfactory, the pump can only be restarted manually.

Following an initial shut-down, the operator restarted the pump at 10.41 am then set it to automatic mode. The nitrogen pressure immediately fell and the pump stopped once again. For reasons unknown, although probably associated with a representation error despite the indications provided on the diagram, the operator selected and manually opened the nitric acid valve. Acid once again flowed into the reactor (1,500 l/hour). At 10.42 am, the operator restarted the transfer pump manually after noting that it had not started or that it had stopped once again. The transfer operation was finished at 10.53, including the rinsing phase.

At 11.45 am, an abnormal temperature was detected at the reactor level. The operator noted that the acid valve was open and attempted to shift to manual mode, the position that it was already in. The valve is then closed shortly thereafter. The rupture disc then burst due to a rise in reactor pressure and temperature. The workshop was secured and the establishment's POI (Plan d'Organisation Interne, internal contingency plan) was put into action in the minutes that followed.

The consequences:

At 11.48 am, the 102 m^3 of nitrous vapours were released in 1 or 2 min. The resulting cloud was carried away by the wind (7 m/s) and passed a minute over a few homes and a school located 350 m away, then completely dispersed 5 or 6 min. later. Between 4 pm and 8 pm, 13 people, including 12 high school students, were hospitalised, and 4 remained under observation (less than 48 h).

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

Nitrous vapours consist of nitrogen oxides, including namely nitrogen dioxide, a substance which is classified as highly toxic in Appendix 1 of the 'Seveso' Directive. As such, the index relative to the amount of 'dangerous materials released' is thus at least 1 (parameter Q1).

The accident resulted in 13 members of the public being hospitalised (parameter H5), 4 of whom stayed less than 24 h (parameter H4). This brings the 'human and social consequences' index to 3.

Finally, the lack of information concerning the accident's environmental and economic consequences prevents the evaluation of the last two indices of the accident scale.

ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

The accident was caused by a chemical reaction that was slow to start although strongly exothermic, between the excess nitric acid and the reaction mixtures contained in the reactor.

The excess nitric acid resulted in the accidental opening of the nitric acid valve by an experienced operator, most likely due to an installation representation error. The manual control of a step of the process had become necessary owing to an inerting defect of the rector, itself associated with a recent pump change on the installation: the new pump's output, greater than the previous pump, regularly led to an excessive drop in the inerting nitrogen pressure in the reactor causing the installation to shut down as a safety measure. The shutdown thus required the pump to be restarted manually.

ACTION TAKEN

The manufacturing procedures were re-examined at all workstations in the facility using nitric acid. Additional safety measures were undertaken in the workshop concerned:

- The operators can no longer manually actuate the reagent valves.

- A temperature monitoring device was installed on the reactor. Except for nitrogen inerting, the supply valves close once the temperature exceeds 25°C.

- Test procedures for the safety devices and alarms were set up.

- The safety devices associated with the injection of reagents into the reactor were doubled. Fail-safe operation is ensured by level monitoring in addition to the checks made on the outputs and the durations.

- The transfer rates are physically limited to avoid pump shut-downs due to an inerting loss.

LESSONS LEARNED

Two types of lessons can be learned from this accident, one concerning the management of modifications in industrial establishments and their other relating to the human factor:

- Even a minor modification in an installation process or piece of equipment is a risk that must be carefully considered and the impact of the modification on the installation's safety must thoroughly studied.

- While the experience of the operators is an undeniable asset in industrial safety, it can sometimes be considered risky as they may become less vigilant due to routine, habituation to the risks…