Discharge of hydrochloric acid
June 06 1994
St Pierre La Garenne – [Upper Normandy]
France

Phytosanitary products
Toxic discharge
Organisation/procedures
Operating Methods
Management of modifications
Maintenance
Alarm
Procedures/Field of security

THE INSTALLATIONS CONCERNED

Installation concerned

The plant, created in 1952 is in a rural zone, between the Seine and the PARIS-ROUEN railway; it employed 200 people. Its activities included the synthesis and the formulation of phytosanitary products, fluorescent brightening agents and products for the textile and leather industries. The site was subject to the SEVESO directive.

The accident took place at the level of the manufacturing group for fluorescent brightening agents in one of the buildings of the "Fine Chemistry" unit of the factory. This installation is subject to an authorisation for the handling and storage of toxic or flammable products (categories 1111, 1131, 1430, 1433 in particular). The prefect's authorisation was dated May 1994. The workshop, with a low level of automation, employed 25 persons (of whom 3x4 employees in teams). The brightening agents are obtained by nucleophilic substitution, in the presence of sodium, of 3 atoms of chlorine from chlorate of cyanide by 3 different aminates among which is sulfanilic acid. The first substitution, which is rapid and exothermic, requires cooling with ice and brine. The reactor is then heated to obtain the two following substitutions. In 1978, a new operating procedure had been in a test phase for one month when the accident involving the first substitution took place.

THE ACCIDENT, THE SEQUENCE OF EVENTS, ITS EFFECTS AND ITS CONSEQUENCES

The accident

Another synthesis started on June 6th at 8h45. Water, sulfanilic acid and chlorate of cyanide were loaded into a reactor with a capacity of 8 000 litres. Following the new operating procedure, 1 t of ice should then be introduced just before the sodium (according to the previous operating procedure, the ice would have been loaded before the introduction of the chlorate of cyanide). However the pneumatic feed valve was blocked and the agitation in the reactor was continued without cooling while awaiting repairs. In relation to knowledge acquired concerning this procedure, this status is normally without danger

A 9h23, while repairs were ongoing, the unattached cover plate of the manhole of the reactor lifted up. A cloud of gas containing 107 kg of hydrochloric acid was released through this aperture and through the ventilation system of the reactor. The 4 persons present evacuated the workshop and raised the alert. The vapours diffused through the workshop and then escaped during 40 minutes through the aeration chimney of the building.

The factory firemen intervened. At 9h35, a first team noted a temperature of 103 °C in the reactor and observed that the agitator in the apparatus was not working. The circulation of brine (between -24 and -27° C) was put into service manually in the double envelope to cool the reacting medium. However, the agitator of the reactor remained blocked, thus slowing the cooling process. The manholes on the other reactors were closed and since no other reaction was taking place, the installations were secured (heating halted, emptying and agitation) At 9h45, a second team flooded the reactor with 1 900 litres of water and closed the release valve leading to the Seine for the residual water of the plant. Products released onto the ground and acid vapours were neutralised with an ammoniac solution diluted to 12 %.

The consequences

The operator visited the 7 closest neighbours to advise them to stay indoors during the period of the alert. Measurements of concentrations were taken in several places using a Draëger. These were below detectable limits with this device (< 2 ppm). The alert was lifted at 10h20 and the neighbours were informed by telephone between 10h45 and 11h15. The emission of hydrochloric acid was evaluated at 107 kg in one hour, the major part having escaped by the chimney.

No victim was to be deplored. No notable consequence to the environment was observed. The authorities requested the suspension of operations at the plant.

Material damage was evaluated at 18 KF and operating losses at 200 KF.

European scale for industrial accidents

Using the rules for scaling by the 18 parameters of the scale formalised in February 1994 by the Committee of Competent Authorities of the Member States in application of the 'SEVESO' directive and taking into account the available information, the incident is characterised by the following 4 indices:

The parameters comprising these indices and the method of evaluation are available at the following address: http://www.aria.ecologie.gouv.fr.

The 0.1 tonnes of hydrogen chloride represent 0.05 % of the corresponding Seveso threshold (200 t), which is the equivalent of level 1 of the index « dangerous materials released » according to parameter Q1 (Q1 < 0,1 %),

Parameter H7 of the index « human and social consequences » reached level 2: 7 persons were confined for a period of 2 hours (N < 500 with N = number of neighbours evacuated or confined at home > 2 h * number of hours).

THE ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

The reaction started, in an unforeseen manner at ambient temperature, despite the absence of reagents, (sodium). Between 8h45 and 9h23, the temperature rose from 20 to 105 °C in the reactor. A laboratory test was conducted the day following the accident to mitigate the lack of information on the procedure. This test showed that cyanid chlorate and sulfanilic acid can react in the absence of sodium if the temperature of the reacting medium is sufficiently high (30° during the test, 26 °C the day of the accident). Indeed, 80 minutes after the mixing of the reagents, the reactive medium reached boiling point. On the day of the accident, there was probably an initial reaction between the cyanic chloride and the sulfanilic acid, followed by hydrolysis of the cyanic chloride. The reacting medium, which reached its boiling point, caused the ejection of the solution at the moment when the ice feed valve was undergoing repair

This accident had 5 principal causes:

- ⇨ The malfunction of the pneumatic ice feed valve.
- ⇨ Lack of knowledge of the possible reaction without the addition of sodium.
- ⇨ The novelty of the operating method (undergoing trials for one month)
- ⇨ Insufficient risk analysis
- ⇨ Absence of a temperature alarm high up on the reactor.

RESULTING STEPS TAKEN

Activities of the workshop, suspended from 6 to 15 June, were re-started after the following measures had been taken:

- Return to the former procedures (loading with ice before the cyanic chloride),
- stock of one tonne of ice maintained close to the reactor (manual loading if necessary),
- preventive maintenance of ice feed valve,
- installation of high temperature alarms independently of measurements on all reactors generating exothermic reactions,
- institution of a "safety guide" covering all procedures involving chemical reactions.

LESSONS LEARNED

The unit concerned is a polyvalent installation. The accident was due to the unexpected initiation of a chemical reaction followed by a thermal situation spiralling out of control.

Several lessons can be learned from this accident:

- ✓ It is recommended that all elements relative to the security of all procedures be assembled and if necessary completed by laboratory tests or appropriate experiments concerning the stability of raw materials, the reactive medium and the finished products…
- ✓ If there exists a risk of the reaction running out of control, the technical choices adopted for the procedure must enable the safe shut-down and stopping of the reaction (injection of ice, flooding of the reaction, inhibition, “rapid emptying”…).
- ✓ The procedure was reputed to be safe as from its entry into service, the operating method had been changed several times, with an under-evaluation of the consequences of these modifications. The safety consequences of any modification, however minor, to a procedure or to the installation, must be analysed
- ✓ The temperature of the reactive medium is measured in the reactor but there is no high temperature alarm. This underlines the necessity to define the safety aspects of the procedure, the parameters and alert levels and alarms, with the corresponding human or automated reactions. Risk limiting measures must be defined in relation to the required safety level, implying special requirements as regards organisation on the one hand and, on the other hand, equipment handling.
- ✓ The necessity of organising a programme of preventive maintenance (ice feed valve in the case of this accident).