Electrolysis
Sulfuric acid
Residual effluent
Modifications

Release of a chlorine gas cloud in a chemical plant

January 12, 2003

Saint Auban – [Alpes de Haute-Provence] France

THE INSTALLATIONS IN QUESTION

The site:

The St Auban chemical plant synthesises three types of products from chlorine manufactured on site: polyvinyl chloride (PVC), chlorinated solvents (trichloroethane, trichlorethylene, javel water…) and acids (hydrochloric acid, monochloroacetic acid…).

This complex facility is classed as a "High Threshold" SEVESO establishment for the use and/or fabrication of chlorine, bromine, hydrochloric acid, vinyl chloride monomer, and solvents… Its special intervention plan covers a radius of 5 km and its 2 urban planning control zones extend over radii of 350 and 700 m, respectively.

The unit concerned:

The chlorine manufacturing facility includes 141 mercury electrolysis cells, through which 120 kA of current passes. It can produce chlorine (21 t/h), hydrogen and soda. The chlorine extracted by a network under a slight vacuum, is then cooled, dried and used directly, or liquefied and stored.

THE ACCIDENT, ITS BEHAVIOUR, EFFECTS AND CONSEQUENCES

The accident:

On **January 12, 2003 at 1 pm**, the high pressure alarm on the chlorine production shop's brine regeneration tank went off. As a safety precaution, the residual chlorine was automatically directed to the javel water network via the tank's vent.

At 2 pm, an increase in pressure on the chlorine intake systems of the electrolysis room lead to successive drops in the load until the electrolysis room shut down completely on the high pressure safety threshold.

At 2.25 pm, the chlorine detection alarm in the drying building next door was triggered. Two PBA-equipped agents reported turbulence in a liquid seal and chlorine cloud formation.

At 3.10 pm, the chlorine detection alarm outside the building was triggered.

At 3.30 pm, the foam operations conducted by the firemen in the drying facility enabled the alert to be called off one half hour later. The site nevertheless remained under surveillance until 6 pm.

Consequences:

Approximately 2 kg of chlorine was released into the atmosphere, i.e. approximately 600 L of chlorine gas.

The establishment's internal contingency plan was initiated. Informed by the operator, the French national railway company "SNCF" (with a rail station located 200 m from the site) decided to delay the Briançon-Marseilles train 50 minutes.

European scale of industrial accidents

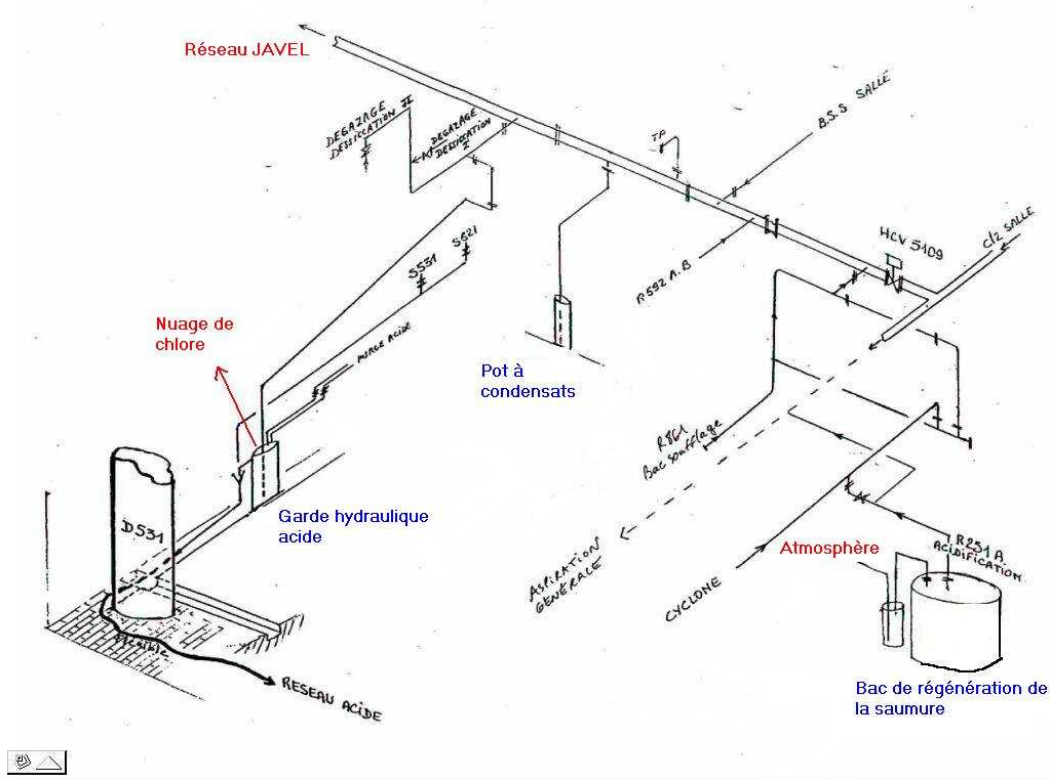
By applying the rating rules of the 18 parameters of the scale made official in February 1994 by the Committee of Competent Authorities of the Member States which oversees the application of the 'SEVESO' directive, the accident can be characterised by the following 4 indices, based on the information 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

The "dangerous materials released" index is 1 as 2 kg of chlorine, e.g. 0.008% of the Seveso threshold (25 t), were released into the atmosphere (parameter Q1).
The withdrawal of public transport (parameter H8) explains the "human and social consequences" rating of 2.

ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

The accident was caused by an unexpected influx of air into the tank used to regenerate the brine coming from the mercury electrolysis cells. This influx of air, resulting from an insufficient water level in the liquid seal protecting the tank, lead to pressure fluctuations in the installation and triggered a high pressure alarm in the tank. The excess pressure lead to the regeneration unit being secured and particularly the automatic connection of the tank valve on the javel water network collecting all of the residual chlorinated gaseous effluents (see diagram below).



One hour after the first incident, an increase in pressure on the chlorine manifolds connected to the electrolysis cells lead to a pressure drop, then the automatic shutdown of the cells, with a very significant amount of chlorinated water entering the javel water system. The start-up of the fans, enabling the rapid degassing of the electrolysis cells, caused a sudden peak flow in the network also disrupting the discharge of chlorinated condensates in the manifolds.

Furthermore, heavy condensation of the water vapour contained in the chlorinated effluents released in the javel water system, condensation associated with the temperature difference existing between the inside of the pipes and the workshop, promoted the formation of solid chlorine hydrate. As the formed hydrate deposited, it blocked the branch connection connecting the javel water network to a condensate collection drain, thus preventing it from fulfilling its function. The surplus of condensate, water + chlorine was thus evacuated via a liquid seal located in the drying facility and containing 98% sulphuric acid (H2SO4). The water/acid exothermic mixture promoted the vaporisation of the residual chlorine that spread through the workshop and the surrounding area.

ACTION TAKEN

The malfunction of the liquid seal, protecting the brine regeneration tank, was repaired only a month later after the incident happened again, although this time without consequence. The operator will now ensure that it is supplied on a permanent basis.

The branch connection on the condensate tank and the associated pipework was cleaned.

The seal pot containing sulphuric acid, rendered unnecessary by a previous modification, was removed.

The electrolysis facility's procedures and shut-down operations were reminded to all of the operating crews.

LESSONS LEARNED

A few years earlier, an insufficient liquid seal in one of the group's other plants had already lead to the release of chlorine into the atmosphere. It appears that this first accident was not sufficiently developed in terms of feedback; the operator must undertake in-depth reflective thinking on all of the liquid seals within its establishment and revise the danger study of the installation concerned based on this reflective thinking process.

Furthermore, the collection and processing of residual effluents toward safety equipment installed in the plant must for the subject of specific studies.

Beyond this, this accident illustrates the need to systematically consider all installation or process modifications, even minimal, in the danger studies and safety files (see. "Les recommandations dans la chimie fine" (Recommendations in the field of fine chemistry), by the UIC, available at the internet site www.aria.ecologie.gouv.fr).