

## VCM leak in a chemical plant

25th August 1999

Tavaux (Jura)

France

VCM  
Organisation /  
Procedure  
Human / control flaw  
Autoclave

### THE FACILITIES INVOLVED

#### The site:

The Company, created in 1930, covers 100 ha and employs slightly less than 2,000 people on-site and groups together some 700 jobs in various service providing companies.

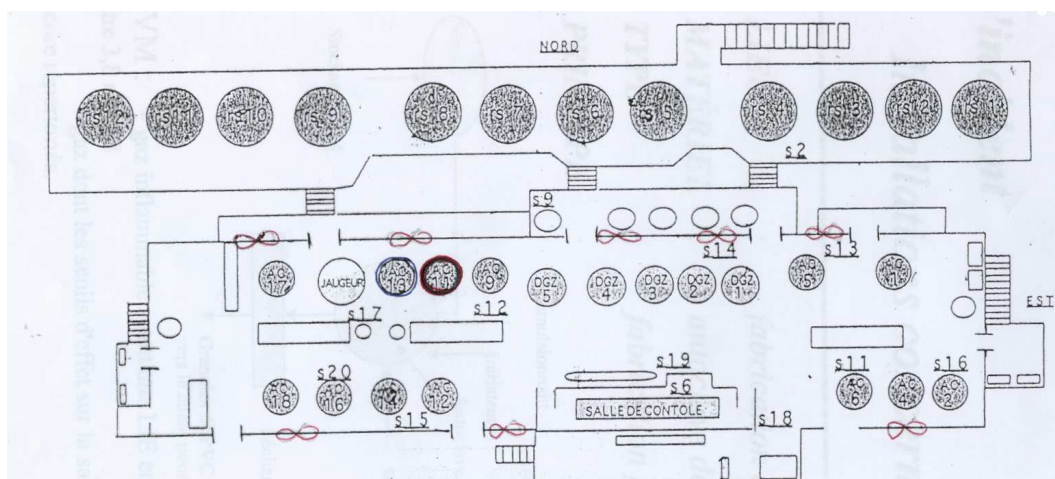
All of the platform's manufacturing operations are based on the transformation of salt into chlorine by electrolysis, which is used to make 3 plastic materials on site :

- √ polyvinyl chloride (PVC),
- √ polyvinylidene chloride (PVDC),
- √ polyvinylidene fluoride (PVDF).

This establishment contains 8 installations which fall directly under the Sevesco directive. The establishment benefits from authorization orders which, on the one hand, set the general operating conditions for the entire operation and, on the other hand, regulate the fifteen or so installations which exist on the site. A POI ("Plan d'Organisation Interne", internal contingency plan) was drafted by the operator. An associated PPI ("Plan Particulier d'Intervention", emergency response plan) was established in 1992 and was revised following an exercise conducted in 1995.

#### The involved unit:

The installation concerned by the accident is the PVC manufacturing facility, itself including 3 workshops. Workshop P69 corresponds to the polymerisation of PVC by a "suspension" process. In order to better understand the progression of the accident, this process is detailed below.



Production is carried out in a discontinuous manner, by "batch", with the reaction taking place in dual-casing autoclaves (a stainless steel tank and steel casing) having a volume of 27.5m<sup>3</sup>. The shop includes 13 autoclaves. The reaction takes place under a pressure of 6 to 9 bar and at a temperature from 40 to 70°C.

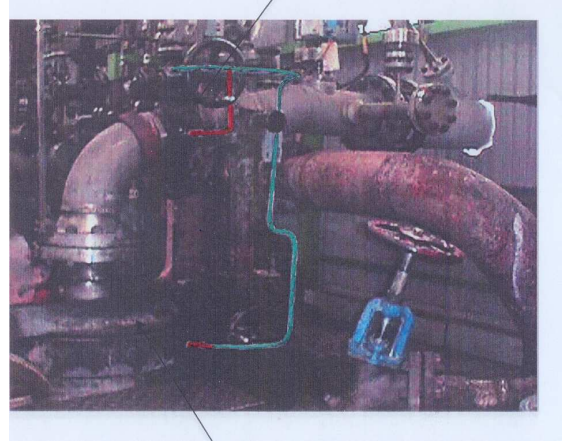
The principle phases are as follows:

- √ demineralised water and dispersing agents are loaded into the autoclave,
- √ agitation,

- √ the autoclave is closed and placed in a vacuum to remove the oxygen,
- √ 10 tons of vinyl chloride monomer (VCM) is loaded into the autoclave,
- √ preheating to the polymerisation temperature by circulating hot water in the dual casing,
- √ polymerisation at constant temperature and the addition of reagents,
- √ depressurisation and transfer from the reaction environment to a different tank,
- √ the autoclave is placed under vacuum,
- √ degassing of the residual VCM,
- √ prior to the launch of a new production cycle, the autoclave is opened by the manhole and cleaned using water at high pressure.

Considering its importance in the train of events, further information is provided about the autoclave's closure mechanism (see photo opposite).

It consists of a pivoting system comprised of the manhole cover and an adjoining elbow-shaped tube section enabling the autoclave to be connected to the overpressure protection system consisting of a rupture disk and a valve mounted in series. A seal is required at 2 levels: one seal is located at the cover/manhole junction, and the other is located at the junction between the elbow tube and the stationary overpressure protection pipe. Two jaws, one at each level and actuated by a lever, ensure the overall tightness of the device.



## THE ACCIDENT, ITS CHRONOLOGY, EFFECTS AND CONSEQUENCES

---

### The accident:

On August 25th, the unit was operating normally. The chain of events which characterizes the accident and how the accident was handled is presented below:

Around 7:30 pm, a leak is detected on the autoclave at the start of the polymerisation phase. Poor visibility in the workshop does not allow the origin of the leak to be determined. Nitrogen is injected to inhibit the reaction in the autoclave.

Between 7h30 to 7h40 pm, the operator checks the concentration VCM in the atmosphere using portable devices in the immediate proximity of the building involved in the accident.

more than 1,000 ppm of VCM in the polymerisation hall are detected at 7:32 pm.

The leak is located at 7:35 pm on the tube connection the roof of the autoclave to the rupture disk.

At 8:02 pm, the operator prepares a foam injection operation in order to reduce the risk of explosion inside the polymerisation hall. He activates the internal contingency plan due to the flammable characteristics of the gas emitted. Additional measurements of the concentration of VCM performed at various locations of the establishment, outside the polymerisation hall.

At 8:55 pm the decision is made to transfer the contents of the leaking autoclave to the neighbouring, empty autoclave. The transfer operation is started at 9:10 pm. The leaking autoclave is depressurised to atmospheric pressure at 9:40 pm. The chromatographs record a rapid decrease in the VCM content in the polymerisation hall.

The rapid improvement of visibility in the hall enables the intervention by an operator and a fireman : they report that the jaws of the closure system on the autoclave/rupture disk junction are loose. The jaws were put back into correct position after having bent the safety rod (preventing the closure manoeuvre).

The transfer is completed at 10 pm and the leak is under control.

### Consequences of the accident:

The accident claimed no victims. Although VCM is a highly flammable and explosive substance, the leak did not result in a fire or explosion.

### The European scale of industrial accidents

By applying the rating rules applicable to the 18 parameters of the scale officially adopted in February 1994 by the Member States' Competent Authority Committee for implementing the 'SEVESO II' directive on handling hazardous substances, and in light of the information available, this accident can be characterised by the four following indices:

Dangerous materials released		<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Human and social consequences		<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Environmental consequences		<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Economic consequences		<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

The parameters composing these indices and their corresponding rating protocol are available from the following Website: <http://www.aria.developpement-durable.gouv.fr>

The overall score of the "Hazardous materials released" index was assigned a "3", as the quantity of VCM released was evaluated at 6.1 tonnes (parameter Q1: quantity lying between 1% and 10% of the SEVESO threshold).

Since no human, environmental or economic consequences were reported, the corresponding indices were all rated a "0".

## **THE ORIGIN, CAUSES AND CIRCUMSTANCES SURROUNDING THE ACCIDENT**

---

The inquiry showed that the launch of the operation was prepared normally and the technician began the habitual procedures, particularly the closure of the autoclave. However, the technician forgot to tighten the jaws of the previously described mechanism.

The polymerisation began after the vacuum operations and the loading of the product were carried out.

The leak did not occur immediately: only when the pressure was sufficiently high, that is to say at the end of the heating phase, the leak occurred suddenly at the "quick" junction. The mechanism remained in place although the seal slipped out of its housing causing the leak.

The VCM spread through the workshop than to the exterior via the facility's mechanical ventilation system.

## **ACTIONS TAKEN**

---

The regulated facility inspectorate carried out their inspection the next day. The operator was questioned about various subjects, including the exposure of the surrounding population to VCM. Beyond its flammable characteristics, VCM is also classified as carcinogenic (category 1 in the European classification, group 1 as per the CIRC - category F+; risk phrase R12-45. It is thus important to have a study relative to the consequences on the surrounding population.

The same day, the inspectorate proposed a draft order in accordance with the emergency procedure, requesting:

- √ that a study be conducted on the consequences of the emissions generated in the environment,
- √ that a study be conducted on the precise circumstances of the accident in order to determine the causes as well as the means to be implemented to prevent such situations from happening again.

According to conclusions drawn from a third-party expert's report, the average concentration of VCM would have remained considerably below the lower explosive limit (roughly 10 times less) over the entire polymerisation facility. On the other hand, the critical concentration range (i.e. between the lower and upper explosive limits) must at times have been reached, yet without triggering ignition.

As for the toxic risk, the most credible estimation of the leak indicates a VCM discharge quantity of 6,100 kg. This calculation furthermore demonstrates that the population living in the closest dwellings along the direction of the wind, i.e. at 1,350 m, was exposed to concentrations on the order of 3 to 5 ppm for a 2-hour duration. By adopting worst-case hypotheses, the concentrations derived yield maximum values in the range of 50 to 80 ppm. In the words of the expert: "The health risk for those exposed remains negligible."

## LESSONS LEARNT

---

In response to the reported human failure, a mechanical device was installed by the operator. It now detects where the jaws are actually tightened during the autoclave vacuum operation.

The device and the corresponding procedures were in place as of late 1999 on all of the autoclaves of the same type and operating discontinuously.

Thought was given to the autoclaves of the other "close process" manufacturing units and which are opened less often. The operating procedures have been completed and now include tests prior to pressurization and depressurisation before the introduction of products in to the reactors. The deadline objective was set for May 2000.

Thought was also given concerning the modification of intervention plans in order to integrate the feedback elements collected after the incident.

