

Chlorine leak in a liquefaction workshop of a chemical plant

January 13, 2004

Vieux-Thann – [Haut Rhin]
France

Electrolysis
Liquefaction
Hydrogen
Chlorine-Iron
reaction
Re-start
Confinement

THE INSTALLATIONS IN QUESTION

The site

The plant specialises in the fabrication of chlorine, and chlorinated and brominated products. It is governed by the "high threshold" of the Seveso directive. The plant is located in an urbanized zone.

Part of the chlorine produced in the manufacturing facility by mercury-cathode electrolysis (200 t/day) is used on site. The other part is liquefied and loaded into rail cars or stored in an 11-m³ tank. The installations containing liquid chlorine are located in closed buildings equipped with a ventilation system and a neutralisation tower to process any accidental releases. A prefectorial order required the company to adopt this confinement installation in 1995.

The unit concerned:

The chlorine coming from the electrolysis facility is compressed and condensed, and then the gas and liquid phases are separated in a floatation pot-type separator. The liquid part is then directed to the storage facilities or to the loading installation. The non-condensed part (referred to as residual gases), containing gaseous chlorine and non-condensable gases (notably H₂ and air) is distributed on site. As the liquefaction rate increases, the concentration of non-condensable gases in the residual gases also increases (the enrichment factor is $[1/(1-\tau)]$). As such, if 50% of the chlorine is liquefied, the concentration of the non-condensable gases in the residual gases doubles, but is multiplied by 10 if the liquefaction rate is 90%.

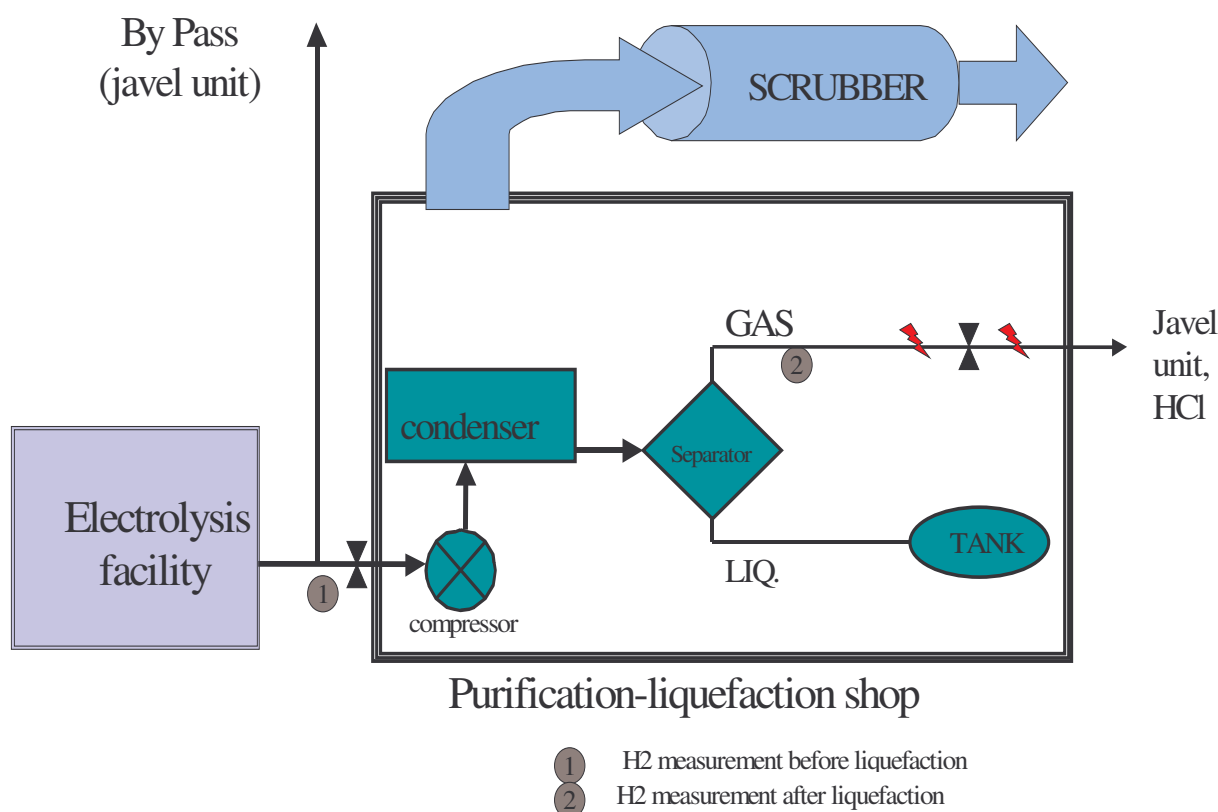
The presence of hydrogen and inert gases, inherent to the chlorine manufacturing process, is particularly important during the installation restart phases, notably after long shutdown periods.

It should be reminded that hydrogen and chlorine react violently, producing hydrochloric acid.

The presence of hydrogen in gaseous chlorine thus requires a that certain number of precautions be taken, including monitoring the changes in its concentration in the installations to ensure that it remains below the lower explosive limit (LEL). The hydrogen contents are measured at the electrolysis shop's outlet and in the gas outlet of the floating pots by means of an automatic analyser, or by manual analysis.

The company's internal procedures require that a maximum hydrogen concentration of 4.7% be respected in the residual gases. The LEL of the chlorine-hydrogen-air mixture is 5% (source: INRS).

The automatic hydrogen analyser is inoperative during the installation's start-up phases due to the excessive quantity of inert gases present. For this reason, during installation start-up operations, the operators perform manual concentration measurements (a measurement every ten minutes, according to the procedures).



THE ACCIDENT, ITS BEHAVIOUR AND CONSEQUENCES

The accident:

In the morning of January 13, 2004, the electrolysis installations were being started after having been shut down due to a lack of cooling water. During the first start-up phase, the chlorine produced is sent directly to the Javel (bleach) unit.

At 9.15 am, the concentrations measured leaving the electrolysis unit at analysis location No. 1 (1.3% H₂, 80% Cl₂) enabled the liquefaction part of the workshop to be put back into service in accordance with the company's internal procedures. Chlorine production was 1,600 kg/h, the output of residual gases 600 kg/h and the hydrogen concentration in the residual gases 3.3% (analysis location No. 2).

The electrolysis facility's production level was progressively increased to 2,900 kg/h. A new series of measurements at the "residual gases" outlet of the liquefaction facility at analysis location No. 2 showed an initial concentration of 4.6% hydrogen in the residual gases. The measurement conducted ten minutes later gave a value of 6.7%. Noting this value, the operator immediately performed the analysis again, which confirmed the first analysis.

The operator then decided to reduce the liquefaction rate by increasing the output of residual gases to 1,000 kg/h in order to lower the hydrogen concentration.

Immediately afterward, a leak was detected at 10.10 am by the alarm and visually in the building. The operators initiated the emergency shutdown; the confinement installations were automatically put into service and directed the majority of the leak to the neutralisation tower.





The majority of the chlorine released by the leak was neutralised in the tower. The operators secured the installations then grouped together to locate and were able to completely isolate the leak in 20 minutes.

The consequences:

No employee or resident of the area was injured. A pipe was damaged in three locations. The quantity of chlorine released into the confinement building was indirectly estimated at 600 kg. The quantity released into the environment was limited to just a few kilos while the confinement building was depressurizing. Nearly all of the chlorine leaked was treated in the neutralisation tower for accidental releases.

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, which 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>

Quantities of dangerous substances		<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"/>

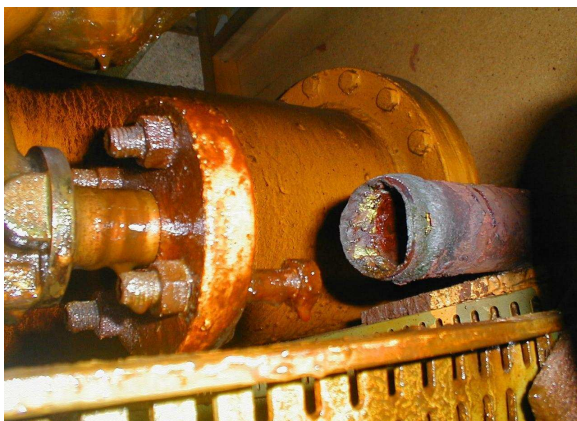
The 600 kg of chlorine from the leak represent 2.4% of the corresponding Seveso threshold (25 t) and result in a level 3 rating in terms of the "quantities of dangerous substances" according to parameter Q1.

ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

The expert assessment conducted immediately following the incident showed that the leak, located along the limit of the confined zone, resulted from the combustion of the steel in the chlorine on a pipe transporting the gaseous chlorine: at two locations (located near zones in which the pipe size was reduced: valve and venturi), the pipe had disappeared over several centimetres, including a flange. A hole of diameter equal to that of the pipe (8 cm) was created in a third location.

The combustion of steel in chlorine is a process that is initiated when the steel is brought to a temperature above 130 °C. Once this reaction begins, it is self-sustaining until all the chlorine has been consumed.

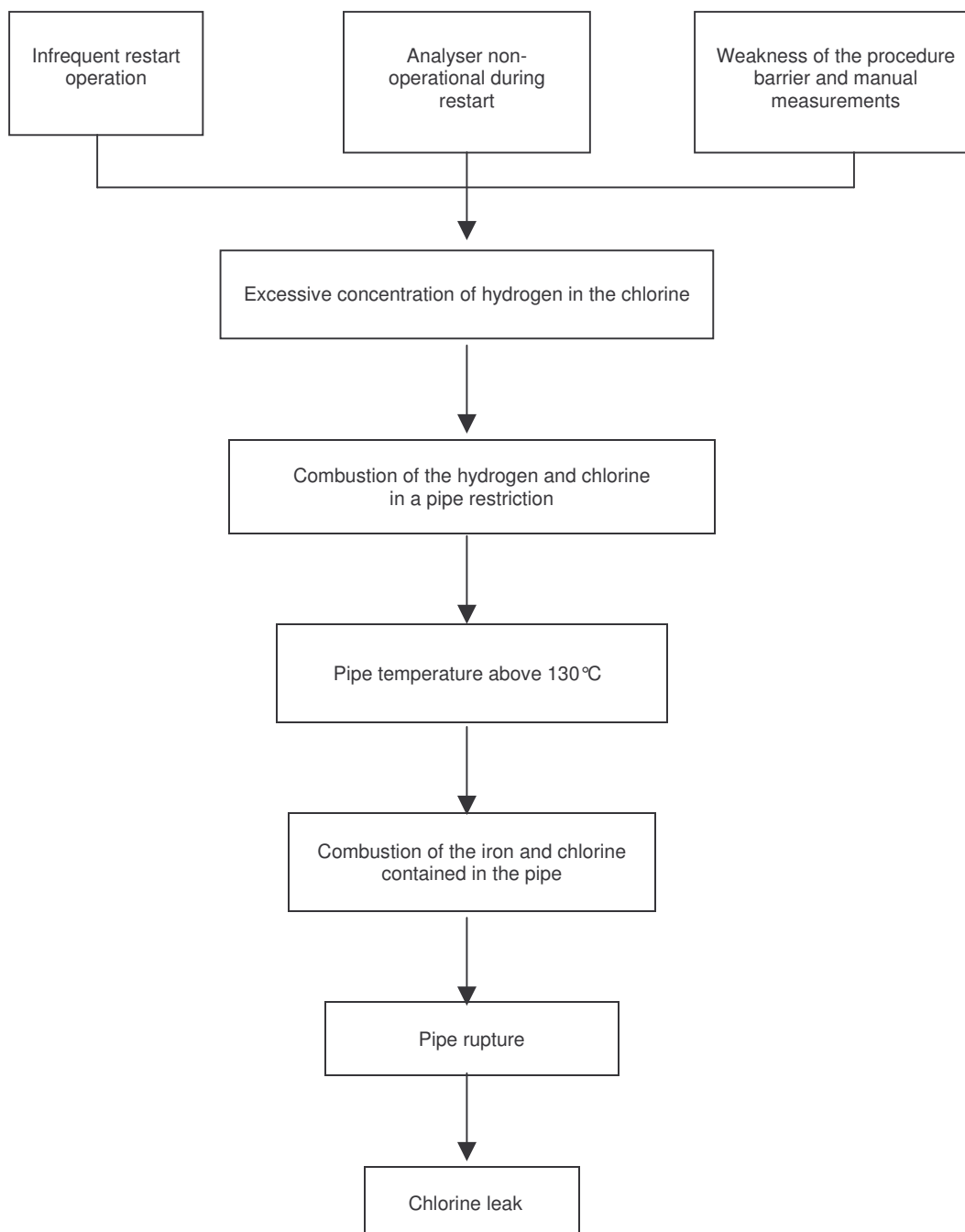
The operator identified the cause of the iron/chlorine combustion process as a hydrogen-chlorine fire whose ignition energy is sufficiently low to start spontaneously due to an output restriction or a significant flow rate. The increase in the output to 1,000 kg/h could have also supplied the ignition energy required.



The value of the hydrogen concentration leaving the electrolysis facility and the liquefaction rate could only result in the LIE being exceeded (the hydrogen enriching factor being 5 just prior to the accident) as soon as the operator did not act immediately when he measured a concentration of 4.6%.

The non-operation of the automatic analyser and related safety devices during the start-up phases made the security of the installations rely only upon action by the operators, who are particularly busy during the rare start-up phases. This point was brought up during the last risk analysis of March and December 2003, when the operator was searching for a new analyser.

This incident can be broken down in the following manner:



ACTION TAKEN

Besides the verification of the installations and the replacement of damaged parts, several actions were implemented to prevent the incident from happening again:

- A material assessment was set up to monitor the hydrogen concentration in the residual gases according to the liquefaction rate and the hydrogen content at the electrolysis facility's outlet.
- Implementation of two continuous hydrogen analysers that can be used in the presence of inert gases (cost: 150,000 euros).
- Supervision of start-up phases by a manager.
- Modification of the instructions.
- Re-examination of post-accident actions.
- The installations are shut down if the hydrogen concentration is exceeded by more than 3.5%.

LESSONS LEARNED

The main feedback elements to remember concern:

- The correct operation of the confinement installations during an incident without the building increasing in pressure.
- The guillotine rupture scenario that is not a textbook example.
- The analysis of transitory phases and the specific security arrangement to be implemented and not neglected.
- The weakness of the operator barrier associated with the instructions that were not necessarily explicit (the number of measurements, respect of the limit concentration of hydrogen in the residual chlorine, shut down of the electrolysis facility).
- An organisation to be improved through the modification of instructions and better operator training as well as the reinforcement of the supervisors' role during delicate phases.
- The relatively significant delay in isolating the leak (20 min.) following problems relating to the intervention and locating the leak in a building in a chlorine atmosphere.
- The drainage of upline and downline chlorine systems by depressurisation, particularly concerning the 11 m³ liquid chlorine storage tank which supplied the leak for 5 minutes until it could be isolated.
- The low ignition temperature of combustion between iron and chlorine (130 °C).