Cyclohexane leak in a chemical plant

December 16, 2002

Chalampé (68 – Haut Rhin)

France

Chemical plant
Ground water table
Pipeline
Abandoned channel
Freezing temperatures
Soil decontamination
Late detection
Organisation

THE INSTALLATIONS IN QUESTION

Chalampé chemical platform

Installed at the site since 1957, the Chalampé chemical platform employs 1,200 salaried employees, extends over 93 hectares covering 3 communes and consists of 2 plants. The common general manager and the personnel of the first company operate the units of the second on its behalf.

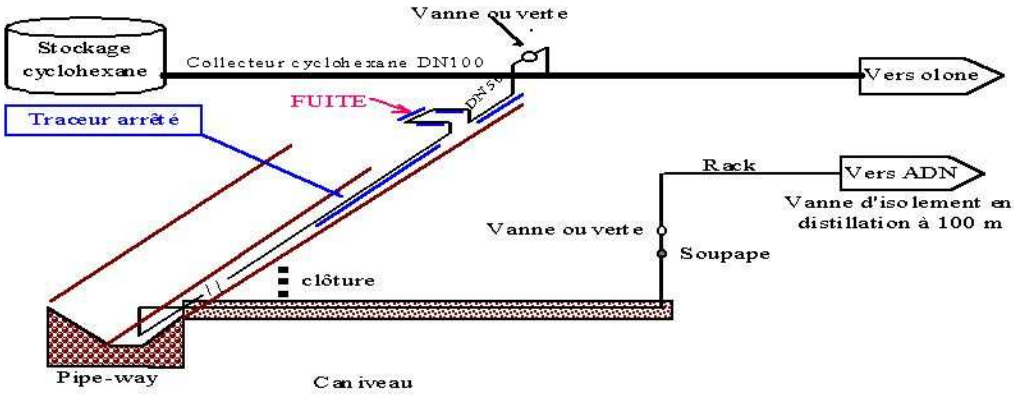
The Chalampé chemical platform specialises in the fabrication of "nylon" salt (a basic chemical intermediate product for threads, fibres and plastic materials).

The site stocks a significant amount of raw materials: two tanks of cyclohexane with a capacity of 5,000 and 10,000 m^3, two 2,500 m^3 tanks of butadiene, two 300 m^3 ammonia tanks and numerous storage facilities for finished and intermediate products.

The Chalampé chemical platform is governed by the "AS" section of the nomenclature for installations classified for its industrial manufacturing activities requiring the implementation and storage of toxic products, flammable liquids and liquefied combustible gases. The last prefectoral order, which followed a public enquiry dates back to November 23rd, 1999.

Installation responsible for the leak

The 10,000-m^3 cyclohexane storage tank (B10000) is connected to the OLONE production shop (a mixture of cyclohexanol and cyclohexanone produced from cyclohexane) via a ND100 mm pipeline. A ND50 mm manifold connected to this pipe supplies the adiponitrile (ADN) production facility. This ND50 mm manifold is routed in a pipeway (a group pipes that are half-buried in a trench dug in the ground featuring intermediate mounds of earth) and features an expansion loop located above the other pipes in the pipeway, a manual valve at each end, a valve and heat lagging equipped with steam tracing to maintain the cyclohexane in liquid form (melting point of cyclohexane = 6.47°C).



The OLONE shop continuously draws 800 tons of cyclohexane per day. The ADN shop draws a few tons of cyclohexane only once every 6 weeks.

The OLONE shop and the 10,000 m^3 cyclohexane storage tank are used by 2 different departments of the first operator, the ADN shop is operated by the second company.

THE ACCIDENT, ITS BEHAVIOUR AND CONSEQUENCES

The accident:

On December 16, 2002 at around 9.00 am, the OLONE shop's shift personnel noted an incorrect supply of cyclohexane. The filters were changed, the pumps checked and the ND100 mm pipe visually inspected and the ADN shop was queried. The next day, the disturbances continued and a visual inspection of the ND50 mm manifold was organised. The cyclohexane leak was located by its odour: the leak occurred on the expansion loop of the DN50 mm manifold that supplies the ADN shop.

The consequences:

Approximately 30 hours went by from the time the initial cyclohexane output disturbances were noticed and the leak being stopped. The leak was initially estimated to be in the order of a few tons. A material assessment conducted by the operator 10 days later re-evaluated the leak between 850 and 1,200 tons.

Cyclohexane is a "Category 1" flammable product, of relatively low toxicity, moderately miscible to water (solubility = 55 mg/l), less viscous and lighter than water.

After the leak, the cyclohexane infiltrated for the most part into the soil which was made up of gravel. Only a few small puddles of solidified cyclohexane were visible at the location of the leak; a fraction of gaseous cyclohexane also was released into the atmosphere.

At the upper level of the underground water table, located at depth of 15 metres, the cyclohexane tended to spread out rapidly (supernatant layer). After a few days, the spilled cyclohexane could be found in four different forms underground:

✓ A layer of superlatant cyclohexane above the underground water table represents 70 to 85% of the tonnage released by the leak;

✓ Cyclohexane trapped underground by a capillary phenomenon represents 15 to 30 % of the tonnage released;

✓ Cyclohexane dissolved in the underground water table (less than 1% of the tonnage released);

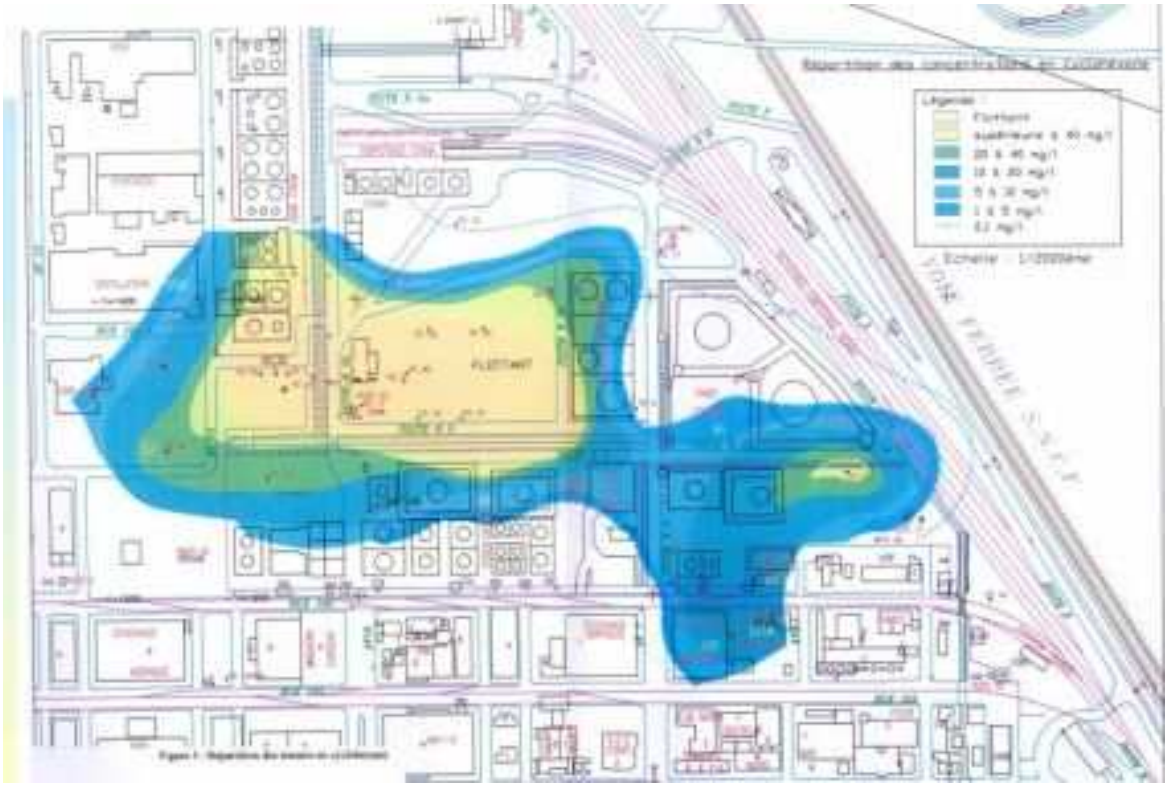
✓ Gaseous cyclohexane underground (less than 1% of the tonnage released).

The layer of supernatant cyclohexane formed the largest part of the cyclohexane released. It was also a supply source for the cyclohexane trapped underground by capillarity, for the cyclohexane dissolved in the underground water table and the gaseous cyclohexane.

The pollution of the water table, one of the largest in the region over the last 10 years, presented a risk of contamination of the community's drinking water reservoirs and agricultural pumping stations located downstream.

The cyclohexane released did not ignite or explode. The internal contingency plan was not put into action.

The overall cost of this leak and the resulting actions was estimated at 2 million Euros.



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

Between 850 and 1,200 tons of cyclohexane were released, representing between 4.2 and 6 times the Seveso threshold which is 200 t (a substance that is highly toxic for aquatic organisms). The index relative to the amount of 'dangerous materials released' is thus 5 (parameter Q1). The "environmental consequences" index was rated as 4 owing to the amount of underground water to be decontaminated: between 10 and 50 ha.
As the cost of decontamination is greater than 1 M€ (parameter €18), the "economic consequences" index is 4.

ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

The ND50 mm manifold's outlet valve is permanently open. Only the ADN shop's inlet valve is closed (the latter valve is opened only in case the ADN shop requires cyclohexane). The ND50 mm manifold is thus maintained under pressure on a permanent basis (2 to 3 bar).

The steam tracing, controlled by a valve, had been turned "off" for an unknown length of time and for an unknown reason. It not longer maintained the cyclohexane in liquid form.

In early December 2002, freezing temperatures caused the cyclohexane to solidify in the manifold. As the temperature varied greatly over the weekend of December 15-16, and owing to the play of the expansion and the retraction of the cyclohexane in the manifold, the manifold broke near the expansion loop (an oblong hole approximately the size of the

palm of your hand), which was the part the most exposed to temperature variations due to its shape and raised position in relation to the pipeway.

ACTION TAKEN

The outlet valve of the ND50 mm manifold was closed as soon as the leak was detected, immediately stopping the leak. The supply of the OLONE shop returned to normal. An existing well, located 30 m from the leak (well No. 23), was used to create a cone of depression (output = 900 m3/h). The existing hydraulic barrier (a network of 25 wells distributed around the chemical platform creating a depression of approximately 2 m aiming to prevent all migration downstream of the water table pollution) was adapted to guarantee that the pollution was confined inside the industrial site.

In late August 2003, the following operations were undertaken:

✓ 55 piezometres (115 mm in diameter) were drilled at the site in order to determine the extent of the pollution, to pump the supernatant cyclohexane, to draw off the gases (venting), and to perform analyses. These operations required special precautions to prevent the risk of explosion during the drilling operations;

✓ 2 cyclohexane fixation wells with a water table barrier were drilled (300 mm in diameter);

✓ 1 sparging barrier measuring 300 m long was set up along the site's northern limit to reinforce the existing hydraulic barrier (injection of air into the water table and recovery of the gases using 18 well doublets);

✓ 4 control piezometres were drilled downstream from the site (in addition to the 3 existing ones);

✓ Several hundred cyclohexane analyses were conducted (on site and downstream) by an independent laboratory (detection limit at 5 µg/l for a potability limit at 10 µg/l).

These operations limited the expansion of the pollution that continued to extend under the industrial site in August 2003 over a surface area measuring 600 m long by 300 m wide. The thickness of the supernatant cyclohexane layer varies from several centimetres to roughly ten or so centimetres.

In **July 2004**, 590 tons of cyclohexane were extracted from underground (more than 90% of which was in supernatant form), using the 3 recovery systems in place: skimming of the supernatant, venting, sparging. However, stabilisation in the quantities recovered was noted at the start of the year (a dozen tons per month). As such, a long term remedial plan is required to treat the pollution.

Studies are underway aimed at bio-remediation of the pollution using bacterial strains, specifically intended to denature the cyclohexane, detected along the periphery of the polluted zone.

The action by the administration lead to the following:

✓ Observe and report the facts,

✓ Conduct 5 inspections January 8, March 7, June 13, July 2 and 3, 2003;

✓ Propose 2 prefectoral emergency orders on January 9 (circumstances of the leak, cleanup operations, monitoring, feedback, information provided to the authorities) and March 12, 2003 (reinforcement of pumping operations, downstream monitoring, third-party expert assessment);

✓ Organise 7 meetings with the operator (including 3 relative to the information provided to the authorities);

✓ Draw up a large number of reports, communiqués and letters intended for the *prefect,* the operator and elected officials, environmental protection associations, judiciary department and the media.

A working group made up of the DRIRE, DDASS, DDAF, and DIREN, was specially compiled to follow-up and evaluate the consequences of the leak and to provide the *prefect* with a proposal to require possible safeguard actions relative to public heath and safety.

The working group's action was primarily based on:

✓ The operator's control of the efficiency of the hydraulic barrier in place in order to contain the pollution inside the industrial site and to avoid all contamination downstream;

✓ Recovery of the cyclohexane;

✓ Monitoring of the water table downstream from the chemical platform.

LESSONS LEARNED

Various actions were conducted aimed at preventing such a leak from reoccurring:

✓ On the leaking cyclohexane manifold:

× Installation of output measurements on all cyclohexane lines with remote reporting in the OLONE control room (material assessment display equipped with an alarm system),

× Preparation of a procedure in case the line is not used (closure of the inlet valve, drainage);

× Annual inspection of the steam tracing;

× Regular verification of the status of pipeway lines;

× Taking into account of the hypothesis of a leak whenever an anomaly is detected (information for the personnel + instruction).

✓ On the site's other transfer dangerous fluid transfer lines:

× A procedure for sharing responsibilities between the site's various units;

× 67 scheduled modifications on the dangerous fluid transfer lines;

× Definition of inspection and servicing of the tracings.

A procedure for providing the authorities with information in case of an incident was drawn up in cooperation with the internal departments of the *prefecture*. It was tested in early 2003. This procedure contains a rating scale for the incident established using a grid based on the characteristics of the chemical product (toxic, flammable, …), the extent of the leak, and the impact both on and off the site. A separate rating deals with the potential impact based on the volume of the system (potential leak), the controllable character of the event, the operability of the safety devices, the potential impact on and off the site, and the estimated cost of damages and operational losses. The information is submitted to the governmental departments (CODIS, Préfecture, Gendarmerie, DRIRE, labour inspectorate, CRAM, SAMU) and to the municipalities. The application of this procedure resulted in the company declaring 16 incidents from January to November 2003.

The Chalampé chemical platform has become a pilot site within the company's group in terms of the information made available to the authorities.

This leak highlighted the following elements:

✓ Technical malfunctions: failure of the steam tracing, lack of real-time information (material assessment) and an alarm enabling the leak to be detected;

✓ The lack of verification programs for the equipment involved (manifolds, steam tracings, …) and the actual designation of the individuals in charge of conducting these checks;

✓ The lack of appropriate instructions in case of a leak;

✓ Communication problems between the operators of the 3 departments involved;

✓ The presence of a large size dead branch without a catchpit due to the inlet valve of the ND50 mm manifold being maintained open;

✓ The inappropriate reactions of the operators associated with the above-mentioned technical and organisational deficiencies and the lack of diagnostic tools should an alarm be triggered;

✓ Incomplete information about the incident.

This leak lead to the following:

✓ Confirmation of hydraulic barrier efficiency (installed in the 1980s following pollution of the community drinking water reservoirs due to the chemical platform);

✓ Retrofitting and implementation of action programs to prevent an major leak from reoccurring;

✓ Re-engineering of the information sent to the authorities and the neighbouring communities;

✓ The manufacturer was reminded of its duty to remain vigilant and to control the processes and the risks presented by its installations;

✓ Quick assessment of the skills and experience of the various departments in charge of overseeing public health, the conservation of natural environments, the water police and the registered installations through the work group.