Leak on effluent pipeline in a chemical plant

August 05 – 11, 2002

Le Havre – [Seine-Maritime]
France

THE INSTALLATIONS IN QUESTION

The chemical plant, located in Le Havre (76 – Seine Maritime) since 1957, is classed as a “Low Level” Seveso facility and employs 420 individuals at the site.

It essentially produces titanium dioxide, which is used as a pigment in numerous markets (paper, rubbers, ceramics, plastics, paints, and inks… as well as in the pharmaceutical and cosmetics industries). The Le Havre site has a maximum production capacity of the approximately 95,000 tons/year. Titanium dioxide can be produced industrially either by the chlorine process or by the sulphate process. The Le Havre manufacturing process uses the sulphate process.

The titanium oxide fabrication operation employs a mixture of natural minerals (ilmenite) and steel industry slag containing a variable quantity of TiO2. The process can be broken down into a series of operations that enables it to be extracted and subsequently purified.

The attack of these minerals by sulphuric acid (also manufactured at the site) generates acid effluents.

Part of this acid process water (the most acidic is referred to as "mother water") is conveyed, via a pipe measuring 18 km in length (ND 300 mm), to the Hode site for treatment before being released into the Seine River.

The other part of this acid water (referred to as "wastewater", with a flow rate of approximately 14,700 m3/day) was released via a dispersal tube into the Baie de Seine, without any specific treatment whatsoever. As of July 31, 2002, the operator had planned to sent its water to the Hode neutralisation installation via a second 18 km long pipe made of SVR ("stratifié verre résine", laminated, fibreglass-reinforced) installed during 2001-2002 (SVR piping ND 400 mm).

July 31, 2002 was a cut-off date as the Baie de Seine drainage line had to be partly dismantled in order to allow the Le Havre port expansion works to continue. In the scope of the “Port 2000” project corresponding to the expansion of port capacities, the operator was required to move its drainage line located in the Baie de Seine in order to move further away from the port's new future access channel.

The two acid water pipes are installations that are related to the registered installations but are also governed by the ministerial decree of December 6, 1982 which outlines technical regulations for the pressurised transport of fluids in pipes other than hydrocarbons and combustible gases. In this respect, the prefectoral order of September 3, 2001 authorising the extension of the Hode installations required the operator to observe specific instructions regarding the location and operation of the SVR ND 400 piping.

The SVR ND 400 piping was installed in compliance with the technical provisions stipulated by the order of December 6, 1982, namely, tubes adapted to the service conditions (nature of the fluid, temperature and pressure) and assemblies correctly installed and checked. The piping, having a design pressure of 10 bar (for a service pressure of approximately 4 bar) successfully completed the water resistance test at 15 bar on July 16, 2002.

On July 31, 2002, and in compliance with the prefectoral authorisation of September 3, 2001, the release of "low-acid" effluents into the Baie de Seine was stopped and the effluents were sent to the Hode facility via the new pipeline, beginning at the start of the week of August 5nd 2002.
THE ACCIDENT, ITS BEHAVIOUR, EFFECTS AND CONSEQUENCES

The accident:

On August 7, 2002 at 12.01 pm, the pipe's monitoring system (line balance) detected a 100 m³/h leak (with a nominal flow rate of 500 m³/h) of wastewater (diluted sulphuric acid: concentration less than or equal to 15 g/l of sulphate), at 5 bar. An inspection performed by the operator in the field and in the set of galleries all along the line from Le Havre to Hode enabled the leak to be located. The leak, evaluated at approximately 20 m³, was due to a 40 cm crack on a tube located on the grounds of the Le Havre plant. After replacing the faulty section, the entire pipe was again tested and the equipment placed back into service.

Four days later, on Sunday, August 11, 2002 at 8.05 pm, a new leak occurred and was immediately detected by the monitoring system. The rated output is 440 m³/h (diluted sulphuric acid), at a pressure of 3.9 bar (these conditions are significantly below the maximum operating conditions and much below the test conditions). The leak was located on the outside of the Le Havre plant, on an underground part of the pipeline, near a section that passes underneath some railroad tracks behind a LPG storage and filling station. The leak was evaluated at between 100 and 200 m³.

In all, between August 5 and August 11, 2002, eight problems were reported, six of which were on the first 2 kilometres of the pipeline. Two failures occurred while in service, in similar conditions, near elbows and changes in direction, while this pipeline had only been in operation roughly ten hours in service conditions where the pressure had never exceeded 5 bar in a diluted sulphuric acid environment (concentration less than 15 g/l) and at temperatures less than 35°C (temperature allowed for SVR tubes 50°C).

On August 11, 2002, the pipeline was shutdown due to a systematic defect. Experts were appointed by the contracting authority and the operator in order to determine the causes of the pipeline failures. In November 2002 and January 2003, leak detection tests using a nitrogen + helium mix enabled two additional leaks to be detected.

The consequences:

All of the soil polluted by the various leaks was treated with sodium carbonate and used as backfill to fill in the trenches. The soil analyses conducted after each of these incidents showed no significant impact on the soil or on the installations located in within the perimeter of the leaks’ potential impact zone.

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.

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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](http://www.aria.ecologie.gouv.fr)

The cost of installing a new PEHD pipe (5.5 M€), intended to replace that made of SVR, explains why the "economic consequences" index is at least 3 (parameter €15).
ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

All of the faults observed on the pipes are similar in the following respects:

✓ the main direction of the cracking: longitudinal along the invert (lower generatrix),
✓ location: near a specific zone, namely a slope or angular change (45°, 30°, 22°, 11° elbows or high point).

It was clearly shown that the damage to the installation was due to a stress corrosion mechanism in an acid environment. Stress corrosion is a cracking mechanism that requires the participation of the following three elements:

✓ A stress (or a permanent deformation),
✓ A material that is sensitive to this phenomenon,
✓ A corrosive environment.

All of the pipeline’s basic dimensioning data were analysed when the damage was discovered. Several facts were established following this analysis:

✓ Soil / structure interaction

As far as the soil is concerned, the installation specification requires a minimum of compacting for the footing and the sides. Soil analysis conducted around the pipeline revealed compacting values lower than those specified. The ovaling of the pipe could have thus exceeded the maximum acceptable value locally.

✓ Hydraulic dimensioning

In order to protect the pipeline from excess pressure (hammering at start-up) and vacuum (pumping shut-down/start-up step), a hammering tank of 20 m3 was installed at the start of the line. In order to be efficient, it had been specified that the cylinder must be initially pressurised to 0.5 bar; during the expert assessments conducted following the various incidents, it was noted that the cylinder had been pre-pressurised to 1.7 bar. The entire pipeline had thus experienced a more violent fall of pressure when pumping had stopped (the greatest negative pressure having occurred in the first 2 kilometres). Furthermore, the potential existence of air at the high points, owing to the fact that there were no vents at the highest points, could have the same hydraulic consequences, in terms of both overpressure and negative pressure.

✓ Service life of pipelines made of composite materials

The pipeline’s design curve relative to the stress corrosion, coupled with a few experimental values in the field of significant deformations, shows that the rupture time of composite pipelines is roughly ten hours for the major deformations.
In summary, the safe-T-tree of the incidents that occurred on the pipeline in August 2002 is as follows:

- **Failure**
  - Stress corrosion
    - rupture time is roughly ten hours for the major deformations.
  - Stress
    - hydraulic transitions
      - pumping shut-down/start-up step
      - potential existence of air at the high points
      - overpressured hammering tank
  - Deformations
    - low compacting values of the soil
      - divergence between calculation assumption and installation device
      - difficulties to correctly compact the soil (nearby pipeline and concrete well)
  - Environment
    - corrosive environment

The failures occurred near or at high points and near a change in direction, which confirms the role played by hydraulic transitions. Certain failures occurred in a zone where it was difficult to correctly compact the soil (nearby pipeline and concrete well). Finally, the majority of the failures (6 out of 8) occurred in the first two kilometres, i.e. in the zone where hydraulic stresses are greatest.

**ACTION TAKEN**

Following the incidents of August 7 and 11, 2002, the pipeline connecting Le Havre and Hode was shut-down; the operator was no longer able to send its "low-acid" effluents to the Hode neutralisation facility. As the flow rate of the "low acid" effluents was approximately 15,000 m³/day, the operator could not use the existing pipeline in service that was used to transport the "mother water" (the most acidic), as the pipeline was not designed accordingly.

The operator thus requested authorisation to release its "low acid" water into the Seine, as it did prior to commissioning the new pipeline, in order to do away with the time needed to replace the leaking pipes and conduct a thorough investigation of the pipeline. The plant cannot operate without creating these effluents and the available catchpit, despite its 30,000 m³, could only accept the equivalent of roughly sixty hours of effluent. A draft order proposed by the DRIRE indicating emergency measures was signed by the Departmental Préfet on August 13, 2002, authorising the operator to release its effluents into the Baie de Seine for a maximum period of one month, provided that the requirements relative to the characteristics of the release be observed (pH at 50 m from the release point must be 5.5 and 9; the maximum average flow rate over 24 h is equal to 12,500 m³/day…).

As the emergency measures order of August 13, 2002 ran out on September 13, 2002, the operator requested an extension of the aforementioned order until December 2002. The Prefect signed a new emergency measures order proposed by the DRIRE on September 17, 2002:

- It took into consideration the true characteristics of the effluent, which thus lead to an increase in the amount of effluent released (with a maximum average flow rate over 24 hours equal to 14,760 m³/day) and to extend the distance at which the pH is greater than 5.5 from 50 m to 80 m;
It foresaw the implementation of a new temporary and back-up Baie de Seine drainage pipe in order to continue investigation operations on the pipeline connecting Le Havre to Hode and the progress of operations on the Port 2000 project.

Until December 31, 2002, the operator thus released its effluents into the Seine, via the old drainage pipe (used prior to the commissioning of the pipeline connecting the Le Havre site to Hode) which was partly amputated due to the Le Havre port expansion operations. At that time, the status of the Port 2000 operations required that this drainage pipe be dismantled as it was located in the zone that had to be backfilled in order to construct the terminals. As the commissioning of the new pipeline connecting the Le Havre plant to the Hode neutralisation facility was not foreseen before the end of the 3rd quarter of 2003, the operator decided to build the new drainage line as an intermediate solution. In compliance with the emergency measures order of September 17, 2002, the file relative to this new temporary and backup drainage line was submitted in mid-October 2002.

A prefectoral order was then signed on January 7, 2003, temporarily authorising (for 6 months, renewable):

- the release of effluents into the Seine estuary,
- the modification of the Baie de Seine discharge point.

As the regulations limited the possibility of temporary provisions, the operator may request that the temporary authorisation be renewed for 6 months, which was undertaken by mail on April 8, 2003. A new prefectoral order was thus signed July 2, 2003 thereby renewing the temporary authorisation for a maximum duration of 6 months.

The operator thus had until January 2, 2004 to discontinue the release of effluents into the Baie de Seine and put the pipeline connecting the Le Havre site to the Hode neutralisation facility back into service.

Furthermore, as the establishment had reported numerous accidents in just a few months time, an emergency measures order of October 21, 2002 prescribed an audit of its Hygiene, Safety and Environment management system in order to ensure that it was sufficient and that it operated correctly.

Finally, a prefectoral order was signed December 12, 2002 requesting that all of the danger studies relative to the Le Havre site be revised. The last danger studies conducted were specific to certain units and were more than five years old. In light of various incidents that occurred at the site, it seemed necessary to take stock of all of the site's dangers and not only on certain specific units.

From the technical standpoint, the operator replaced several leaking pipes. On July 22, 2003, the pipeline successfully completed a new water test at 15 bar held for 2 hours. Acid water tests were undertaken since early August 2003, two other high point tubes that suffered damages were repaired. In November 2003, the plant was shut-down as the acid production unit was being overhauled. New tests were planned as soon as acid effluents would be available.

Finally, a prefectorial act had been signed on the 8th March, 2004. It requires the implementation of a new pipeline until the 30th of June, 2006. It will follow the same route as the previous one but will not be made of SVR but of PEHD (Polyethylene high density).

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1 June 8, 2002: overflow of the effluent storage tank
June 28, 2002: leak on the buffer tank filling pipe
August 7, 2002: leak on the Le Havre – Hode pipeline
August 8, 2002: leak on the Le Havre – Hode pipeline
August 14, 2002: leak on the catchpit
September 15, 2002: fire on an oven feed line
September 23, 2002: fire on a liquid sulphur storage tank
LESSONS LEARNED

The lessons to be learned from this series of incidents concern as much the technical aspect as the organisational component.

**On the technical level**

If the pipes and their assembly were in compliance with the regulatory provisions foreseen by the order, which was approved July 16, 2002 by a satisfactory resistance test, the installation of the pipeline and the pressure control equipment, however, was not completed in accordance with recognised trade practices (disregard for the installation specifications, incorrect dimensioning of the buffer tank and underestimation of the number of vents).

Obviously, this site's project management, involving several parties (internal and external engineering offices, the pipeline constructor, the public works contractors and their sub-contractors, and the operator…), was not optimal. In particular, the prior and systematic verification of calculations, the pipeline installation conditions and the respect of a certain number of rules relative to the pressurisation of the system.

**On the financial level**

This series of incidents generated significant costs for the operator (operating losses, leak repair, modifications of the Baie de Seine discharge point, investigations following the incidents, and the repair of the pipeline…). For example, the shortening of the former drainage line and the reconstruction of a dispersal tube cost 329,300 € (exclusive of VAT) and the installation of a new discharge point was estimated at 5,500,000 €. This work had to be undertaken for conjunctural reasons (the Port 2000 project) by temporarily replacing the new pipeline connecting the Le Havre plant to Hode and would never have been initiated if the new pipeline had been operational as early as the 4th quarter of 2002.

**On the organisational level**

The operator must improve its HSE management system.