Hydrocyanic acid
Adiponitrile
Hexamethylenediamine
Flashback
Transient phases
Safety field
Organization
Communication
Humain failure
Instrumentation

Successive accidents on a chemical platform

March, the 20th , August, the 23rd , September, the 29th and October the 18th 2000.

Chalampé – [Haut-Rhin] France

THE INSTALLATIONS IN QUESTION

The platform :

The Chalampé platform includes 4 chemical plants:

× One plant (A) specialises in organic and basic inorganic chemistry, from which Nylon intermediates. More than 30 prefectorial orders govern the activities of the Chalampé plant which operates various installations subject to authorisation (A) and authorisation with public easements (AS). The establishment is subject to the following directives :

✓ **SEVESO I** of June 24th, 1982 for the use of liquefied flammable gas (propylene) up until its discontinuation, for the use of flammable liquids under special conditions (for the fabrication of Olone), and the use of very toxic preparations and substances (T+)

✓ **SEVESO II**, both for certain sections exceeding the AS limits (use and storage of Ammonia, storage of flammable liquid for instance) as well as under the terms of the addition rule (‘règle de cumul’, required by French regulations).

× A second plant (B), 50% subsidiary of the previous one (A) and 50% of a international group and a producer co-operative, the finished products of which (Nylon intermediates too) are exclusively earmarked to supply the 2 associates.The plant operates various installations subject to authorisation (A) and to authorisation with public easement (AS). Its activities are regulated by **the codificative prefectoral order of November 23rd, 1999**, taken within the scope of a project based on the extension of adiponitrile and hexamethylenediamine production. The establishment is also subject to the following directives:

- **SEVESO I** of June 24th, 1982 for the use of liquefied flammable gas (Butadiene) and the use of very toxic (T+), toxic (T), (O), explosive (E) substances / preparations.

- **SEVESO II**, both for certain sections exceeding the AS limits (use or storage, fabrication of very toxic, toxic, (even with special toxicity) preparations and substances, storage of liquefied flammable gas, storage of flammable liquids, for instance) as well as under the terms of the addition rule.

× Two other gas plants (C and D) set up on the chemical platform contribute to its activity: one produces hydrogen for the on-site plants and the other produces nitrogen and oxygen for the on-site plants, as well as for various outside customers.

The two entities (A and B) which have the same general manager, place products, goods and various services at mutual disposal:

✓ Plant A personnel also operate all of the site's units, including the plant B’s workshops,

✓ a common POI ("Plan d'Organisation Interne", internal contingency plan) was last updated in late 1999,

✓ a common PPI ("Plan Particulier d'Intervention", special intervention plan) (radius of 4,900 m) defined by the prefectoral order of April 15th, 1997:

The worst case scenario retained for the site, a leak on an ammonia tank, includes that of hydrocyanic acid. This scenario considers the rupture of a pipe carrying HCN : release of 15.8 kg/s over a period of 360 seconds, a limit zone of irreversible effects (ZOLERI) of 1,400 m and a limit zone of deadly effects (ZOLEM) of 780 m.

In 2000, the chemical platform experienced a series of 4 significant accidents :

- ✓ On March 29th, 2000 in the hydrocyanic acid workshop of plant B,
- ✓ On August 23rd, 2000 in the installations producing adipic acid in the plant A,
- ✓ On September 29th, 2000 in the adiponitrile workshop of plant B,
- ✓ On October 18th, 2000 at the phosphorus trichloride unloading station, in the plant B.

The first accident is presented in this sheet, the 3 other accidents are mentioned only to illustrate the generic problems encountered and the successive actions of the DRIRE in charge of the classified installations inspectorate

The plant :

The plant A is located 17 km east of Mulhouse, next to the Grand Canal d'Alsace (Rhin - navigable). It is spread over 120 ha, 93 ha of which are enclosed by fencing, belonging to the communities of Chalampé, Bantzenheim and Ottmarsheim.

The development of the site :

Following exclusive production of adipic acid from 1955 to 1959, the plant A put into service and operated workshops used to manufacture plastifiers and vinylic derivatives between 1959 and 1964. From 1965 to 1972, the establishment completed its Nylon line, increased production (400,000 t/year in 1972) and employed 1,240 people. From 1973 to 1976, the site diversified its production with polyester and oxalic acid synthesis units. The production of intermediate products increased to the detriment of the plastifiers and vinylic derivatives.

The subsidiary B moved to the site in 1976. The company, which employs 1,700 people, started hydrocyanic acid and adipontrile (ADN) synthesis workshops. In 1981, the Nylon intermediate products formed 90% of the chemical platform's production and the workforce grew to 1,600. The fabrication of dry N salt (nylon salt) was launched in 1985. In 1993, Nylon intermediate products represented 97% of the site's production. In early 1998, the chemical platform employed 1,150 people.

Between 1999 and 2001, the project of extension which would increase ADN and HMD production by 60%, was being put into place:

- ✓ The installation of 2 new workshops (HCN synthesis, processing of natural gas),
- ✓ The increase in the capacity of the ADN and HMD production shops.

The installation at stake :

The damaged installations, used for the synthesis of hydrocyanic acid (HCN), belong to the plant's adiponitrile production unit. HCN is obtained by a chemical reaction between ammonia and methane.

$$NH_3 + CH_4 \rightarrow HCN + 3\ H_2$$

Liquid ammonia (NH_3) arrives in the unit via a pipe from a neighbouring plant or from a storage tank.

The methane, taken from the natural gas, must be purified before reaction with the ammonia in order to eliminate heavy hydrocarbons (ethane, propane, butane, etc.). These substances, which hamper proper yield of the synthesis process and the service life of the catalysts, would also give excessive amounts of superior nitriles.

The HCN shop includes:

- ✓ **A natural gas purification shop** (TGN) in which the treatment of the gas takes place in 4 phases:
  - ◆ **Heating** of the raw gas,

- **Hydrodesulphurization** : the gas is mixed with hydrogen (H_2) to eliminate molecules sulphated by the catalytic reaction,

- **Reforming-cooling** : the desulfited gas is mixed with steam at 25 bars, converted into CO and H_2 then into CO_2 and CH_4 before being cooled.

- **Methanation-cooling** : the reforming gas is treated by H_2 ; the CO_2 and the CO are transformed into CH4 with the production of water.

✓ HCN synthesis: the reaction produces a temperature between 1,100 and 1,200°C, ammonia, natural gas an d air coming into contact with the catalyst (Pt). The synthesis gases (HCN, water, excess NH3 and incondensable gases) which leave the converters, contain approximately 10% HCN. They are cooled before being sent to an absorption tower where the ammonia is eliminated by spraying using phosphate solutions; 98% of the NH3 and 2% of the HCN are absorbed. The gases cleansed of the NH3 are sent to the HCN purification/recovery section.

✓ Recovery of NH3 (NH3 train): the phosphate solution is sent to a HCN-phosphate stripping tower. The HCN vapours are sent back to the gas input of the NH3 absorption tower and the liquid is sent to the NH3 stripping tower. The stripping of NH3 takes place using steam; after condensation, the NH3/water vapours are sent to an enrichment tower. In the tower, NH3 is separated from the water by distillation and recycled at the supply side of the converters.

✓ **Absorption/recuperation of the HCN (HCN train)** : the HCN train consists of 4 towers

- **stabilisation** : the gases are stripped of traces of NH3 by counter-current spraying with a H2SO4 solution.

- **HCN absorption** : the gases are cooled and stripped of the HCN by counter-current washing with an acid solution. The residual gases are incinerated (CNIM boiler). The washing solution, containing 3.5 to 4.5% HCN, is sent to the next stripping tower.

- **HCN stripping** : the HCN is stripped by steam heating (HCN/water vapours containing 80% HCN).

- **purification** : this tower is used to eliminate all residual water.

The HCN cooled to 5°C is then sent to the relay tan ks which supply the ADN workshop.

THE ACCIDENTS, THEIR BEHAVIOUR, EFFECTS AND CONSEQUENCES

The accident of March 29th, 2000 (ARIA n°17528)

The accident occurred on the HCN production installations, at the level of the separator tank on the residual gas transfer line between the head of the HCN absorption tower and the boiler. Several incidents were noted on previous days :

Liquid extraction difficulties at the base of the HCN purification tower (tower H2243) noted from March 20 to 26, required that a second pump be used. On March 27th, the decision was made to shutdown the distillation train to clean the HCN polymers that had formed. The produce implemented required

✓ deplete the HCN from the train, up to 2% HCN in the drainage water, by directing it toward the ADN unit,

✓ conduct air stripping until an acceptable concentration of HCN is achieved for opening the equipment, the residual gases being burned in the boiler.

On March 28 and 29, the distillation train was drained (shutdown of the HCN converters, as well as the natural gas heaters and the upstream TGN). Draining remained difficult due to extraction difficulties at the base of tower H2243 (purification tower). On March 29th at 1 p.m., it was decided to forego the air stripping phase. The concentration of 1.2% HCN measured in the towers, measured at the base of the HCN desorption tower (H2242), was greater than the value habitually encountered although was below the limit value of 5% tolerated in the operating mode.

In compliance with the instructions in force, the workshop was evacuated by security on March 29th at 4.15 p.m. before the stripping operation was launched. The order to evacuate was cancelled 15 minutes later and 9 individuals returned to the workshop.

The explosion occurred at 4.40 p.m. at the level of separator tank (H1191) at 5 m high on the gas line. Two analysers (Toxguard) nearby (10 to 15 m) indicated 30 ppm of HCN; the concentration dropped after 5 minutes. Other equipment located 100 m from the unit detected values in the order of 4 to 5 ppm of HCN from time to time.

The shop personnel were evacuated to a withdrawal zone and the stripping operation was shut down immediately. The unit's Toxguard detector which triggered the alarm at 4.45 p.m. for a HCN concentration greater than 5 ppm, activated a gas alert and the 300 people present in the establishment were required to confine themselves. The POI was put into operation at the same time and the site firemen intervened with SCBA. Water curtains were set up around the installations. Concentration measurements conducted on the periphery of the workshop gave values less than 2 ppm of HCN.

The header line of the HCN absorption tower was isolated from the HCN desorption tower (H2241) at 5.30 p.m. Only the detector located near the separator unit indicated, still 30 min later, a concentration of 15 ppm of HCN.

As no consequences for the personnel or the environment was signalled at 7.00 p.m., the operator felt there was no need to initiate the PPI (special intervention plan) and lifted the POI (internal contingency plan), as well as the employee confinement order. The classified installations inspectorate (DRIRE) and the mayors of the 3 surrounding communities were informed, although the “préfecture” was not informed by the operator.

The consequences

The operator evaluated the quantity of HCN released into the atmosphere at 25 kg and the property damage was limited: the line to the boiler was expanded over 1m in length and a the collar of the separator tank was ripped over 400 cm². No consequences were observed on the personnel and the plant's environment.

On April 5th, the classified installations inspectorate requested that the operator submit an accident report, as well as the measures taken or to be taken and to check if this type of accident had been contemplated within the scope of the project of extension.

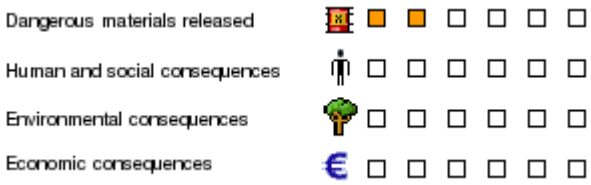
A factual and succinct article published in the local press, also on April 5th, recounted certain comments of the plant's union representatives estimating that plant management had minimised the accident, that the accident could have resulted in deaths and that a series of small incidents had recently occurred.

On April 10th, the operator presented the inspectorate with the conclusions of his post-accident analysis and the measures taken or which would be implemented in the near future in order to prevent such an accident from happening again. It took note of these measures and no objection was made concerning placing the installations back into service.

The cleaning of the installations, the repair of the separator unit and the damaged piping, then the progressive restart of the HCN shop then the TGN (natural gaz purification shop) took place Monday the 10th through Thursday the 13th of April, 2000.

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.



The parameters that comprise these indices and the corresponding rating method are available at the following address : http://www.aria.ecologie.gouv.fr

Hydrogen cyanide is classified as a “very toxic” substance by the 'SEVESO' directive. The 25 kg of HCN released into the atmosphere during the accident correspond to 0.125% of the threshold (20 tonnes), which explains level 2 for 'dangerous materials released' (Q1 parameter).

The accident of August 23rd, 2000 - Emission of nitrogen oxides (ARIA n°18051)

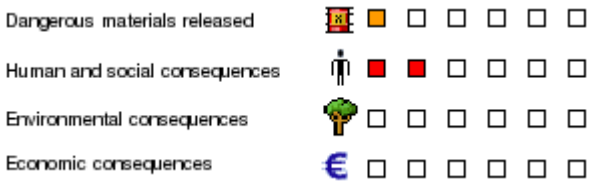
A safety system triggered the emergency shutdown of an adipic unit (AAD4). The safety system was short-circuited due to improper electrical wiring connections made following servicing of the installations.

- Reaction: adipic acid (AAD) is obtained by oxidation of a mixture of cyclohexanone and cyclohexanol by nitric acid (HNO3). The resulting nitrous vapours (N2O and NOx) are drawn in by a compressor and sent under pressure into an RVN oxidation reactor where the nitrogen dioxide (NO2) is transformed into HNO3.

- The emergency shutdown of the AAD4 unit caused a compressor to shutdown and an automatic valve to open allowing the reactor to return to atmospheric pressure.

During this shutdown, a release of reddish brown nitrous vapours occurred 20 m above the AAD4 unit, as well as smaller releases above the adipic reactors. As there was no wind and according to standard tactics, the plant's firemen dispersed the coloured plume using a fire hose. While the fire hoses were being set up, a fireman, not exposed to the nitrous vapours, died - most likely due to heart failure.

By applying the rating rules of the 18 parameters of the european scale of industrial accidents, the accident can be characterised by the following 4 indices :



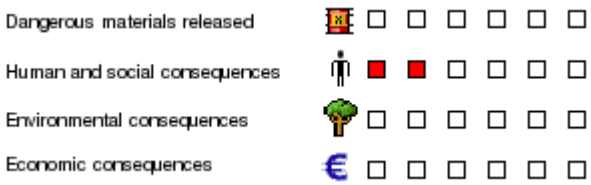
Nitrogen dioxide (NO2) is classified as a very toxic substance, which explains level 1 for 'dangerous materials released' (Q1 parameter). The death of a fireman on the site (without no apparent relation to the toxic substance released) explains level 2 'social and human consequences' (H1 parameter).

The accident of September 29th, 2000 - Emission of « pentenes nitriles » (ARIA n°19185)

According to the operator, 150 kg of nitrile pentenes was released into the atmosphere in less than one minute. No incidence on the environment outside the establishment was observed. At the site, 1,000 people from external companies were working near the extension construction site. The alert was declared immediately, 11 of the sub-contracting personnel were disturbed by evacuating their work stations.

Further to a human error committed during an operation performed while the installations were in transitory operation, a valve was closed instead of being opened.

By applying the rating rules of the 18 parameters of the european scale of industrial accidents, the accident can be characterised by the following 4 indices :



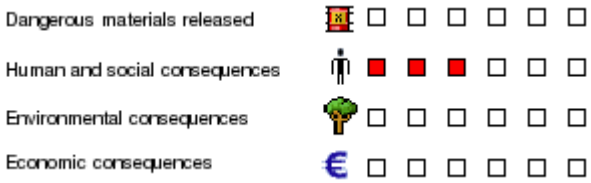
Level 2 for the 'human and social consequences' parameter is explained by the fact that 11 employees were unwell due to exposure to gas and treated on site (H5 parameter).

The accident of October 18th, 2000 - PCl_3 accident (ARIA n°19185)

The accident **occurred in the morning while unloading a rail car of phosphorus trichloride**. The gas alert was triggered and the plant personnel were confined. The internal rescue services intervened immediately and very rapidly controlled the leak, although 22 persons from external companies working at the neighbouring extension construction site were effected and examined by the 2 company doctors; 4 were hospitalised and placed under observation (following intervention by an anonymous call to the Mulhouse fire brigade and SAMU (paramedics) who finally examined 44 individuals). The operator assessed that the level of the incident was not exceeded and did not place the establishment's POI (internal contingency plan) in to operation.

No consequence is observed outside of the site.

By applying the rating rules of the 18 parameters of the european scale of industrial accidents, the accident can be characterised by the following 4 indices :



Level 3 for the 'human and social consequences' parameter is explained by the fact that 44 employees were unwell due to exposure to gas and treated on site (H5 parameter)

THE ORIGINE, THE CAUSES AND THE CIRCUMSTANCES OF THE ACCIDENT

Accident of March, 29th, 2000 : (ARIA n°17528)

The analysis of the accident was conducted by an interdisciplinary work group. It potential causes were examined using the failure tree method. A safe-T-tree was then constructed after having eliminated the highly improbable potential causes **: a flashback produced from the boiler was stopped by the separator tank (H1191).**

According to the operator, the accident was caused by:

- ✓ the presence of polymers in the tower which slowed down the drainage of HCN,
- ✓ at the start of the air stripping phase, an operation conducted with an HCN content higher than normal in the residual gases, the normal drainage of the trains not having been conducted,
- ✓ the presence of several inconsistencies in the implementation procedure:
  - ◆ since 1989, the stripping procedure consists of a blocking phase based on a safety threshold level set at 5% HCN in liquid phase. This threshold is erroneous, stripping at 10°C with an HCN concentration > 1.2% in the liquid leading the lower explosive limit (LEL = 6%) of the hydrocyanic acid in gas phase to be reached.

    At the time of the accident, the HCN concentration of the liquid at the base of the HCN desorption tower (H2242) was **1.2%**, compatible with the threshold.

  - ◆ the sample of liquid analysed at the base of tower H2242, containing 1.2% HCN, was not representative of the real HCN amount of the train.

    A posteriori, the average concentration of the amount analysed was 2%.

  - ◆ the gas phase HCN analyser present at the tower head was not adapted and did not allow the operators to be alerted.

    The device was limited to "normal" operating ranges: alarm at 0.9% and no measurement beyond 1.2%.

  - ◆ the operating mode did not explicitly indicate the action to be taken for a concentration greater than 0.9%.

    By reducing the air outputs, the operators:

    - reduced the speed of the gases in the line toward the boiler,
    - promoted flashback,
    - increased the HCN content in the air and the risk to exceed the L.E.L.

ACTIONS TAKEN

The accident of March 29th, 2000 (ARIA n°17528)

Actions correctives initially proposed by the operator :

- ✓ modification of the shutdown procedure,
- ✓ replacement of the air by nitrogen during the stripping operation,
- ✓ the installation of an analyser at the tower's gas outlet, independent of that of the process and triggering the fail-safe of the stripping operation upon detection of HCN > 0.9%),
- ✓ installation of a flame arrestor between the separator unit and the boiler to avoid flashback.

Measures taken by the Administration:

The inspectorate wrote a report, dated April 27, 2000. On May 4th, the Prefect took note of the modifications proposed by the operator, while giving formal notice for it to :

- ✓ Within **2 months** :
  - ◆ set up criteria and procedures for informing the elected officials and the media consulted together with the Administration, even for minor accidents,
  - ◆ improve the follow up of the HCN contents during installation shutdown phases and to define the means to be implemented to prevent flashback from the boiler.
- ✓ Within **4 months** :
  - ◆ determine and quantify the possible worse case scenarios of the accident of March 29th,
  - ◆ implement a verification program regarding the quality of the procedures and instrumentation used in transitory conditions on all of the company's dangerous installations.

Corrective measures undertaken by the operator :

- ✓ After 2 months, (operator's letter of June 26th, 2000 to the Prefect):
  - ◆ The POI (internal contingency plan) is modified: prefecture, DRIRE and gendarmerie are informed of all gas alerts (even triggered at very low levels) lasting more than 30 min,
  - ◆ A flame arrestor is installed upline from the boiler installed during the next major shutdown of the installations,
  - ◆ The operating procedure is modified for phases after the drainage of the HCN train:
    - Stripping started using nitrogen to lower the HCN concentration in the liquid as in the gaseous phase and to remain below the LEL,
    - Shift to air stripping below 0.7%,
    - Lowering of the alarm threshold and installation of a safety device acting on the recirculation output of the liquid phase,
    - Stripping continues to 1 ppm of HCN in the liquid.
  - ◆ In addition, the operator proposes to improve spraying by an acid solution in the tower to combat the risk of polymerisation due to acidification defects.

- ✓ After 4 months: (letters of September 1st and September 26th, 2000):
  - ◆ Examination of 2 possible worst case scenarios of the incident of March 29th, 2000:
    - **Non closure of valves:** the release would have continued to 1 t/h of N2 at 2.6% HCN → release of 26 kg/h and ZOLEM of less than 50 m.
    - **Explosion propagating after the separator tank up to the head of the absorption tower and resulting in its opening**: the release at the head of 30 t/h of air with 5.6% HCN at a height of 30m and in the presence of a puddle on the ground with a maximum HCN concentration of 5.6%,
      - First release at 0.5 kg/s: ZOLERI 230 metres.
      - Evaporation of the puddle: ZOLERI < ZOLERI worst case scenario of the extension project.

      Such an accident would not exceed the limits of the site.
  - ◆ Launch of a procedure and instrumentation verification program regarding the operation transient phases:

38 situation sheets established: 13 HCN, 10 ADN and 15 HMD will be studied until late 2001.

The accident of August 23rd, 2000 : (ARIA n°18051)

Following an inspection of the site the same day, the DRIRE sent a report to the Prefect on August 30th. This report requested that the operator perform the following, September 7th and within one month's time:

- ✓ Evaluate the quantity of NOx released into the atmosphere, as well as the risks for the neighbouring villages,
- ✓ Study the possibilities of preventing NOx releases during shutdowns,
- ✓ Study the risks of opening the valve while in operation and the means to detect this opening, as well as quantify the releases,
- ✓ Specify the corrective actions implemented at the automatic controller level.

On October, the 6th, the operator answers all the points of the letter and plans the installation of a new abatement column within the end of 2001.

The accident of September 29th, 2000 : (ARIA n°19185)

The operator conducted an analysis of the causes which shows the need to:

- ✓ Clearly identify the valves which must remain open, throughout the rest of the installation,
- ✓ Check the rest of the installation and the extension installation,
- ✓ Define the operations at risk to be performed outside of the extension site's business hours,
- ✓ Set up respiratory protection instructions in the zones difficult to evacuate.

The PCL3 accident of October 18th, 2000 : (ARIA n°19185)

The DRIRE was informed belatedly by the operator, initially by telephone, then by fax (copy of the press release) in late afternoon. On October 19th, it proposed the Prefect to issue an emergency order to suspend phosphorous chloride unloading operations. The Prefect signed the order the same day, making the continuance of these unloading operations subject to the submittal of an evaluation of the circumstances and consequences of the incident, as well as a proposal of corrective measures.

Following an initial refusal on November 17th, justified by the absence of this analysis, the Prefect authorised the activity in question to continue on December 4th.

LESSONS LEARNED

The accident of March 29th, 2000 (ARIA n°17528)

Concerning the technical aspects :

- The operator under-estimated the accident,
- The procedures and the instrumentation in the transient phases were insufficient,
- This accident showed the need to implement a program to verify the quality of these procedures and the instrumentation, encompassing all the installations,
- The accident had limited immediate consequences although led to long-term actions for the operator.

Concerning communication with the exterior:

- The accident highlighted the operator's poor communication with the Administration (limited to the DRIRE while forgetting to notify the Prefecture) and the need to limit the latter beyond the DRIRE to only accidents and incidents described in the POI (internal contingency plan),
- Also, poor communication with the elected officials and the media: information limited to only the mayors, provided late and by channels exterior to the media, information which should take the environment of the site into account (launch of alerts...).