Release of acrolein into the Rhône

10th July 1976

Pierre-Bénite – [Rhône] France

Water pollution
Petro-chemicals
Tank-wagon
Acrolein
Maintenance work
Organisation
Communication
Safety study

On 10/07/76, the release into the Rhône of the contents of a tank wagon filled with acrolein caused one of the most serious incidents of industrial pollution in French history.

Derisory means to hold back the pestilential tide which is invading the Rhone banks at Vienne…THE BATTLE OF THE RHONE 500 soldiers, nets, boats to recover 100 tonnes of rotting fish…Tonnes of dead fish were floating on the Rhone downstream from Lyon.

LES INSTALLATIONS CONCERNÉES

Acrolein had been manufactured in Pierre-Bénite since 1965. The plant, the only one of its kind in France, produced on average 35 t/day of acrolein.

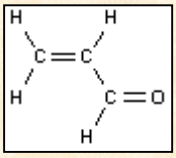
Acrolein was obtained from the catalytic oxidation at high temperatures of propylene supplied by pipeline from a nearby refinery. Apart from acrolein, the compounds present at the end of the reaction were excess propylene, propane, nitrous oxide, water and by-products such as acrylic acid, acetic acid and polyacetaldehydes. The acids and polymers were extracted by scrubbing and incinerated. All other aqueous solutions were detoxified by hot alcalinization.

The acrolein produced at Pierre-Bénite was then transferred to another site where it was used in the synthesis of methionine, an amino acid used in animal feed.

In 2004, a change in manufacturing procedures, to a system known as "the direct method" from propylene, caused the final closure of the plant.

Acrolein

(file INRS n° 57, http://www.inrs.fr/htm/acroleine.html)



- *Also known as acrylic aldehyde or propenal.*
- *Highly toxic product (irritant effect on the mucous membranes and on the skin).*

The mortal dosage for fish varies from 1 to 12 mg/kg, according to the species , which corresponds to a concentration in water of a few mg/l.

- *A highly reactive product which polymerises easily (exothermic reactions which may become explosive):*
  - *in the presence of bases, aminates, strong acids or peroxides*
  - *in the presence of water (violent polymerisation)*
  - *dimerisation in air, heat or light.*

  It must therefore be stored stabilised under inert gas..
- *Reagent used in numerous industrial and chemical reactions, in particular in the manufacture of methionine, acrylic acid and glutaraldehyde.*

THE ACCIDENT, THE SEQUENCE OF EVENTS AND THE CONSEQUENCES

The accident :

➢ The plant operations were halted on Friday 2 July 1976 for maintenance work. The personnel were reduced to 2 operators per shift and mainly occupied by the supervision of sub-contracting companies.

➢ ON July 8th, 2 2 wagons n°385 and 387 each containing 20 t of acrolein were awaiting dispatch and were placed, as a precaution, beneath sprinkling lines.

➢ On Saturday July 10th, wagon n°384, which arrived empty for repairs, ha d to be de-gassed and rinsed. The acrolein, being highly inflammable, these two operations were also conducted under sprinkling lines. As a consequence, empty wagon n°384 was parked beside filled wagon n°387. Few members of the personnel being present on the weekend, the rinsing was postponed until Monday July 12th. The operator therefore wrote on a board in the plant control room "Fill wagon 387 with water" (or it could have been 384, badly written), and wrote in a diary on July 12th the words "Fill wagon 384 with water".

➢ On this same July 10th, an operator coming on duty took notice of the board and began to rinse wagon n° 387 at 15h30. The acrolein being transferred under nitrogen overpressure, the wagon has a plunger tube and a ventilator. During the rinsing, the ventilator was connected to a tube plunged in a sodium neutralising bath while the water enters the wagon via the plunger tube which has a flow-rate of 15 m³/h. The operation presented no difficulties and no abnormal smell caught the attention of the operator who left the scene to undertake another task.

➢ One hour later, the operator returned to the scene and noticed the presence of abundant foam and a crust of polymer in the neutralising bath. He halted the release, consulted the despatch log, realised that he had emptied a wagon filled with acrolein and vainly attempts to reach his supervisor by telephone. Ill informed about the conditions for intervention in the event of accidents and the possible consequences, he added 1 t of sodium to the neutralising trench and, by the use of fire-hoses, injected a large quantity of water into the trench. Fearing the formation of polymer in the wagon, he decided to end the rinsing and drained the rest of the contents of the wagon into the drains. On the next shift, the operator, informed of the accident, continued the cleaning of the trench and the rinsing of the wagon.

➢ Heavily acrolein charged effluents were generally treated with concentrated sodium at high temperature (90 °C) in a specific reactor within the plant. The acrolein was thus destroyed within 15 minutes. On the other hand, the caustic soda in dilute solution can polymerise effluents with low concentrations of acrolein; this is what occurred in the 15m³ neutralisation trench into which flowed the water used in rinsing the tank wagons. .

➢ The basin being designed to neutralise a few litres of acroleiin and not some twenty tonnes, only a very small part of the acrolein present in the neutralisation trench was polymerised (in the form of a crust) prior to its release into the Rhône.

The RHONE at Pierre-Bénite

The consequences

➢ The acrolein has a catastrophic impact on the river until its concentration fell below 1 mg/l. For a week, hundreds of firemen, soldiers and volunteers gathered 367 t of dead fish along 90 km of the river (5 départements were involved). The pestilential smell obliged the emergency teams to wear gas masks. The dead fish were then incinerated or buried in a vast ditch in a quarry, where they were treated with quicklime.

➢ Safety measures were taken to :

- forbid all bathing downstream from Pierre-Bénite
- survey the water catchments and wells fed by the Rhône
- check regularly the distribution of drinking water.

➢ The company had to pay to various fishing associations an indemnity of almost 4 MF calculated on the basis of a flat rate of 10 to 25 F/kg of fish (white fish or carnivorous species).

European scale of industrial accidents

Using the scoring rules of the 18 parameters of the scale approved by the Committee of Competent Authorities of the Member States in February 1994 for the application of the 'SEVESO' directive, each accident can be characterised by the following 4 indices taking into account the available information.

The accident at Pierre-Bénite is characterised by the following indices:

The ¨parameters comprising these indices and the corresponding methods of scoring can be found at the following address: http://www.aria.ecologie.gouv.fr

The level 5 index relating to the release of dangerous substances (parameter Q1) relates to the release of 20 t of acrolein, a product classified as highly toxic in the directive 96/82/CE known as 'SEVESO 2'.

The 367 t of dead fish collected explain the level 6 of the index of environmental consequences (parameter Env10).

Finally, the measures taken to rehabilitate the environment, costing 4 MF 1976 (or the equivalent of 1.8 M€ 1993) are characterised by the level 4 on the index of "economic consequences" (parameter €18). .

THE ORIGIN, CAUSES AND THE CIRCUMSTANCES OF THE ACCIDENT

➢ The primary and determining cause is human error: an erroneous indication "fill wagon 387 with water" (figure badly written or mental confusion in the numbers) noted on the board by the foreman of the previous shift. This also reveals the lack of organisational rigour in the transmission of information between shifts and also the inadequate level of supervision (management on call…) as well as in the operating practices.

➢ Other major elements, at the origin of this pollution, reveal organisational shortcomings:

- the parking of two wagons, one full, one empty, beside one another and with closely resembling numbers (384 and 387).

- the shutdown since 4 months of the effluent storage and control-before-release trenches, while awaiting a new waterproof lining. The volume of these trenches (2 x 250 m³) would have been sufficient

to recover the acrolein charged effluent. Normally conducted in these trenches, the rinsing operations were "provisionally" conducted in a neutralising corridor with a far lower capacity.

- a partly inappropriate reaction by the operator, who was ill informed of the intervention procedures and the possible consequences – and could not reach his superiors. The plant management was only made aware of the accident 36h after it occurred.

- a below strength surveillance system and a slower discovery of the anomaly, the plant being under seasonal stoppage and having reduced personnel..

THE MEASURES TAKEN

The penal and administrative measures taken following this accident were heavy:

➢ the director of the plant was condemned to one month's suspended prison sentence and to the payment of a fine of 5 000 F for the misdemeanour of releasing acrolein and 2 000 F for the offence of non respect of a decree from the Prefect,

➢ the company also had to indemnify a consumer association (5 000 F) and a neighbouring businessman (2 000 F) but above all to indemnify various fishing associations (4 MF),

➢ dispositions, taken as a follow-up, for the major industrialists of the region, included:

- a programme of equipment with high capacity storage and retaining tanks,

- follow-up analysis, prior to release, of cooling and heating water supplying exchangers or devices in which circulate water which, by virtue of its quantity of its characteristics, may involve discernable consequences to the natural milieu. The operators must supply to the Inspectorate of Classified Installations a list of installations which are systematically or occasionally concerned.

- a detailed examination of the causes of all abnormal variations in the characteristics of effluents susceptible to lead to accidental pollution,

- the preparation of an anti surface-water pollution file covering the principal toxic elements used or manufactured in the plant. This file must be regularly updated to take into account the evolution of knowledge and techniques and will include all elements known on::

1. the toxicity of the products released
2. their evolution and conditions of dispersion in the natural milieu
3. the definition of zones which risk being attained by concentrations of pollutants likely to lead to consequences to the natural milieu or to the various uses of the water (bathing, industrial procedures…) The definition of these zones must be founded on either life-size or modelled dispersion tests.
4. methods of elimination of pollutants to be implemented
5. remedial measures to be used to treat persons and the fauna and flora exposed to this pollution.
6. analytical methods or methods for the identification of the substances in question and the competent bodies to conduct such analyses. The operators of chemical industries located close to the Rhone have grouped themselves to implement tracing and thus develop a model for the diffusion of pollutants accidentally introduced into the Rhone. This model, baptised " DISPERSO" allows for the determination in a few minutes of the true impact of a release into the natural milieu.

➢ This accident and several others which occurred between 1972 and 1978 are at the origin of one of the first safety studies conducted in France. Completed between 1978 and 1980, this study covers the entire acrolein unit and cost 1.5 MF. Modifications to 'installations and new preventative dispositions were then proposed and subsequently implemented. The corresponding investment amounted to 12.4 MF.

THE LESSONS LEARNED

➢ The annual shut-down is often the occasion for a "mini demographic upheaval" in the plant. Production having ceased, the personnel of the plant is reduced and makes way for employees of outside companies responsible for maintenance works who have less knowledge of the installations and safety rules.

A mistake which would have remained benign during a period of normal operations can easily become serious if the activities on the site are not supervised by a sufficient number of internal personnel. It is thus necessary, in this type of situation, to clearly designate responsibility for oversight of the maintenance works to a sufficient number of people or, failing that, to organise the scheduling of the works in order to reduce the number of works operations conducted simultaneously.

- When works take out of operation one of the organs of a plant, it is necessary to put into place a suitable replacement. As regards this, the neutralisation corridor, ”provisionally” provided to gather the products issuing from the empty tanks did not constitute a sufficient solution (far lower capacity, absence of control of effluents…).

- If these « simple » human errors are easily identifiable, they must not hide organisational deficiencies which require a deep re-examination (on-call management, working instructions, training, intervention procedures…).