Water pollution after a fire in a chemical plant

June 15, 1985

Roussillon – [Isère]

France

- Fire
- Chemistry
- Warehouse
- Pyrocatechin / oxadiazon
- Organisation
- Firefighting water
- Dead fish
- Water distribution

The water used in fighting a fire in a chemical products warehouse, and highly charged with toxic substances, made its way to the Rhone River. Seventy tons of dead fish were recovered from the river. The drinking water supply was disrupted for 2 days in 3 departments.

THE INSTALLATIONS IN QUESTION

Created in 1915, the plant is located 60 km south of Lyon. It operates on 95 ha of land, extends more than 2 km along the banks of the Rhone and has a workforce of 1,900 people, including 75 executives.

The plant operates roughly twenty production facilities which produce numerous intermediate chemical products with 4 highly diversified production lines:

- phenol and its derivatives (nitro and aminophenol, salicylic acid, and paracetamol),
- acetic acid and its derivatives,
- methylchlorosilanes (raw materials used in the fabrication of silicones),
- methionine (amino acid for animal feed).

The Rhone River near Roussillon

THE ACCIDENT, ITS BEHAVIOUR AND CONSEQUENCES

The accident:

On June 15, 1985 at around 10.15 pm, flames were noted in a 1,600 m² building that had been converted into a finished product warehouse. The fire spread throughout the building despite rapid intervention by the internal fire department based nearby.

The operator alerted the public fire department which arrived at the scene around 10.50 pm. Reinforcements arrived at approximately 11.10 pm. Significant resources were employed to combat the fire and prevent it from spreading to the neighbouring installations. The building was located just 40 m from a nitric acid production unit and ammonia tanks. These firefighting resources also were used to cool down thirteen 1-ton containers of dimethyl sulfate (DMS), a highly toxic product, stored near the facade and which had to be moved.

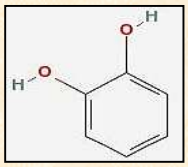
At around 11.00 pm, the building's metal roof and framework collapsed in flames. The tangle of beams and roofing sheets complicated firefighting operations, significantly reducing the efficiency of the extinguishing agents employed. The emergency services thus had to use large quantities of water.

At 11.40 pm, the rescue personnel were informed of the exact nature of the products stored: 639 tons of pyrocatechine (a product similar to hydroquinone), 88 tons of oxadiazon (herbicide) and 80 tons of diphenyl-propane or DPP (a raw material used in the manufacture of plastic resin). As the firemen were familiar with the high solubility of pyrocatechine and its high toxicity in an aqueous solution, an attempt was made to minimise the amount of firefighting water used by spraying foam on the fire and by limiting spraying, but these measures were inefficient.

Pyrocatechine

(http://www.cdc.gov/niosh)

- *$C_6H_6O_2$: also designated Pyrocatechol, 1,2-dihydroxybenzene or 1,2-benzenediol.*



- *Generates irritating smoke during combustion.*
- Irritating for the skin, and respiratory and digestive tracts.
- *Solubility in water: 430 g/l*
- *Toxic for aquatic organisms (LC 50 24 hours of 5 mg/l for fish). The American Conference of Industrial Hygienists (ACGIH) has classified this substance as a carcinogen in animals.*

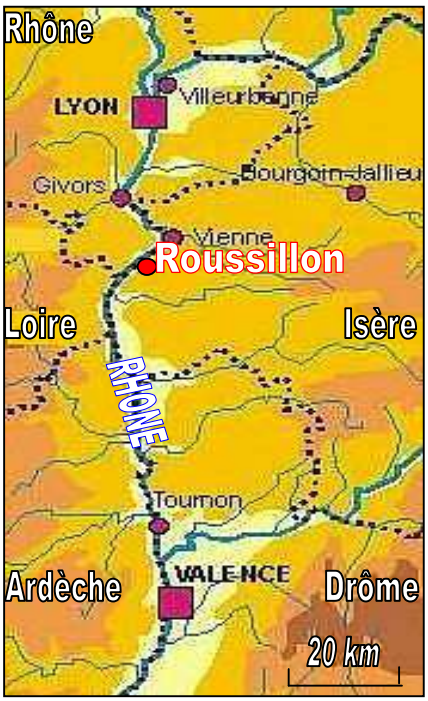
In order to protect the DMS warehouse and the nitric unit, and thus prevent serious toxic atmospheric pollution, extinguishing and cooling operations using water were resumed with full knowledge of the facts. Part of this water polluted the Rhone. Approximately 200 tons of pyrocatechine and an unestimated quantity of oxadiazon and DPP flowed into the river. In addition, oxadiazon is classified among the highly toxic substances for aquatic organisms under the terms of the 'SEVESO 2' directive, 96/82/CE.

Pollution monitoring equipment was installed to monitor the Rhone at 11.45 pm. Samples were taken and analyses were performed on the establishment's releases and in the river water, flowing at a rate of 1,100 m³/s. The first analyses indicated a concentration of pyrocatechine in the releases of 1.2% by weight. The maximum concentration was noted at 0.05 am (1.5%) although remained strong throughout the night (0.25% at 4 am). Samples taken in the Rhone and 3 km downstream from the plant gave a concentration of 25 ppm at 3.30 am and 15 ppm at 6 am.

The fire was brought under control at around 5.30 am and finally put out at 6.15 am; spraying was then stopped.

Pollution monitoring operations were maintained throughout the day of June 16th. At 11.30 am, dead fish were reported at distances up to 75 km downstream from the discharge location. The operator performed two series of tests along the river which allowed the pollution front to be located: it was located at 35 km at 3.20 pm (8.8 ppm) and at 68 km at 9 pm (3.5 ppm).

From June 16-18, specific measurements were taken to ensure that both the water and the population were protected (pumping was suspended in the water table, fishing and swimming were prohibited, and clean-up of dead fish).



The consequences:

The 1,600 m² warehouse and all the products stored there were destroyed.

The Rhone was polluted over nearly 70 km and approximately 70 tons of dead fish were recovered and incinerated.

The drinking water supply of numerous cities was disrupted for 2 days along 200 km of the Rhone River valley. More than 130,000 inhabitants were concerned.

Damages within the company were evaluated at 36 MF and operating losses at 3 MF. Fishermen would receive 2.6 MF in compensation.

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 Roussillon 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 available at the following address: http://www.aria.ecologie.gouv.fr

The level 4 rating relative to the quantities of dangerous substances released (parameter Q1) corresponds to **88 t of oxadiazon**, which is classified as highly toxic for aquatic organisms under the terms of the 'SEVESO 2' Directive 96/82/EC.

The 130,000 people deprived of drinking water for 2 days explains the level 6 rating of the 'human and social consequences' index (parameter H8).

The 70 t of dead fish explains the level 5 rating for the 'environmental consequences' index (parameter Env14).

And finally, the 36 MF in property damage within the establishment account for the level 3 rating of the 'economic consequences' index (parameter €17).

ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

The origin of the fire could not be determined. The products stored were non-flammable powders, stable at ambient temperature although combustible.

ACTION TAKEN

Technical actions

The polluted water within the building was pumped into a tank and treated by a specialised company.

All of the products recovered, including rubble and chemical products, were stored in an abandoned building pending destruction.

Administrative actions

The administration noted offences against legislation relative to the ICPE and requested that the operator reinforce the protective equipment resources and improve management and emergency plans.

Legal actions

The Magistrate's Court of Vienne (Isère) discharged the director in April 1986 for nullity of the proceedings. The District Attorney entered an appeal. The Court of Appeal of Grenoble (Isère) sentenced the operator to pay a total of 2.6 MF to roughly twenty fishing companies and associations in the Drome, Ardèche and Isère departments effected by the pollution in the Rhone.

LESSONS LEARNED

- Intervention difficulties:

The firemen's progression was hindered by the collapsed roof, which created an entanglement of beams and roofing sheets. The collapse of the roof also significantly hindered firefighting efforts with foam which could have avoided the massive water pollution that followed.

- Following this accident, the establishment was required to reinforce its prevention program. Completed in 1987, the program is broken down into 4 main categories:

  ✓ Reinforcement of fire detection and monitoring (implementation of an internal alert network, monitoring of explosive atmospheres, additional leak detection...). Alarms are reported in the control rooms and in the plant's fire control department.

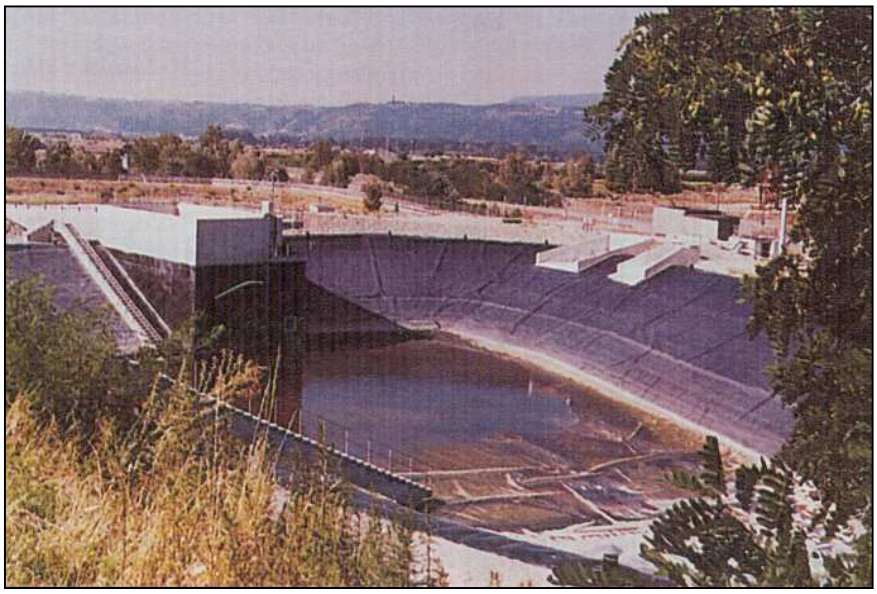
  ✓ Permanent monitoring of aqueous releases on 3 levels:

  - in the workshops (pH, COT, phenols, conductivity…),
  - in the 4 main sewer drains (output, COT, pH),
  - in the plant's general effluent (output, COT, pH, phenols, conductivity, Redox potential).

The information collected are then sent to the site's central laboratory where someone is always on duty. This system, the purpose of which is to isolate the network where the pollution has originated, renders the production workshops more accountable by requiring them to improve their process in an attempt to achieve minimum pollution.

✓ Installation of a containment sump for accidentally polluted water (10 MF).

A 10,000 m³ gravity fed containment sump was made on a branch of the site's main sewer system. It was designed to contain, for 6 hours, the output of the most charged main sewer drain, increased by the foreseeable volume of firefighting water in case of a fire in the largest workshop on the network. The sump is hermetic thanks to a 3 mm thick welded membrane.
Shut-off valves, located on each main drain and remotely controlled, are used to channel the waste water to the sump if the alarm thresholds are exceeded. A 250 m³ secondary concrete sump allows the polluted effluent to be treated prior to release into the natural environment.



Source DR

Spill containment sump built following the accident

✓ Modelling of the dispersion of toxic effluents into the Rhone during the accident.

At the request of the Classified Installations Inspectorate, the region's Chemical Industries Group ("Groupement des Industries Chimiques") developed a calculation program entitled "DISPERSO". By knowing the duration of the release, the quantity and the toxicity of the product involved, and the flow rate of the river and its main tributaries, the program determines the progression of the spill within 45 minutes (front, maximum concentration, trail) and the changes in concentrations at a given location. The program was validated from reports compiled at the time of the accident and by tracing and measurement operations in a 100 km zone downstream from Lyon.