

A series of accidents in a chemical plant

Between 2003 and 2004

Auzouer-en-Tourraine – [Indre et Loire] - France

Fire / Explosion Flood Aquatic pollution Chemistry **Organisation / Management Training Procedures** Safety data information package **ATEX** (explosive atmosphere) **Property damage**

THE INSTALLATIONS IN QUESTION

The chemical plant employs 135 people, including 25 engineers and executives. It operates around the clock, manufacturing approximately 400 chemical products and uses numerous toxic and/or flammable substances. The company's activities are governed by the "upper" threshold of the "Seveso 2" directive, owing to the nature and quantities of the substances stored, formulated and used.

THE SUCCESSION OF ACCIDENTS: BEHAVIOUR, EFFECTS, CONSEQUENCES, ACTION TAKEN AND LESSONS LEARNED

In 2003 and 2004, five accidents or incidents were reported to the Classified Installations Inspectorate:



Press articles

- February 2, 2003: pollution of a river as the result of a leak on a filter in a workshop;
- **December 15, 2003:** an explosion followed by a fire in a R&D building;
- January 13 and 14, 2004: partial flooding of the site. As the reactors were being washed during this period, the wash water mixed with the flood waters via the piping;
- Night of February 27, 2004: ammonia released for an hour
- July 19, 2004: pollution of a river. The analyses conducted at the discharge point of the plant's treatment plant indicated that the standards established under the authority of a prefectorial order had been significantly exceeded (7 times the authorised threshold for phenols, 5 times that authorised for COD, and 3 times that authorised for nitrogen). A few days after having noted this pollution, the Supreme Council for Fishing estimated that 80% of the piscifauna (approximately 400 to 500 kg of fish) had disappeared downstream from the site.

February 2, 2003: pollution of a river as the result of a leak on a filter in a workshop (ARIA No. 30077)

× The accident:

On Sunday, February 2nd, between 5am and 8am, 20 m³ of an iron complex likely to contain phenols and other toxic substances were released from a filter system located in a workshop. The leak, resulting from the expulsion of an element on the upper part of the filter, resulted to the release of polluting substances into the river.

× The consequences:

The liquid substance spread out over the ground and entered the wastewater network. As the 2 day pools located downs line from the station were unavailable, the polluted water did not pass through a buffer tank enabling it to be checked before being sent to the pools of the plant's treatment plant. It was thus not possible to process the polluting load.

On Monday morning, when the Inspectorate arrived at the site, the releases from the station were highly coloured and visible over approximately fifty meters.

The results of the analyses conducted on a sample taken Monday morning showed that the discharge standards had been exceeded:

	Sample	Standard
- chemical oxygen demand (COD):	1,826 mg/l	350 mg/l
- overall nitrogen:	99.7 mg/l	32 mg/l
- iron :	265 mg/l	5 mg/l

The significant flow rate of the river at the time of the release limited the environmental impact of the accident.

× 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.

Dangerous materials released	181			
Human and social consequences	$\dot{\P}$			
Environmental consequences	4			
Economic consequences	€			

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

The Env12 parameter of the "environmental consequences" index is rated 1 by default, as the volume of polluted water had not been determined.

× Lessons learned and action taken :

The consequences could have been reduced by the proper application of the safety instructions.

The significant quantity of substance released (20 m³ over a 3-hour period) is the result of the operator not being at his workstation for an extended period of time. The operator in question had been working in another workshop at the time of the accident. Filtration takes place without monitoring.

In addition, the malfunction was discovered Sunday morning, but the non-compliant effluent continued to flow toward the river until the following Monday.

These two elements point to a problem in the application of safety and emergency procedures.

The Classified Installations Inspectorate recorded the facts and implemented the corresponding actions.

December 15, 2003: explosion followed by a fire in a R&D building (ARIA No. 26064);

× The accident :

On December 15, 2003, around 5pm, an explosion and fire was reported in a laboratory on the first floor of the research and development building.

× Causes:

According to the subsequent investigations, it appears that this accident was caused by the explosion and fire of a mixture of highly flammable solvents (tetrahydrofuranne and hexane) contained in an open 15-liter container and in 2 open jars. All three of these containers were located in an operating extractor hood in the laboratory, while the laboratory technician was absent (3 to 4 min.).

It appears that the electronic heating regulator of a heating mantle (placed in the hood) caused the ignition of the solvent/air mixture that had formed in the hood. The electrical defectiveness of this regulator, not designed to be used in explosive atmospheres, was thus the cause of the accident.

× 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.

Dangerous materials released	X 🔲			
Human and social consequences	ர் □			
Environmental consequences	🌳 🗆			
Economic consequences	€□			

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

By default, parameter Q1 is given a rating of 1, as the quantity solvents involved is unknown.

As the effects of the explosion had not been characterised and windows were broken at distances less than 300 m, parameter Q2 was given a rating of 1.

The overall "dangerous materials released" rating is thus 1.

× Lessons learned and action taken :

In this accident, in which no one was injured but which destroyed the laboratory and blew out several windows on the first three floors of the R&D building, it appears that:

- the laboratory operators did not take all the adequate safety measures,
- the equipment that they were using was not compliant for use in areas with explosive atmospheres.

As regards the regulations, it is the operator's responsibility to define the explosive atmosphere zones and to adapt the electrical equipment to the regulatory requirements stipulated for use in these zones. In any event, this rule was not respected at the site.

The inspectorate of classified installations recorded the facts. A prefectorial order was issued to collect and process the toxic waste produced by the accident. Extensive investigations were also ordered concerning the R&D unit's workstations.

The operator was formally instructed to delineate safety zones, to bring the electrical equipment used in explosive atmospheres up to standards and to install additional firefighting equipment in the R&D buildings.

January 13 and 14, 2004: partial flooding of the site (ARIA Nos. 27920 and 28558)

× The accident:

Due to the sudden rise of the river on January 13 and 14, 2004, water entered part of the site and was polluted by spreading over the ground and mixing with the wastewater in the networks. This led to further pollution of the natural environment. Traces of spillage of coloured substances, containing iron and aluminium, were noted in various locations.

× 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.

For accident No. 27920, the indices are as follows:

Dangerous materials released	181			
Human and social consequences	min (
Environmental consequences	P			
Economic consequences	€			

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

The Env12 parameter of the "environmental consequences" index is rated 1 by default, as the volume of polluted water had not been determined.

× Lessons learned and action taken :

In this accident, it should be noted that the consequences of the pollution were compounded by the fact that the reactor cleaning operations were continued during this period. The wash water mixed with the floodwaters via the piping, which could have been avoided had the emergency instructions been applied.

The Classified Installations Inspectorate recorded the facts and a supplementary order of the prefect called for a study relative to the flood hazards, operations designed to insolate the site and a study relative to the origin of the spillages.



July 19, 2004; pollution of the river (ARIA No. 27923)

× The accident:

On July 19, at approximately 7 pm, after having noted dead fish downstream from the plant, the Supreme Council for Fishing visited the site, accompanied by the plant operator to take a sample at the treatment plant's outlet. There were no visible signs of pollution in the area surrounding the discharge points.

On the morning of July 20, after having checked the results of the effluent sampled at the treatment plant's outlet, the manufacturer noted that they were significantly above the standards and stopped their release.

A deviation in the plant's operating procedures, primarily over the weekend of July 17/18, 2004 resulted in the releases exceeding the standards established under the authority of a prefectorial authorisation (7 times the authorised threshold for phenols, 5 times that for COD, and three times that authorised for nitrogen).

The analyses, conducted on the samples taken automatically at the station's discharge point and maintained refrigerated by the operator, provided the following results (in mg/l):

	Release of 07/16	Release of 07/17	Release of 07/19	Standard
- chemical oxygen demand (COD) :	433	586	1690	350
- overall nitrogen	26.1	35.9	110	32

In addition, analyses conducted on the sample taken at the plant's discharge point by the Supreme Council for Fishing in the evening of July 19th, confirmed the malfunction: significant Suspended Solids (SS), phenol content of 0.255 mg/l which is well above the authorised value of 0.05 mg/l.

× The consequences:

The high content levels largely contributed in downgrading the receiving environment, notably its oxygen content required to sustain aquatic life.

The treatment plant's malfunction killed several hundred kilos of fish over 3 to 4 km downstream from the discharge point and, according to the Supreme Council for Fishing, also destroyed a large portion of fauna along the river.

According to the operator, "fixed-term contract" and temporary personnel washed the containers used to transport chemical residues over the weekend. This washing operation may have been the origin of the malfunction.

× 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.

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Three parameters are involved in determining the level of the "Environmental consequences" rating: Env10, Env12 and Env14.

- Level 2 of the Env10 parameter is associated with the 300 kg of fish killed in the water (Env10 between 0.1 t and1 t).
- The Env12 parameter is rated 1 by default, as the volume of polluted water had not been determined.
- Level 3 of the Env14 parameter corresponds to the river pollution over 3-4 km (Env14 between 2 km and 10 km).

As a result, overall "Environmental consequences" rating is 3.

× Lessons learned and action taken:

The washing operations conducted without supervision by a foreman contributed to sending large amounts of chemical pollutants to the treatment plant, that the facility was unable to process, inasmuch as the operator did not first check the plant's ability to process the water collected in the buffer tanks located upline.

This event once again shows that there is a problem relative to the application of procedures and a lack of supervision of the personnel.

The Classified Installations Inspectorate recorded the facts and a complementary prefectorial order was issue bearing on the reinforcement of daily inspections and the implementation of specific drum cleaning procedures.

FOLLOW-UP - MEASURES TAKEN

The disregard for safety instructions, faulty or non-compliant equipment, tasks performed by insufficiently trained personnel, the installation operating without surveillance, and instructions not followed, are all causes of the accident at the site. These elements were detailed in reports made following inspection visits during which the organisation and the management of the safety management system (SMS) were regularly found to be faulty.

Some of these characteristics findings, established during the in-depth inspections conducted in 2003 and 2004, are presented below.

2003 inspection

The main findings concentrated on the disregard of procedures related to the management of procedural modifications, the consistent delays on the inspection of certain safety-related elements owing to a lack of personnel to conduct the preventive maintenance operations, as well as the storage of an abnormally high quantity of containers outside retention facilities.

× Deviations concerning the management of procedural modifications :

Certain manufacturing operations were conducted in reactors whose volumes were greater than those indicated in the safety study. The Inspectorate questioned the operator about the procedure followed to ensure that this modification did not present a hazard.

The reliability study for an operation of this type was conducted without formalisation and in the following manner:

- the reaction was carried out in the reactor of volume V1, using the quantities of product stipulated for the reactor of volume V2 (V1>V2)
- the reaction volume was progressively increased up to V1, while checking that the cooling power is sufficient for the next reaction volume.

This procedure was not compliant with the SMS which specified that the change in reaction parameters (quantity of reagent, temperature, pressure and output conditions...) must form the subject of an in-depth examination, updating of the safety studies and possibly laboratory testing.

The manufacturer must also ensure that the new reaction conditions remain safe, which requires a minimum level of investigation and validation by sufficiently-trained agents.

It was also found that certain recommendations outlined in the safety studies were not followed (notably the temperature recordings).

28558, 27923, 30077

x Deviations concerning the management maintenance operations :

During the visit of two workshop facilities, the Inspectorate wanted to check the follow-up of safety-related equipment. For the 13 instruments (thermometers, pressure switches...) declared as safety-related for these two workshops, only one had been inspected during the 12-month periodicity indicated for the inspection of safety-related elements and some had never been inspected since they had been installed.

Conversely, certain non safety-related instruments had been inspected during this period, thus demonstrating a total lack of ranking of instruments to be inspected first.

The same was true for a phosphorous trichloride (PCI₃) storage tank, a product that is highly corrosive and toxic. The danger study stipulated that the tank was to be drained and inspected on a yearly basis, and to change the bottom valve. While this operation had been performed following corrosion problems and leakage on these elements, the inspectors noted that the valve had not been replaced since 1999.

2004 inspection

The findings concentrated on the storage conditions that did not ensure a sufficient level of security.

Certain containers were outside confinement zones and the lack of passageways prevented easy access to the products stored in case of an accident. The fixed storage retention zones which were flooded two weeks earlier still held a considerable amount of water, making their capacity insufficient.

Once again, the inspection of maintenance operations was determined to be faulty. While a danger study stipulated that the high temperature alarms must be tested on a daily basis, the operator was not able to describe this test.

The equipment conditions (logging system, the crampedness of the facilities, archiving possibilities) appear to be insufficient to ensure the management and follow-up of more than 1,000 instruments, sensors or equipment.

Training programs were nevertheless conducted and programmed for maintenance crew personnel, whose workforce had been increased since the 2003 inspection.

Findings

The inspections described above lead to numerous administrative and penal actions designed to require the operator to take corrective action.

In autumn 2004, legal action consisted of two hearings before a tribunal. IN November 2004, the company was fined 75,000 euros and the director received a 3-month suspended jail sentence and a 10,000 euro fine. The manufacturer appealed the first ruling. In late June 2005, the magistrate's court sentence the establishment's director to a 3-month suspended jail sentence and a 10,000-euro fine. The company was fined 120,000 euros. The manufacturer also appealed the second ruling. These legal cases, as well as the various accidents presented above, received significant media coverage.

PERSPECTIVES FOR IMPROVEMENT

An improvement in the situation, notably in terms of management of the site's storage facilities, was noted in the second semester of 2004.

It should be noted that following the administrative and penal actions, the manufacturer, through its CEO, undertook strong commitments with the Prefect, the DRIRE and the CHSCT to improve the situation by implementing an investment program.

The administrative actions are continuing and a complementary prefectorial order was issued on January 7, 2005. The provisions notably bear on the critical analysis of the danger study and a study of the health hazards.



In order to evaluate the pertinence and the proper application of the procedures that had been deemed faulty in the past, an external audit was also prescribed relative to the implementation of the SMS and specifically on the following:

- -the personnel's knowledge of the SMS and the respect of procedures,
- -the operator's ability to implement the SMS and to check that is applied properly,
- -the pertinence and the efficiency of the safety organisation.

This 21/2-day audit should be able to identify the organisation's weak points and the origin of the problems, on which the operator must undertake corrective actions.

In early 2005, the group's CEO expressed his desire to reduce hazards, fulfil regulatory requirements and improve the company's image, with the assistance of an external advisor.

The action plan proposed by this consulting agency was forwarded to the Classified Installations Inspectorate in April 2005. The initial actions concentrated on improving the storage areas and on the reorganisation of the HSE department.

In parallel, in April 2005, the manufacturer presented his revised multiyear investment plan, which outlines significant investments in terms of reducing risks, and proposed additional changes at the request of the labour inspectorate and the Classified Installations Inspectorate.