



Meeting – REIMS, June 2001, 12<sup>th</sup> and 13<sup>th</sup>

## « LESSONS LEARNT FROM INDUSTRIAL ACCIDENTS

ICPE / IMPEL inspectors



# | Thanks

We do thank the participants to the meeting for their presentation and their contribution in the achievement of the following synthesis.

The speakers' names are listed below in alphabetic order (but grouped for each presentation).

- *Mr Wilfried BIESEMANS (Environment Ministry- Belgium)*
- *Mr Charles-Guillaume BLANCHON (DRIRE Ile-de-France - France)*
- *Mr Laurent BORDE (DRIRE Aquitaine - France)*
- *Mrs Catherine CASTAING (DRIRE Champagne – Ardennes - France)*
- *Mrs Fausta DELLI QUADRI et Mr Graziano CARLI (Environment Protection Agency– Italy)*
- *Mr Chris DIJKENS et Mr Wim MOLHOEK (Environment Ministry– Netherlands)*
- *Mr Philippe FARENC (DRIRE Lorraine – France)*
- *Mr Claude FERRAND (DRIRE Alsace - France)*
- *Mr Jean-Claude GUILLAUMIN (DRIRE Picardie - France)*
- *Mrs Laurence LE SOUFFACHE (STIIC - France)*
- *Mr Laurent MARTIN (DRIRE Rhône Alpes –France)*
- *Mr John PEAK (Environment Agency – Royaume-Uni)*
- *Mr Hubert SIMON (DRIRE Haute-Normandie - France)*
- *Mr Christian TORD (DRIRE Champagne – Ardennes - France)*
- *Mr Bruno VAN MAËL (DRIRE Auvergne - France)*
- *Mr François VILLEREZ (DRIRE Alsace - France)*
- *Mr Norbert WIESE (Land Rhénanie du Nord –Westphalie - Germany)*

# | Summary

## Introduction

Opening speech for the 2001 edition of the meeting

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Enschede (The Netherlands).  
May, the 13<sup>th</sup>, 2000

### 2 – Fire in a warehouse

Marly-la-Ville (95)  
August, the 1<sup>st</sup>, 2000

### 3 – Fire in a rubber gum warehouse

Clermont-Ferrand (63).  
January, the 20<sup>th</sup>, 2000

### 4 – Thermal runaway of a styrene-acrylonitrile copolymerisation reactor

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Villers St Sépulcre (60)  
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October, the 6<sup>th</sup>, 2000

**13 - Explosion of an unconfined cloud of vapour coming from a tank storing drain water mixed with hydrocarbons**

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Closing speech of IMPEL meeting of June, 12<sup>th</sup> et 13<sup>th</sup>, 2001

# | Introduction

**Welcoming of participants**

**Opening speech**

**Meeting of June, 12<sup>th</sup> and 13<sup>th</sup>, 2001**

## Welcoming of participants

### Marie-Claire BELTRAME-DEVOTI

Regional Director of the CHAMPAGNE-ARDENNE Industry, Research and the Environment

I feel both a great pleasure and interest to welcome in Reims the third IMPEL meeting dedicated to the experience feedback relative to technologic accidents. DRIRE Champagne Ardenne is particularly concerned by the analysis of industrial accidents. Two of its inspectors will present cases on which investigations were carried out. Different acts were also proposed in order to reduce the occurrence probability and possible consequences on people and goods. Indeed, as soon as there are hazardous substances and processes, the risk cannot be denied and it is necessary to face all its implications.

Just like its European or French "colleagues, DRIRE Champagne Ardenne is highly involved in the checking of the implementation of Seveso II directive. What is at stake presents a high interest to me. We have to do our best with the means available to answer our co citizens' wishes. It is an ambitious challenge that we have to face every day, for, so far as security is concerned, experiences are never definitely got.

Reminding the lessons learnt from accidents must contribute to feed the mitigating action of the inspectorate in order to curve the risk. Here lies the main idea of these two days. Let me give the flow to Denis Dumont who will present you the agenda of this meeting.

But, before describing these technical and organisational aspects, I hope the best conditions for your stay in Reims that could afford enrichments for your missions of inspection.

## Seminar introduction speech

### Denis Dumont

Director of the BARPI (bureau d'analyse des risques et des pollutions industrielles).

I readily agree with the opening words of the Director of the DRIRE Champagne-Ardennes. I would sincerely like to thank her for being here for the opening of the seminar and for her organisation's contribution in organising this event.

I would like to welcome you all to this 7<sup>th</sup> seminar on industrial accidentology. This is the third time that it has been organised within the scope of the IMPEL network (European Union network for the IMPLementation and Enforcement of environmental Law) of European Union inspectors. The presence of inspectors from various member states is an enriching factor for our operations, in both technical and practical terms concerning inspection.

I am very delighted that so many of you were able to join us, as I am familiar with the workload of the classified installation inspectorate and know how difficult it can be to "reserve" 2 days in an agenda. I particularly appreciate the participation of the European Union inspectors who spontaneously accepted to come to Reims to conduct a presentation.

I hope that the work and reflective thinking that we will engage in during these next two days will help you in conducting your various missions.

The stakes of feedback clearly consists in making available information and assessments based on real cases to those individuals in charge of risk prevention.

This means completing the studies and theoretical models with concrete elements

- in order to improve risk reduction at the source,
- to evaluate the consequences of possible accidents in order to develop urbanisation control and external contingency plans,
- to improve strategy and emergency response means.

The objective is also to provide you with, in a format as directly usable as possible, arguments for your discussions with industrialists.

In this case, it is also the subject of the ARIA database. At present, ARIA is considered a "knowledge base" including 20,000 industrial accidents recorded since 1992. Currently, more than 2,000 accidents are recorded per year.

The main sources of information include:

- the classified installation inspectors,
- the civil protection services and fire brigades,
- the "water police",



- the powder and explosives inspectorate,
- the department in charge of pressurised equipment and piping at the Ministry of Industry,
- international organisations,
- the press.

Exploitation of the ARIA database particularly enables the following:

- to produce customised studies in response to questions frequently asked by industrials or consulting agencies,
- to establish research studies on specific themes,
- to supply elements of information to training organisations.

BARPI's current orientation is to intensify relations with the classified installation inspectorate

- by supplying the copy of responses sent to the industrials,
- by establishing annual regional reports,
- by participating in initial inspector training programs.

For a limited number of accidents, which deserve further scrutiny, we also wish to gather more detailed information from you concerning the circumstances, the kinematics and the geographic extension of the consequences, particularly in the form of observation notes, drawings and photographs.

As for myself, I am convinced that the detailed reminder of the causes and circumstances of accidents can contribute to providing a realistic and convincing dimension to our discussions with industrialists, elected representatives and the prefects.

Before starting our presentations, I would like to remind everyone that the organisation of this seminar would not have been possible without the efficient assistance of the DRIRE Champagne – Ardennes, the contribution of the inspectors, both foreign and French, who have prepared the presentations, and the active participation of the BARPI agents.

At the end of the day, Jean-Luc Claret will present a new element: the BARPI web site. If you like, you can go "surfing" during the breaks on a workstation, which has been made available for this purpose.

Tomorrow, Marie-Claude Dupuis, Head of the SEI, will moderate the day's program and will close the seminar.



# | Sheets of the accidents presented

# 1 - Explosion of a fireworks warehouse Enschede (The Netherlands). May 13th, 2000

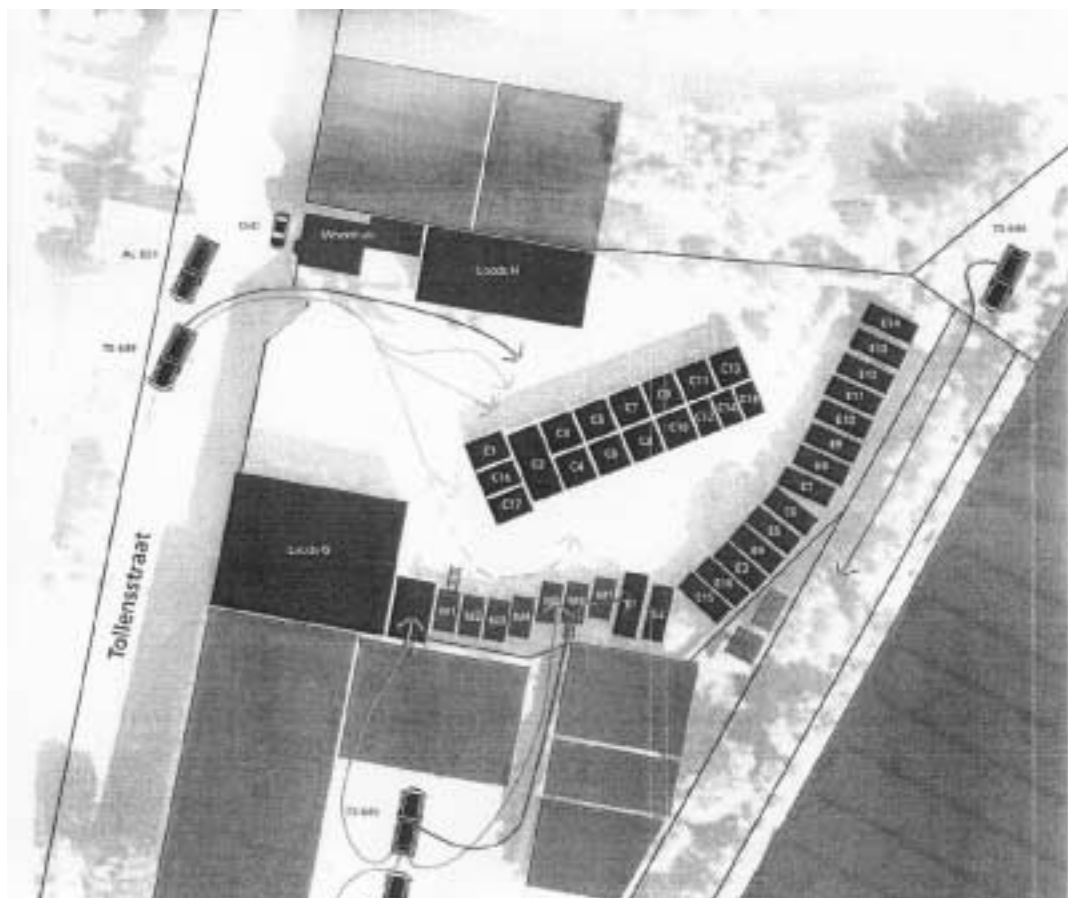
## THE INSTALLATIONS IN QUESTION

The company operates a fireworks warehouse in the city of Enschede, in a residential district near town centre (Tollensstraat). The city has a population of approximately 150,000, with about 2,500 people living in the surrounding neighbourhood.

The company stores and repackages explosive products consisting essentially of entertainment fireworks imported from China. The site includes the following facilities:

- 17 "bunkers" used in the operations performed on the fireworks (particularly for repackaging),
- 16 metal containers (20' ISO type),
- 7 light concrete structures, prefabricated garage type (MAVO box).

The diagram below indicates the location of these various structures.



**M: MAVO box**

**C: central zone cells**

**E: containers**

*(The diagram indicates the position of fire fighting vehicles, prior to the explosions)*

### History:

The installation was created in 1976 in a zone which, at the time, did not appear to be highly urbanised. In the late 1970s, the operator installed the MAVO boxes. Around 1990, the company's activities developed to include fireworks for professionals. This resulted in "regulatory regularisation" which was undertaken only in 1996 and granted in 1997 (10 bunkers with a capacity of 7 t each, 3 "small" bunkers of 5 t each, 7 MAVO boxes of 2 t each and 3 containers of 2 t each). The maximum quantity of explosive was 105 t.

The operator purchased the depot in 1998 and then expanded operations: 11 containers were added (authorisation in 1999). Two unauthorised containers were subsequently installed, bringing the total number to 16. Furthermore, the quantity capable of being stocked in the boxes and the containers increased to 3.5 t each. The maximum quantity of stored explosives increased to reach a total of near 159 t. Authorisation had been granted for 1.4 division explosives and in accordance with various structural details. Considering these quantities, the depot was not subject to the Seveso 1 directive.

## THE ACCIDENT, ITS BEHAVIOUR AND CONSEQUENCES

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### The accident

The accident occurred Saturday, May 13th, 2000, at around 3.30 p.m. The chronology of events was established based on various witnesses and investigations. The diagram locates the structures concerned as well as the position of the firemen during the rescue operations:

🚒 Slightly prior to 3 p.m., a fire broke out in workshop C 2 (used for working on the fireworks). The fire brigade was summoned for a standard fire.

🚒 The doors were blown outwards under the effect of the fire,

🚒 The fire spread via ignited rockets to containers located opposite, particularly E 15.

🚒 At 3.08 p.m., the fire brigade arrived on the scene, determined that the site was a pyrotechnic storage facility and called for reinforcements. Operations to fight the fire were organised: several fires had already broken out on the site. The fire brigade took up the positions as indicated in the diagram above.

🚒 Rockets fired from the various facilities: during this sunny afternoon, many people who were in streets of town centre approached the site. The emergency services pushed the onlookers back in order to clear them away from the edge of the site.

🚒 The heat produced by the fire caused a container of heavy explosive charges to explode. That was the first major explosion. The firemen had to move back and take shelter.

🚒 The fireworks stored in the MAVO boxes then exploded.



✚ The succession of explosions and the resulting shock waves destroyed the doors on the various storage facilities: the central bunker was then next to be invaded by fire. The exploded violently, generating an enormous plume of smoke and devastating effects on the surrounding area,

✚ The fire-fighters were no longer able to contain the fires; everything in the direct vicinity having been destroyed by the explosion (including the rescue vehicles in particular).



### The consequences:

The damage caused by the catastrophe is excessive.

✚ 22 deaths were reported, including 4 firemen, with 3 persons missing.

✚ Nearly 1,000 individuals suffered various injuries, 50 of which were seriously injured (hospitalised at least 5 days)

✚ In a radius of 250 m around the site, homes and other structures were obliterated



✚ Buildings within a zone of 750 m were subjected to extensive damage. It was impossible to live in the zone following the accident. The municipality of Enschede decided to remove and demolish everything else that remained. The neighbourhood was temporarily erased from the map.

✚ In all, 500 homes or business establishments were destroyed or severely damaged,

✚ Property damage was estimated at 1 billion guilders or 500 million Euros.

## ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

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🔗 The day of the accident, the fire began in building C 2. The initial cause of the fire remains unknown. It may have been started in a variety of ways: either through human error or through malicious mischief, or due to a technical malfunction such as a short-circuit or spontaneous ignition. The inquiry was difficult due to the fact that the facilities were destroyed. The inquiry lasted several months after the accident.

🔗 Nine hundred kilos of explosives were stored in the facility. In theory, fireworks are not authorised in this type of zone if re-packaging operations are not under way. The day of the accident, nobody was working in the depot. Once started, the fire reached the fireworks which initiated the smoke and ignited the first rockets.

🔗 The rockets flew into other parts of the depot, particularly into the triangle formed by E 2 and E 15. This last container, which was added later, is not authorised and forms a triangular zone with E 2 and the fence, difficult to access. One of the fires was located in this zone, which was also obstructed by various equipment (trailer, ...). Their presence in this area fed the fire which spread to the containers nearby. The firemen attempted to get as near as possible although experienced difficulties reaching the zone on fire with their nozzles (see diagram on page 1).

🔗 The depot, initially built to hold 18 t of fireworks for private individuals, eventually held 180 t of fireworks intended only professional use (of which only 159 t was authorised as 2 unauthorised containers were added since 1999, including E 15). At the time of the accident, the following quantities were present:

🔥 16 t of class 1.4 explosive (1.4: fireworks for private individuals, non-explosive although highly flammable)

🔥 154 t of class 1.3 explosive (1.3: professional fireworks with high heat release and highly flammable),

🔥 5 t of class 1.2 explosive (1.2: professional fireworks, highly flammable, explosives such as a bomb with projections possible),

🔥 1.5 t of class 1.1 explosive (1.1: professional fireworks of the heaviest category, high-mass explosive with shock wave formation).

🔗 The structures and boxes did not provide sufficient security against the risk of explosion. Even the permit's structural provisions, nevertheless relatively light, were not respected: distance between the containers of at least 1 m, for example.

🔗 The MAVO boxes and the containers were not subjected to any specific testing.

🔗 The various structures and the containers were not or sparingly equipped with fire detection and extinction devices. Alarm devices were also non-existent. The automatic fire extinguishing network in the bunker was poorly designed.

🔗 One of the walls of the central cell had a hole through which the fire spread.

## ACTION TAKEN

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On the request of the public authorities, a Board of Inquiry was set up, the Oosting Commission, in order to conduct a large-scale investigation on the circumstances and the responsibilities engaged in this accident. The inquiry concentrated on the manner in which the various operators worked although



also analysed the operating mechanisms of the various authorities, on both national and local levels, implicated in the drawing up of texts or the control of fireworks. In this manner, responsibility was sought in the various organisations. The report, dated 02/28/2001 is quite thick (2,000 pages). A few of the conclusions are presented below:

9 **The successive operators, managers of their depot**, formed the subject of the following observations:

- They committed various serious offences in terms of managing pyrotechnic materials, equipment of various structures, and the use and location of light-weight, inadequate structures.
- Over several years time, certain parts of the depot were unauthorised. In addition, the operators failed within the scope of their requests by not sufficiently considering the regulation's requirements in their dossiers, which were presented late to the authorities.
- No risk assessment, rendered mandatory by labour legislation, was undertaken.
- They could not ignore the fact that the classifications of products coming from China are generally underestimated. During previous inspections by official organisations, this fact was established.
- A passive attitude on the part of the operators was discovered: no recourse to an external specialist, an interprofessional organisation or a branch union was undertaken. They limited their interaction to the public authorities only, which is insufficient considering their responsibility. The commission indicated that this attitude led to a transfer of this responsibility to the public authorities, which is not acceptable. In addition, it was indicated that a highly-limited inspection on the part of the administration in no way justifies the disregard for the texts.

9 **The national public authorities** are also the subject of the commission's observations, particularly in terms of organisation. It is clear that, in so doing, the commission was looking for ways to improve the system and not to blame the authorities, be it local or national. The various elements mentioned could have contributed, at vary diverse degrees, to preventing this accident from happening:

- No lessons were learned from the Culemborg accident of 1991. At this time, the problem of the accuracy of the classification as indicated on the products was brought up.
- The organisation of the departments and the distribution of tasks among them resulted in a complicated system: the RVI (the national transports inspection organisation), the DMKL (environmental investigating bureau "Department of substances of the Royal Armed Forces of the Department of Defence"), the VROM (Dutch Ministry of Housing, Spatial Planning and Environment), intervene in the field of fireworks with, for each, a different role or activity. In addition, following reorganisation, traditionally competent branches were done away with over the last 10 years (KCGS – dangerous materials inspection agency) or withdrew (Environmental Hygiene Inspectorate) or do not have sufficient manpower (drastic reductions in some departments since the 1990s).
- Regulations are complex and not very accessible due to the partitioning of the various departments concerned.
- A lack of communication between the various departments is detected: this was particularly the case within the framework of handling the aftermath of the Culemborg accident. The information held was not distributed between the departments and not much more to the municipalities, particularly that of Enschede.

- The file relative to regulations governing professional fireworks was handled slowly: for example, an extensive consultation of the sector was made on the possibility to engage in certification of the profession. After several years of discussion, the process was finally abandoned. If the commission approves this decision, it considers it as late. The VROM was in charge of this process. A lack of harmonisation is also detected on the subject of the review of the regulations between the various ministries (VROM and the transportation department).
- A certain amount of ambiguity apparently exists in the role of the DMKL, which plays the role of technical consultant for the authorities and the operators.
- The inspections carried out by the federal agencies appear to be theoretical. The recent inspections conducted by the police were essentially based on the final consumers of the fireworks.

9 **As far as the local public authorities are concerned**, the essential remarks remain in the following facts:

- No distinction is noted between the roles of consultant, appearing in the scope of the processing of applications, and surveillance, induced by the inspection operations: the same official handles both aspects within the municipality. It should be reminded that, in the organisation of the Netherlands, it is the municipality that controls the terrain through its technical services which also grants the operating permits.
- According to the commission, a "lack of perseverance" on the part of the inspectors to enforce environmental law lead to the pure and simple discontinuation in the application of the texts: few inspections; inspectors not issuing penalties even after having been informed of disregard for regulations; no reports sent to the authority (the Mayor) even informal relationships between the inspectors with their technical support, the DMKL. The municipality counted on the latter to give its opinion. The organisation did not give a clear position on the subject. The relocation of the establishment was brought up...
- A lack of co-ordination between the environmental office, the building permit office and the fire brigade lead to a variety of malfunctions: one of them is the disregard for the cities own zoning plan, regulating the locating distances for industrial activities. Another is the lack of consultation with the fire brigades in the attribution of permits granted by the "environmental" office. The commission, however, recognised that the fire brigades have very few resources.

## LESSONS LEARNED

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The catastrophe was clearly a shock for the public, national or local authorities. As shown above, a board of inquiry was quickly appointed to investigate the accident. Independently and without waiting for the conclusions of the inquiry, various measures of general order were undertaken and are listed below:

- The Department of Justice engaged a judicial inquiry,
- In June 2000, the public authorities decided to accelerate the draft of new regulations concerning fireworks. The regulations, which was under the jurisdiction of various ministries, would now be solely under the direction of the Ministry of the Environment. Furthermore, the provinces would granting the operating permits for pyrotechnic installations, and not the municipalities as was formerly the case.



- Proposals are to be made to establish new regulations on risky situations, one of the causes justifying this project being the lack of information from land use management authorities. The public information about this type of risky situations will also be developed.
- A national inventory of fireworks warehouses was conducted: based on these results, 270 depots were identified. Fifty of them were subjected to a thorough inspection by the Ministry of the Environment.

The Board of Inquiry established a report, accompanied by a series of recommendations which were proposed by the Dutch public authorities. All of the recommendations were approved.

**Technically speaking**, the practical measures which must be implemented rapidly may be summarised as follows:

- A unique safety distance of 800 m is now applicable for all installations in which professional fireworks are located. This would have led to the closure or relocation of more than 50% of the installations.
- A unique safety distance of 30 m was retained for installations which store fireworks for private individuals,
- The majority of the points of sale were required to close or to no longer sell fireworks.

This does not prejudice any other measures which could be taken regarding this subject in the future.



## 2 - Fire in a warehouse

### Marly-la-Ville (95)

August, the 1<sup>st</sup>, 2000.

#### THE INSTALLATIONS IN QUESTION

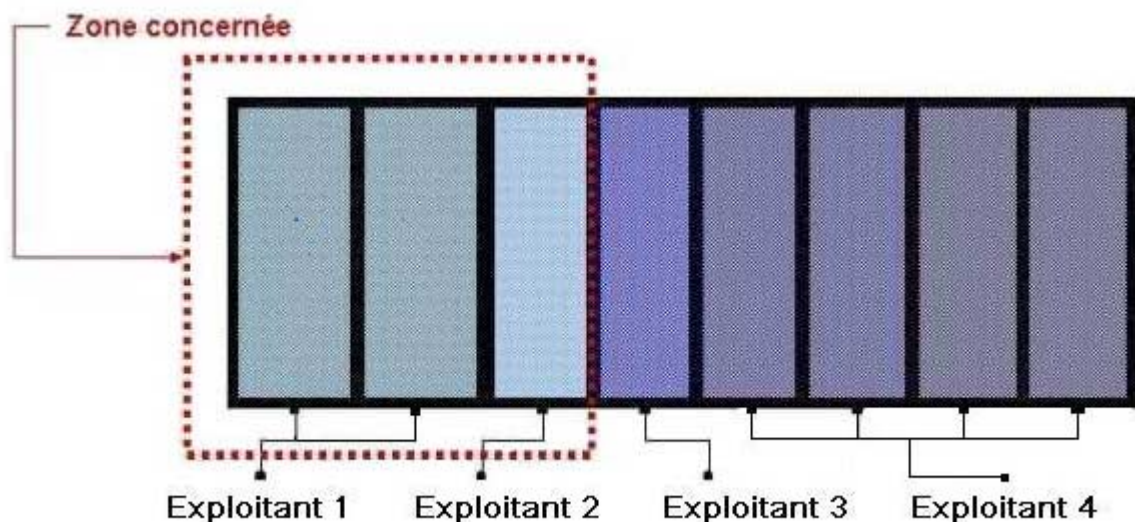
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##### The site :

The building which makes up the warehouse occupies a surface area of 9,600 m<sup>2</sup> and is 10m tall. It is arranged into eight 1,200 m<sup>2</sup> cells.

Its owner rents the building to various renters who occupy 1 or more cells. The day of the accident, 4 renters occupied the 8 cells.

This warehouse is considered a classified installations owing to the storage of combustible materials in quantities greater than 500 tonnes in a building measuring more than 50,000 m<sup>3</sup>.

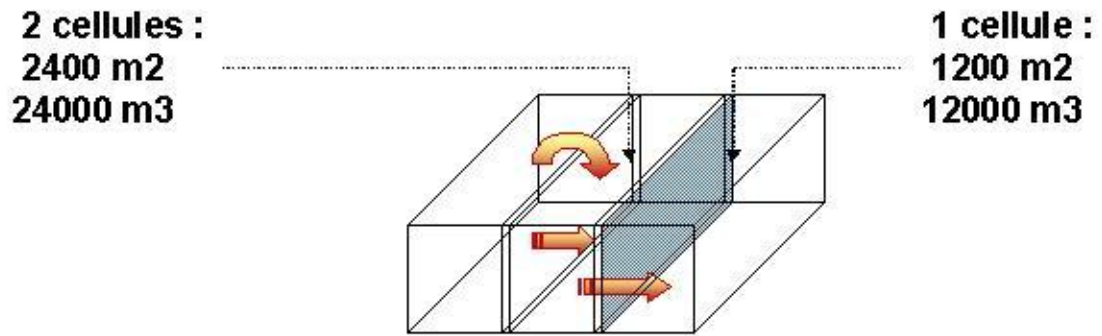


#### THE ACCIDENT, ITS BEHAVIOUR AND ITS CONSEQUENCES

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##### The accident

On August 1st, 2000, a fire started at 11.30 a.m. in the bales of cotton-wool-like cellulose stored in a cells that one of the renters used as a shop for manufacturing napkins, tablecloths and paper for sanitary use.



Employees attempted to put out the blaze using the internal hose station network. Within 20 minutes, the fire spread to the operator's 2 cells via the roof and existing openings in the walls. The partial collapse of a separating concrete block wall allowed the fire to spread to the agro-pharmaceutical products and animal feed stored by the adjacent logistics company.

Thirty-seven fire fighters were overwhelmed by the smoke (7 were hospitalised and placed under observation). The fire protection water (1,500 m<sup>3</sup>) loaded with pesticides, detergents and soaps, collected in a non-hermetic holding reservoir was threatening to pollute the drinking water. Requisition measures were taken to ensure that it was pumped and stored prior to treatment.

The fire was brought under control approximately 2 hours after it had started. Part of the building was spared owing to measures undertaken by the fire brigade.

#### The consequences :

Approximately 1,500 m<sup>3</sup> of the fire protection water collected in a non-hermetic storm water holding reservoir upstream from the site threatened to pollute the water table and the Marly-La-Ville drinking water collection facilities.



The reservoir's soil can be considered as polluted and the rainwater network is tainted. The products initially stored and damaged by the fire remain in the cells.

One of the main consequences lies in the difficulty to find solutions for polluted waters elimination. Besides the high costs of the operations on one hand and the legal as well as administrative proceedings on another hand, the waters treatment will take about 11 months.

## THE ORIGINE, THE CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

The fire broke out while 1999-storm damage repair work was being performed on the roof of the building with a torch.

An inventory of the site conducted by the Classified Installations Inspector showed that numerous sensitive chemical products were stored in the cells which caught fire. This situation might have been a worsening element. The materials stored are mentioned here under :

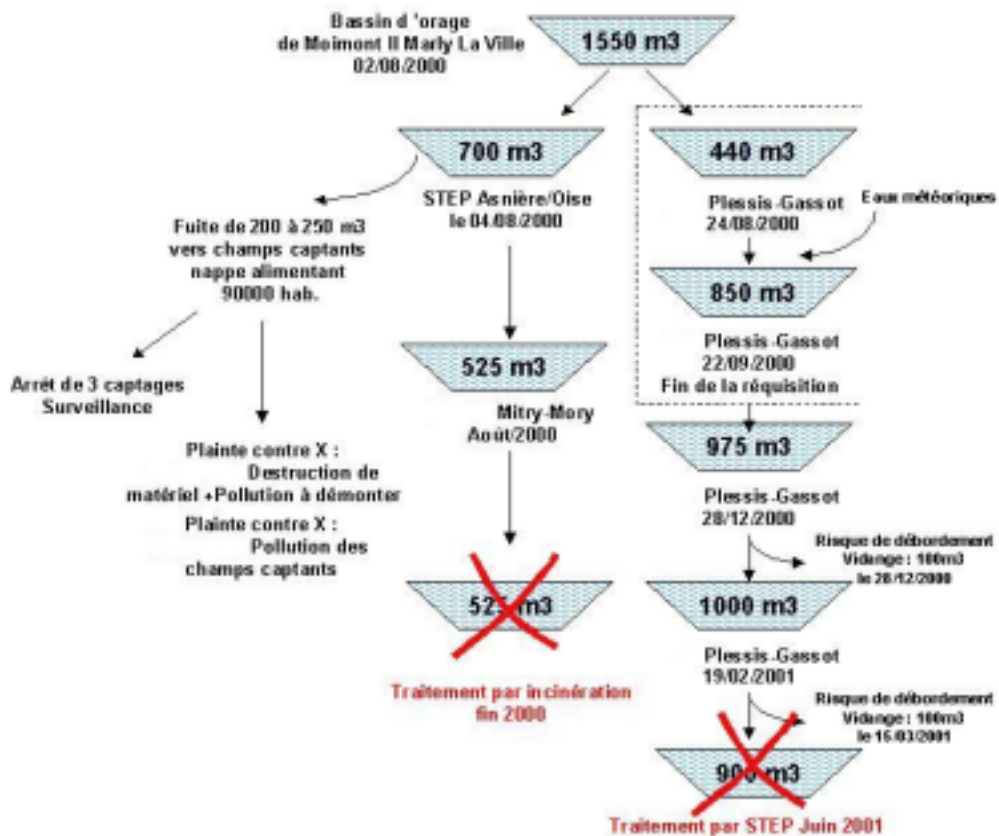
-  Strong bases, soaps, inks... in one of the company's cells where the fire started,
-  Pesticide products, herbicides, fungicides, arsenic trioxide... in the cell of the adjacent transport company. The quantity of arsenic trioxide present at the site (105 kg > 100 kg, Seveso II classifying threshold) is governed by the SEVESO directive.

## ACTIONS TAKEN

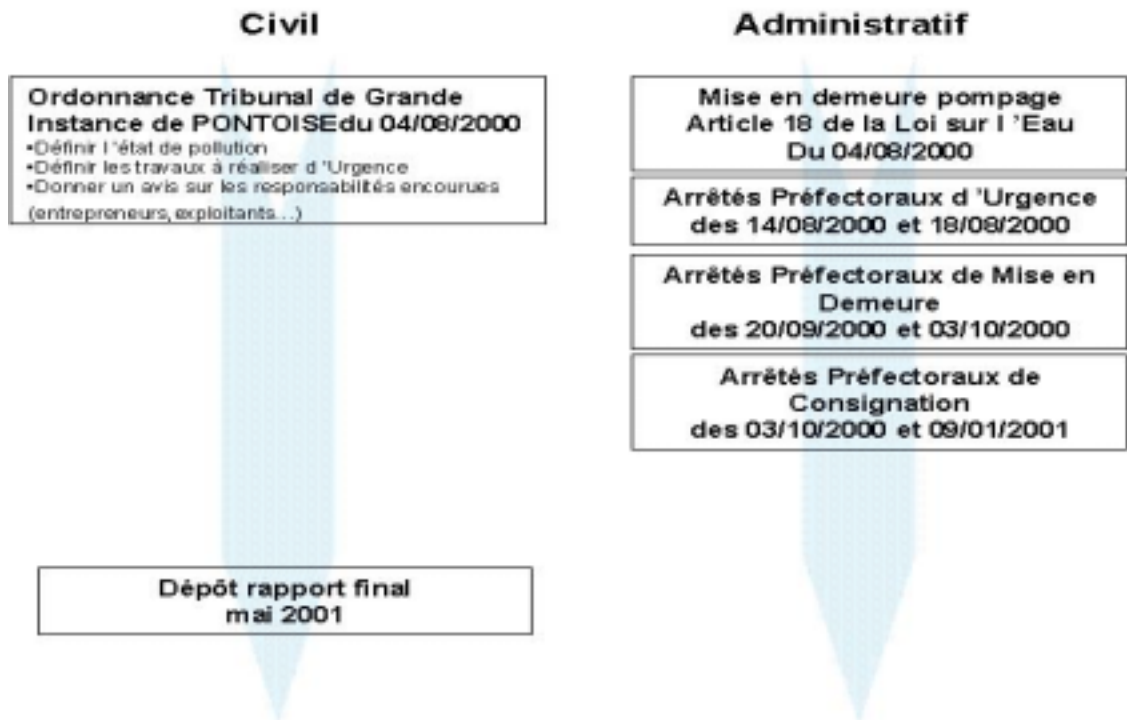
The prime objective of emergency action is to save the water table.

On August 4th, 2000, Prefect of Val d'Oise gave official notice to the operators responsible for the products at issue to pump the fire protection water collected in the Marly-La-Ville holding reservoir within 24 hours under the terms of Article 18 of the Water Act. Faced with the refusal of the 2 operators, as of August 5th, 2000, the Prefect undertook requisition measures under the terms of the Acts of July 22nd, 1987 and July 11th, 1938 relative to the following points:

- ✈ The pumping and transport means of a specialised company,
- ✈ The means required to store the fire protection water prior to elimination consisting of the leaching tank of the Asnière-sur-Oise treatment plant (800 m<sup>3</sup>) and the aeration tank of a class 2 technical burial center (700 m<sup>3</sup>),
- ✈ The monitoring of the water table by the installation of 2 piezometers upstream from the Bellefontaine drinking water collection station.



A series of judicial redress procedures and administrative decisions complicate and slow down the technical aspects of the pollution problem's management.



## THE LESSONS LEARNT

The rapid spread of the fire to a cell occupied by a third part shows that vigilance is required vis-à-vis the constructive provisions imposed and implemented on the site.

The presence of a quantity of arsenic derivatives equivalent to a SEVESO classification requires observation relative to the materials stocked and their risk potential.

The pollution in the holding reservoir which threatens the water table shows the need for a hermetic fire protection water retaining tank.

In the case of overlapped installations operated by multiple companies, possible situation resulting from division of platforms or addition of units, it is important to check that all technical as well as organisational questions in connection with pollution and risk prevention had been answered with appropriate measures whose responsible is clearly identified.

In the case presented, the problems rose particularly :

- since the moment when the operators refused to comply with the regulations included in the prefectorial orders taken successively after the accident : emergency prefectorial order (Environment "code", article L 512-7) and official notice (article L514-1).
- due to the long delays added because of administrative followed by legal recourses.

The requisition of service provider companies makes the necessary works possible. The final payment of the works will be settled by the responsible for the accident and its consequences. Their procrastination only increased the total cost of the operations.



### 3 - Fire in a rubber gum warehouse. Clermont-Ferrand (63). January 20th, 2000

#### THE INSTALLATIONS IN QUESTION

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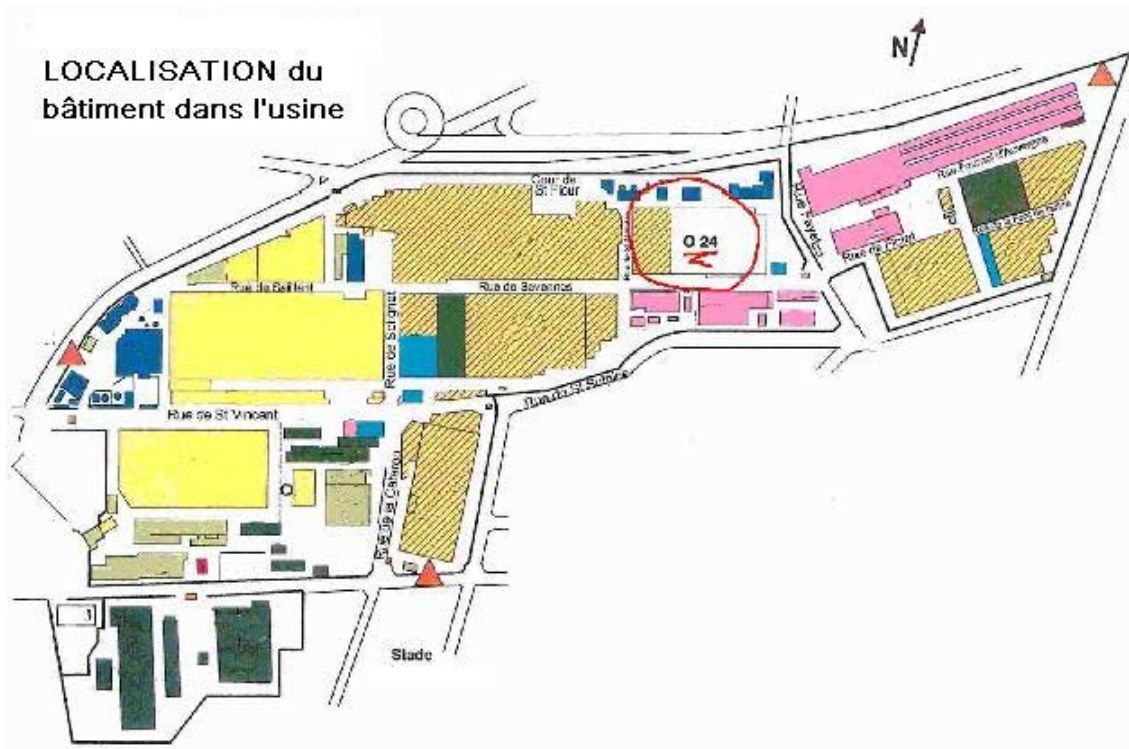
##### The plant :

The plant is subject to classified installation authorisation, primarily for its combustion plants. The facility destroyed, building O24, was built in 1958. Owing to prior right, it had been classed for the storage of rubber materials (declaration receipt of May 18th, 1987). It had been used as a civil works tyre manufacturing shop for the until the 90's.



Photo DRIRE Auvergne

The fire took place in a building measuring 16,000m<sup>2</sup> at ground level. Largely unused, although undergoing reassignment, the building was used essentially for the basement storage of raw synthetic gums. A machine, referred to as MAC BU, was located in the west part of the building, used for preparing mixtures for gum.



Approximately 2,531 tonnes of gum were stored in the basement, including:

- "PB" gum (polybutadiene),
- "SBR" gum (butadiene-styrene copolymer),
- "extended SBR" gum (extended butadiene-styrene copolymer with petroleum oils).

A certain number of toxic products in transit were located in the building's basement in smaller quantities. These products were primarily stocked around machine MAC BU and were not damaged by the accident (fire and firefighting water), except for colophane (5,75 t), cobalt hydroxide (0.9 t) and a vulcanisation composite stored in the part which caught fire (59 t).

## **THE ACCIDENT, ITS BEHAVIOUR AND CONSEQUENCES**

### **The accident**

On January 20th, 2000 at 4.40 p.m., smoke from the outbreak of fire was detected by an agent of an external company working on the ground floor of a building.

An initial attempt to put out the fire, organised as early as 4.55 p.m. by the Company's fire fighters, proved futile and the city fire brigade were summoned and arrived at 5.41 p.m.

Approaching the fire proved to be difficult and it rapidly got out of hand and managed to reach the majority of the building in just a few hours. Two days were needed, until Saturday, Jan. 22nd mid-day, in order for the emergency services to bring the fire totally under control.

In all likelihood, and subject to the conclusions of the judicial inquiry which was opened, it seems as though the fire began accidentally due to torch cutting operations being performed by an external company.

A major fire at an industrial site, whatever it may be, presents several risks:

- 🚒 Fire, explosion or air blast extension, linked to the ignition of several materials stored, leading to physical effects in connection (high thermal flow, burning sources, compression waves),
- 🚒 The emission into the air of toxic compounds produced or released during the fire,
- 🚒 Pollution of the natural environment by firefighting water when it cannot be contained.

While during the fire and in the following weeks, attention in the press was directly primarily on the plume of smoke observed while the fire was being put out, the intervention by the public authorities and the DRIRE naturally took these three types of risks into account as soon as the accident happened.

It should be noted, however, that the facility has no factor which gives any of these risks major importance (absence of a significant stock of toxic products, easily flammable products or explosives, etc.).

### Chronologie

- January 20<sup>th</sup>, 2000 :

**16 h 50 :** the building's heat alarm in zone 51 was triggered, a significant amount of smoke is confirmed (4.57 p.m.) by the company's fire fighters,

**17 h 35** Reinforcement from the city fire brigade (COMAC) is requested for a rubber gum fire, they arrive at 5.41 p.m.,

**18 h 12** "Drenching" type spraying of the basement is partially implemented (approximately 1/3 of the basement is protected). For the other part, the valves are not accessible. Attempts to reach the valves resulted in the injury of 5 firemen, including 2 seriously following explosions at 6 p.m. and 7.30 p.m.

For this moment on, the COMAC firemen took control of the operations:

- the surface area concerned by the accident is approximately 3,000m<sup>2</sup>, 1,300 to 1,400 tonnes of gum on fire, approximately 1,100 tonnes of gum are protected by the spraying system,
- a thick plume of black smoke rose high in the sky, with good dispersion.

**21 h 15** the Director of the DRIRE arrives on site with the classified installations inspector.

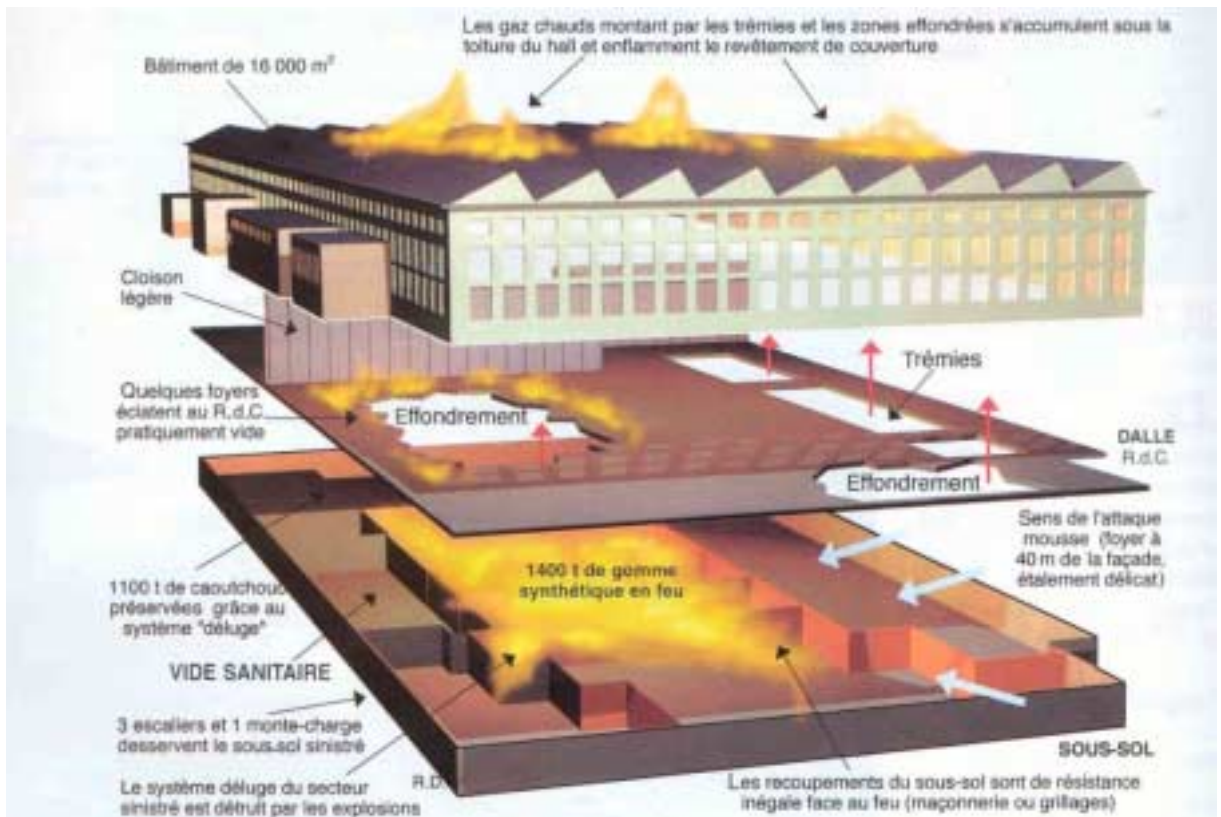
**21 h 30** Reinforcements are requested from the surrounding counties. In all, nearly 500 firemen were called in, with a maximum of 130 operating simultaneously

The gum continued to burn to the evening of **Friday, January 21st**, its intensity was reduced considerably around 7 p.m.

- **January 22<sup>nd</sup>, 2000, about mid-day :** The fire was considered to be out.



Drawn by René Dosne



### Human and material consequences :

Nine persons were injured: 6 company's firemen, 3 external firemen (including a fracture while removing equipment after the fire was put out).

The accident was contained in building O 24, as the firemen's immediate and successful attempts to prevent the fire from spreading to nearby buildings (namely a laboratory, oil and storage warehouses, and electricity transformer).



Photo DRIRE Auvergne



Photo DRIRE Auvergne

Property damage was extensive. The majority of the damaged building will have to be demolished. 1,415 tonnes of gum were affected by the fire. The only important machine in the building, an automatic gravimetric filling machine (MAC BU), separated from the fire by a wall, was protected by the firemen and not damaged, as well as the majority of the chemical products.

The economic consequences were relatively limited. Only the buffer stocks of raw materials and a large portion of building O24 were destroyed. No essential installation was affected. Technical unemployment was not considered and the MAC BU machine was rapidly placed back into service.

### Environment consequence : air pollution

From the start of the accident, the nature of the materials entering into the combustion allowed affirmation that there would be, in all likelihood, little toxic risk although the size of the fire and the incomplete combustion would cause a spectacular smoke plume rich in unburned particles (soot).

The firemen conducted a few elementary air quality measurements, in the immediate proximity of the fire, without detecting toxic compounds.

The ATMO Auvergne network did not detect a spectacular elevation in the pollutants monitored. The air quality remained correct over the community. However, there were numerous requests for information. Real-time measurements communicated as early as January 21st, 2000, the implementation of the network's mobile laboratory in the axis of the smoke cloud and additional measurements, by an approved organisation, of dustfall and particle fallout extended over the following weeks, confirmed that at the highest pollution peak, the concentrations of dust in the ambient air, outside the smoke cloud, remained very much below the O.M.S. recommendation in terms of daily average.

All of the measurements collected today confirm that the cloud underwent several moderate and temporary increases in terms of the level of dusts and sulphur dioxide. Particle fallout remained very localised. These increases remain this side of the rates reached during meteorological circumstances unfavourable to the dispersion of urban pollutants - temperature inversion, anticyclonic period ...

### Environment consequence : water pollution

No major impact was measured during or after the fire (death to fish, plant life, etc.).

Afterwards, significant workshops had been carried out in order to analyse and evaluate non visible effects. The results are detailed in the paragraph "Actions taken".

Long and complex analyses are also continuing on the sediments.

## **ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT**

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The probable cause of this fire is the ignition and slow combustion with pyrolysis of the gum present in the basement.

Photo DRIRE Auvergne

An outside company, in possession of a fire permit, was performing maintenance operations, installation-removal of metal elements, using torch cutting and welding operations. The hypothesis is that a cinder of molten metal initiated the slow combustion of the gum present on pallets for an undetermined duration before the fire broke out.



The favourable dispersion conditions and the absence of strong wind facilitated the operations by the firemen and allowed efficient protection of the buildings in the immediate proximity to the one on fire. A major nearby assembly shop and research laboratories were of major importance for the site's activity and for the factory.

Very rapidly, the company authorities, the firemen and the authorities had a clear idea of the situation:

- ✚ A significant and spectacular accident although without major danger, nor serious economic consequences if it could be contained,
- ✚ A fire very difficult to put out before nearly complete combustion.



Photo DRIRE Auvergne

On the other hand, knowing the difficulty in putting out a widespread gum fire, it appeared a posteriori that the fire could have been much better contained then extinguished if the firefighting means, which were limited, had been implemented faster.

The time between the start of the fire and the decision to flood the storage facility appears long (1'20"). The absence of an automatic device showed that it was not possible to manually operate the devices installed as they were inaccessible, as they were in the immediate proximity of the flames and not on the outside. Everywhere where the sprinklers were able to be activated rapidly, the stocks were protected and the fire pushed back.

Firefighting operations required the mobilisation of significant quantities of emulsifiers beyond the Auvergne region (approximately 100,000 litres, of which 80,000 were used). The analysis of water consumption shows that approximately 90,000 m<sup>3</sup> of water was used to put out the fire, 1/3 of which was using in the sprinkling installations for protection purposes.

The inability to contain the firefighting water, if today there seems to have had any consequence, forms the subject of extensive thinking to correct this, throughout all similar sites.

## ACTIONS TAKEN

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No deliberate fault or negligence was retained against the installation operators, and no administrative or criminal penalty was issued.

In light of the results of the technical inquiry underway concerning the accident, corrective measures were prescribed. Generally speaking, an evaluation of the risks and preventive measures were undertaken (updating of the hazard analyses, consideration of domino effects, possible third-party expert evaluations ...).

The risk of water and environmental pollution through aquatic means has been the subject of in-depth assessment: upon its arrival to the scene of the accident on January 20th, the classified installations inspectorate was worried about the retention of the firefighting water. Considering the small capacity available (1,000m<sup>3</sup>) and the possibility that the fire could spread to a testing laboratory containing toxic products, this capacity was placed in reserve and, finally, was not used.

Few risks were identified during the fire. The site authorities identified a stock of 1,300 tonnes of synthetic gums (in fact 2,530.6 tonnes, even if only 1,415 tonnes were damaged by the fire) and the presence of a few tonnes of chemical products near a machine protected by a wall and by the spray system of the damaged building. A priori, there was no reason to be afraid of a major firefighting water pollution problem.

On January 25th, 2000, the inspectorate was able to verify that the products near the protected machine were not damaged by the fire or the firefighting water. However, according to indications by the operator, "a few big-bags" (a few tons of products packaged in bulk in large 1 or 2m<sup>3</sup> sacks) which were located in the part of the building destroyed by the fire could not be recovered.

However, on February 4th, 2000, the classified installations inspectorate received additional information concerning the presence of greater quantities of chemical compounds in the part damaged by the fire:

- ✚ approximately 60 t of a vulcanisation compound, Vulkanox,

- ✚ approximately 900 kg of cobalt hydroxide,

- ✚ approximately 5.75 t of rosin.

Considering the potential pollution risks by some of these compounds, this important question rapidly formed the subject of significant analysis and impact evaluation studies, through the impetus given by the main public and private authorities.

The inspectorate's attention was rapidly directed toward the Vulkanox, considering the quantities and the nature of the products missing. Including:

- ✚ 600 of the 900kg of cobalt hydroxide were found in the fire debris and residues,

- ✚ In all likelihood, the rosin (purified pine tar) burned up in the fire, considering its high flammability and its water-insoluble properties.

The Vulkanox could have been destroyed in the fire, carried away by the firefighting water or, for part of it, remain the rubble of the building's basement and difficult to access. It is thus important to establish a report as precise as possible of the quantities found in the rubble and in the natural environment and to know the impact of this product and its fate in the environment.



Vulkanox is composed of N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD) having anti-oxidising properties. Although it is identified as "very toxic to aquatic organisms and may cause long-term adverse effects in the environment" according to the material safety data sheet provided by Bayer, it is not very soluble in water and not very biodegradable, although it is very sensitive to photochemical oxidation

### Evaluation of potential pollution and its possible effects :

As soon as the fire started, in the evening of January 20th, the establishments began sampling the firefighting water at regular intervals in the Cataroux plant's outlet channel, and had them analysed by their internal laboratory as well as by the LRPC ("Laboratoire Régionale des Ponts et Chaussées", highway department's regional laboratory).

The analyses were based on commonly evaluated parameters (COD, SS). The results did not seem to present a level of specific dangerousness considering the context (max. SS of 983 mg/l and max. COD of 739 mg/l). A few samples and analyses were undertaken in parallel by an independent laboratory without the operator being informed.

On January 25th, 2000, as soon as the problem associated with the presence of a "few" big-bags of Vulkanox appeared, the inspectorate immediately requested additional analyses concerning this compound in the samples taken by the operator, some of which were performed by one or more independent laboratories (under the co-ordination of the Clermont-Ferrand LRPC).

When the quantities that disappeared were better determined, the classified installations inspectorate officially asked the operator, by fax on February 14th and confirmed by detailed letter on February 23rd, to take water and sediment samples in the water courses downstream from the site, in order to detect and evaluate any pollution resulting from the firefighting water carrying toxic compounds:

- ② 2 sediment samples were performed February 21st in the Bedat and in the Morge in the presence of the classified installations inspectorate. At the same time, the inspectorate requested by fax on February 26th that samples be taken in order to measure the pollution's possible biological impact on the water courses into which the firefighting water may have entered: Tiretaine, Bedat and Morge (water courses of mediocre biological quality),
- ② 3 were conducted in the presence of the inspectorate on February 29th and consisted in sampling then determining the number of oligochaetes (small worms which live in the sediment) for which the systematic distribution of a criteria of evaluation and characterisation of the local pollution.


The results of these measurements received March 7th and the data of the file concerning the fire submitted to the inspectorate by the operator on March 8th, show that pollution of chemical origin is detectable, without it being connected with the fire with certainty.

The quantity of Vulkanox present during the fire has been evaluated precisely at 59 tonnes in the file mentioned above. A meeting held March 13th between the inspectorate and the industrialist bears on the action to be taken concerning the investigations underway.

On March 17th, the work and analyses to be performed were presented in a detailed manner to 2 members of the Group's executive committee by the Regional Prefect, and assisted by the Director of the DRIRE.

These elements were reiterated and confirmed in a letter dated April 10th, 2000 from the Director of the DRIRE to the company, setting the framework of the additional research and investigations to be conducted or provided:

- 🔧 Precise material balances for the various metals and compounds,
- 🔧 Additional analyses and sampling,
- 🔧 Conservation measures to be taken at the site of the fire,

 Theoretical and experimental studies on the degradation of the Vulkanox in the environment and on the possible toxicity of the degradation compounds

On April 6-7, 2000, roughly thirty simultaneous water and fine sediment samples were taken over 25 km of water course downstream from the plant, in the presence of representatives of the company, the classified installations inspectorate and a representative of Clermont Ferrand's Municipal Laboratory.

The purpose of the analytic programme retained, the co-ordination of which was given to the LRPC, was to observe the geographic distribution of the possible Vulkanox pollution as well as any degradation products, derived from this compound, the combustion of elastomers or other products present during the fire.

The initial results, officially sent to the inspectorate on June 8th, show a confirmed significant presence of Vulkanox in the sediments of the Bedat and the Morge.

On June 15th, the inspectorate received a company's file specifying the quantity and the fate of the Vulkanox, following the accident: at the most, 45.5 tonnes of this compound could have entered the firefighting water.

The official report by the LRPC (Laboratoire Régional des Ponts et Chaussées) on the series of analyses was produced June 22nd, 2000. Its conclusions are as follows:

- 🌀 There was an appreciable departure of raw materials containing 6PPD into the natural environment, being carried by the firefighting water,
- 🌀 Other pollutants (metals, primarily lead and zinc) are detectable,
- 🌀 Degradation of the biotic index downstream from the accident is measurable, the origin of which remains to be determined (Vulkanox and/or metals, or another cause independent of the accident).

The classified installations inspectorate, under the authority of the Prefect, requests or confirms on June 23rd, that the operator perform additional and immediate investigations :

- 🌀 Evaluation of the extent of the pollution by a new series of samples and biological indexes,
- 🌀 Theoretical and experimental study of the biodegradability of the Vulkanox in the environment (degradation pathways, toxicity and solubility of the products obtained), with a panel of experts being formed,
- 🌀 Research of any observable toxic effects,
- 🌀 Proposals for rectifying the pollution (cleanup operations which could be required).

The panel of experts, selected jointly with the classified installations inspectorate, held its first meeting on July 6th, 2000.

### Conclusions of the investigations :

Owing to the work of the experts and all of the information available, the following conclusions could be made:

#### **Metals :**

While it could be considered as not very extensive, the pollution of the metals underwent precise evaluation:

- 🌀 in all likelihood, the lead in the water comes from the old x-ray rooms used for inspecting civil works tyres on the site of the destroyed building. The operator indicated that these installations did

not contain radioactive sources. It should be noted that the risk of pollution due to the lead was not, it appears, considered by anyone at the time of the fire, it was revealed by the in-depth analyses.

🔗 the zinc could have come from the roof, part of which was covered with this material.

### Polycyclic aromatic hydrocarbons ou HAP :

Analyses of the firefighting water made by an independent laboratory revealed measurable traces of polycyclic aromatic hydrocarbons without them presenting a risk for the quality of the water.

The presence of these compounds was surprising as they were not present in the gums or in the Vulkanox, and their synthesis conditions do not correspond to those which prevailed during the fire. Furthermore, the search for these components was initially conducted for both scientific and verification purposes.

In all likelihood, it comes from a layer of tar present in the building's roof.

### Vulkanox :

The Vulkanox content in the sediments show the presence, in July, of this product in all water courses concerned up to the Allier, although at levels lower than the first series conducted in April 2000, except in a zone of approximately 8km, at the fork of the Bedat and the Morge.

The comparison of the measurements made in April and July show a drop in the pollution possibly accompanied by a displacement following the heavy thunderstorms since spring. The calculations made in April and July indicate the presence of quantities in the order of 2t and 0.5t, respectively. The difference would be perfectly explainable by a dissolution of the 6PPD by the circulating water.

Even by considering significant uncertainties, inherent to the calculations and sampling, the quantity present in the sediments, evaluated at approximately 0.5 to 1t, is very far from the 45.5t which disappeared during the fire. The maximum concentrations are in the order of 200 to 400 mg/kg of dry sediment. The aqueous solubility was re-evaluated lower, from 1 to 0.2 mg/l at 20°C. Considering the water temperature, it could not have been evacuated a quantity of Vulkanox greater than 2.5t within six months.

The absence of sediment from Vulkanox "tablets", the storage of 59t of this compound in the immediate proximity of one of the two chimney's of the fire (zone where the building's concrete slab caved in due to the fire) and the apparently low 6 PPD content of the sediment and sludge remaining in the building's basement outside certain well-defined zones, render the fact plausible that a significant quantity could have been vaporised or burned.

This last hypothesis is reinforced by several arguments announced by the operator:

🔗 Thick steel elements were bent under the heat near the fire's "chimneys" which confirms the existence of temperatures in the order of 800 to 1,000° C,

🔗 a PVC and polyester (stiffener) closing curtain disappeared. Polyester begins to melt at 280°C and the stocks of 6PPD, rosin and cobalt hydroxide were located between this curtain and the first chimney,

✚ A sheet of melted then solidified 6 PPD was found over approximately 150m<sup>2</sup> confirming that part of this product was liquefied by the heat (the melting temperature under atmospheric pressure is approximately 50°C),

✚ No trace of the big-bags of the products was found, except for a few pieces of pallet although the packaging was destroyed at around 250-300°C,

✚ A laboratory study consisting of placing 6PPD in a flow of increasingly hot air shows that the product begins to disappear at around 220-230°C; the disappearance (evaporation or decomposition) increases suddenly at around 290°-300°C and is total after 350°C.

Photo DRIRE Auvergne



The biotic indexes measured in February and particularly in June, at 10 points of the water courses including 6 in the polluted zone, show that the receiving environment was the site of toxic aggression, although it was not lethal (oligochetes - marsh-worms - were present in all of the samples). Comparison of the analyses conducted in February and July suggest a certain improvement in the environment. On the Allier, after the confluence with the Morge, the impact of a marked toxic effect on the environment does not exist.

There was thus no major harmful effect detected in the natural environment, which seems to be confirmed by the absence of dead fish. This point was brought up during the work conducted with the departmental agriculture and forestry department and then with the supreme council for fishing associated with the last series of samplings in the environment. Les analyses effectuées sous le contrôle de la direction départementale des affaires sanitaires et sociales n'ont pas montré de dégradation de la qualité des eaux prélevées dans l'Allier ou dans sa nappe, après la confluence de la Morge.

The analyses performed under the control of the departmental health and social affairs department did not show degradation in the quality of the water sampled in the Allier or in its water table, after the fork of the Morge.

The bibliographic elements available, notably chemical and toxicological, underline the strong photo-oxidability of 6PPD in the aqueous environment and put its toxicity into perspective. One could thus think that this compound will be slowly downgraded in a natural manner.

The panel of experts continues to meet (meeting of 04/27/2001) to finalise the study of the experiment and analysis results, particularly in the light of theoretical data. In particular, CEMAGREF was asked to perform experimental studies in microcosms (properly equipped aquariums which reproduce a model aquatic environment).

Naturally, a new series of measurements will be conducted in the sediments of the water courses contaminated in 2001 and, if necessary, beyond that in order to verify that the 6PPD pollution is disappearing. The operator will produce a written report containing all of the information and analyses, which will be submitted to the panel of experts and validated by the classified installations inspectorate.

The operator contacted specialised companies to rapidly undertake cleanup operations, if necessary.



## LESSONS LEARNT

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Specifically, attention should be placed on the dangerous products (distribution, storage and traceability), to the rapid and automated rapid reaction capabilities in case of an accident, the implementation of emulsifier tanks, the construction of catchpits sufficiently dimensioned to contain the firefighting water in case of a fire.

A particular attention was given to the underground pipes: indeed, these ones could be damaged by the movements of the ground (expansion of the paving stones as a consequence of thermal effects of the fire).



Photo DRIRE Auvergne

An initial summary report, completed regularly afterwards, was presented to the classified installations inspectorate by the representatives of the company in early March 2000, in compliance with article 38 of Order No. 77-1133 dated September 21st, 1977, which allowed the inspectorate keep the members of the Puy-de-Dôme Departmental Health Council informed by reports of March 13th and September 6th, 2000.

## **4 - Thermal runaway of a styrene-acrylonitrile copolymerisation reactor**

July, the 22<sup>nd</sup>, 2000

## **Leak on a butadiene polymerisation reactor**


May, the 15<sup>th</sup>, 2000


Villers St Sépulcre (60)

### **THE INSTALLATIONS IN QUESTION**

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The Villers St Sépulcre site employs 270 people and specialises in the manufacture of the following plastic materials:

 S.A.N obtained by polymerisation of Styrene and Acrylonitrile. These are intermediate products used in the manufacture of A.B.S and other plastic materials.


 A.B.S obtained by polymerisation of Acrylonitrile, Butadiene and Styrene.

Three types of operations are performed on the site: polymerisation, finishing and composition. Polymerisation takes place in continuously stirred-tank reactors of various sizes, and the duration varies between 1 hour and 15 hours. Following polymerisation, the latex and water dispersions are transferred to storage tanks to await further treatment. The finishing operations consist in separating the polymer from its liquid medium by flocculation, then drying to obtain a dry powder. The composition operations consist in adding pigments and different additives to the powders obtained at time of finishing, in order to obtain the required properties and characteristics.

The annual production capacities are as follows:

 S.A.N resins: 33,000 t

 A.B.S resins: 15,000 t

 A.B.S granules: 45,000 t

A.B.S products have two main properties: good impact resistance and good mechanical strength. They are used in numerous applications: automobile construction, the household-appliance industry, the leisure industry, etc.

The activities have been regulated by a prefectorial order dated February 26<sup>th</sup>, 1993, for an annual production capacity of 109,000 t. The site comes under the European Directive SEVESO II for its storage of acrylonitrile (250 t) and butadiene (340 t).

## THE ACCIDENTS, THEIR BEHAVIOUR AND CONSEQUENCES

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The accidents of May 15<sup>th</sup> and July 22<sup>nd</sup>, 2000 both occurred in the polymerisation sector.

### Accident of May, the 15<sup>th</sup>, 2000 :

The reactor in question (R 13) is a 55 m<sup>3</sup> reactor, fitted with a blade mixer and counter-blades and a heating and cooling system with a "jacket" circuit linked to exchangers supplied with either cold water from cooling towers or steam from the plant circuit (maximum temperature of the reactor: 80°C). It is equipped with valves and rupture diaphragms calibrated at 15 bar, in addition to a degassing system linked to the plant's flare-stack network. It also has, at its low point, a pneumatic remote-controlled drain valve, which is used for wash water drainage. This valve is extended by a sleeve with a plug fitted with a gasket at its end.

Before any polymerisation took place, a series of tests was carried out to ensure that all safety systems were operational. If it had been opened, the reactor is subjected to a pressure test.

The reactor was then loaded: for the production of butadiene, 25 tons of water, 15 tons of butadiene, emulsifier and an initiator are introduced. The water is raised to a temperature of 80°C, and the butadiene is introduced in liquid phase, at a pressure of 8-10 bar. The progress of the reaction, which can last for up to 15 hours, is linked to the lowering of the reactor pressure from more than 10 bar, to approximately 3 bar. The exotherm is at its greatest after between 4 and 10 hours of polymerisation.

In the case of extremely exothermic reactions such as these, agitation and temperature are essential parameters. The latter is precisely adjusted by setting the temperature/output rate of the cooling water.

At the end of the reaction, in the case of polybutadiene production, the butadiene which has not reacted is recovered by stripping.

On May 15<sup>th</sup>, around 3.45 a.m., during a butadiene polymerisation reaction which was taking place in reactor R 13, a butadiene leak occurred in the lower section of the reactor at the level of the plug located downstream from the drain valve. The control room operators detected the ill-timed opening of the drain valve by a flashing light indicator. As far as the operator was concerned, the problem could not be serious, as the circuit was closed by a sleeve and a plug.



The operators tried to close the valve several times, without success. One of them made his way towards the reactor to check the position of the valve and close it. The operator, who could not reach the valve because of the foam mist that was being ejected from the lower section of the reactor, smelt the characteristic smell of butadiene. At that moment, the leak triggered the network of gas detector alarms, one of which is located directly in line with the reactor. Some of them exceeded the upper threshold of the alarm (40% of the lower explosive limit).

The POI ("Plan d'Organisation Interne, internal contingency plan) was put into action, and the operator decided to open the depressurisation valve of the reactor to the flare-stack circuit located on the reactor dome. The pressure of the latter dropped, reducing the leak to zero in less than 30 minutes. The flaring lasted for around 1 hour and 15 minutes, and the sensors reverted to a reading of nothing detected approximately 1 hour after the beginning of the accident.

### The consequences :

The atmospheric tests carried out by the firemen within a radius of 5 km around the site revealed no significant readings of butadiene concentration. The operator has estimated that approximately 340 kg of butadiene was released into the atmosphere. The accident caused no material or physical damage.

### Accident of July, the 22<sup>nd</sup>, 2000 :

The reactor in question (R23) has a capacity of 75m<sup>3</sup> and is fitted with more or less the same fittings as reactor R13. Its maximum temperature is 150°C, and its maximum pressure is 7 bar. In addition, it also has a "dump" tank of 195m<sup>3</sup> which allows rapid evacuation of the contents of the reactor and to flood it in an emergency.

Around 10.40 p.m., during an S.A.N. copolymerisation reaction that was taking place in reactor R23, the control room operator detected an abnormal rise in the temperature of the reactor (125 °C). The visual display screen in the control room confirmed the request for cooling.

An operator then went to the cooling tower to check the water level in the pool, and noted that the water was at the "very low" level: the industrial water supply was no longer operating. His attempts to restore the supply of water did not render it possible to restart the cooling pumps.

The control room operator decided to initiate the emergency procedure in case of reactor runaway: three loads of cold water of a 2m<sup>3</sup> volume per unit were introduced into the reactor to bring the temperature down to a maximum of 121°C. As the temperature was in excess of 125°C and each load of cold water only brought the temperature down by 0.7°C, the procedure was ineffective. Moreover, the volume of the reactor made it impossible to add any further water.

It was then decided, as provided for in the emergency procedure, to introduce a reaction inhibitor, in order to prevent the product from solidifying before the reactor was completely emptied into the "dump" tank placed below the reactor. At the time of emptying, the limits of the process had been reached (a temperature of 140°C, pressure of 5.2 bar).

### The consequences :

The second accident caused no material, physical or environmental damage.

## **THE ORIGIN, THE CAUSES AND CIRCUMSTANCES OF THE ACCIDENT**

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### Accident of May, the 15<sup>th</sup>, 2000 :

Analysis of the accident revealed three concomitant factors:

- 🔧 Failure of the pneumatic drain valve control, in particular failure of the O-ring of the push-button controlling it. The pressurisation therefore became sufficient so as to provoke opening of the valve,
- 🔧 Defectiveness of the seal on the plug located downstream of the valve,

🔧 Faulty installation of the plug, with several incorrect bolts and inadequate tightening. In addition, the plug had not been subjected to preliminary testing.



#### Accident of July, the 22<sup>nd</sup>, 2000 :

The runaway reactor was due to a lack of water in the reactor's jacket circuit, leading to poor heat exchange. This lack of water was itself due to a lack of water in the cooling tower pool, which caused a loss of output towards the cold exchanger of the reactor. The poorly controlled temperature of reactor rose, causing runaway of the co-polymerisation reaction.

A more detailed inspection of the cooling tower pool revealed failure of the "low" and "very low" level sensors on the pool, which detect any abnormal drop in the water level. Removal of the sensors with vibrating blades revealed fouling. The failure of the "low" level sensor did not therefore trigger the automatic opening of the pool water makeup valve. As regards the "very low" level sensor, its fouling was such that the control room alarm was not triggered. Authorisation for the starting of the manufacturing cycle was therefore not refused during the preliminary tests carried out on the reactor.





## ACTIONS TAKEN

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### [Accident of May, the 15<sup>th</sup>, 2000 :](#)

Since the accident, the installation in question has not been re-started. The appropriateness of maintaining the production of butadiene on the site is being analysed. This production is presently being carried out on another site in Holland belonging to the same group. The site is supplied with polybutadiene delivered in highway tanks from the Dutch site.

However, the prefectural order of November 14<sup>th</sup>, 2000 makes any eventual re-start of the butadiene manufacturing unit subject to certain provisions concerning, in particular:

- 🔗 The organisation of prevention of risks,
- 🔗 The setting out of clear operating instructions,
- 🔗 Preventive maintenance of the installations,
- 🔗 Periodic checking of the safety devices instrumental to the correct operation of the installations,
- 🔗 The control devices of the installations,
- 🔗 The safety-related equipment and operating procedures.

### Accident of July, the 22<sup>nd</sup>, 2000 :

Initially, reactor R23 was declared locked out. Subsequently, the operator proceeded with cleaning of the level sensors.

In addition, a programme of checking the condition of the sensors was initiated each time the reactor cleaning operation took place, that is to say, once every two weeks. A series of tests of the "low" and "very low" level sensor alarms was also initiated before each starting of the production cycle. The operator intends to install level sensors with different technologies.

The installation in question was re-started on July 26<sup>th</sup>, in late evening, after being subjected to the checking programmes and tests defined above.

## **LESSONS LEARNED**

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These two accidents reveal a clear defect in the organisation of installation maintenance on the part of the operator.

Over and above these shortcomings, the implementation of a veritable safety management system as provided for in the Ministerial Order of May 10<sup>th</sup>, 2000 appears to be the best way to prevent these types of accidents from reoccurring.

## 5 - Butadiene leak in a chemical plant. Bassens (33). December, the 4<sup>th</sup>, 2000

### THE INSTALLATIONS IN QUESTION

#### The site :

The plant employs 425 people. It produces 120,000 t/year of synthetic rubber derived from butadiene and styrene. The procedure used is a solution-type procedure, the solvent being toluene. The plant is almost the only one which manufactures high-viscosity butadiene, which is essential for the other plants within the group.

The establishment is covered by the AS (SEVESO) regime of the nomenclature for installations classified for the storage of inflammable gas (butadiene) that is liquefied and refrigerated (5,000t) and pressurised (1,790 t). The last prefectorial order, which followed a public enquiry dates back to December 4<sup>th</sup>, 1996.

Within the framework of the PPI (Plan Particulier d'Intervention, special intervention plan), the instructions issued to the population include evacuation within a 600m radius and sheltering in a "restricted zone" between 600m and 1,200m.



### THE ACCIDENT, ITS BEHAVIOUR AND CONSÉQUENCES

#### The accident

On December 4th, around 6.30 p.m., on the U400 high-viscosity polybutadiene manufacturing unit, a valve ruptured downstream from a 12m<sup>3</sup> tank, releasing its contents, 5m<sup>3</sup> of pressurised liquefied butadiene, in 15 minutes (1,250m<sup>3</sup> of gas). The cloud of gas drifted towards the west of the site during the first hour, then towards the south-west, in the direction of the Paris-Bordeaux TGV (French high-speed train) line. The POI (Plan d'Organisation Interne, internal contingency plan) was put into action, and a control unit was installed on the site. The production units were stopped and water curtains were installed around the tank. The SDIS (Service Départemental d'Incendie et de Secours", fire and emergency services) arrived at approximately 6.50 p.m. The road was closed to traffic south of the site at 7.10 p.m.





and in the south east at 7.35 p.m. The TGV line was closed at 8.p.m.

Explosivity measures were taken in the area around the establishment as of 7.10 p.m, first in a random manner by the operator and then from 8.p.m. onwards, in an organised manner by the fire and emergency services and teams of firemen from the plant.

All of these security measures were called off at approximately 10.30 p.m.

There were no victims as a result of the accident. Residents of Bassens complained about the smell following the leak. Olfactory perception of butadiene is possible as of 2 ppm, while the lower explosive limit (LEL) is 20,000 ppm. According to the operator, the explosimeter detection threshold set at 10% of the LEL does not appear to have been reached.

## THE ORIGINE, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

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Spontaneous auto-polymerisation caused a brittle fracture of the valve in question. The valve served as a by-pass for a remote-controlled valve on the pressure control circuit in the butadiene tank. The forming of this polymer, known as "pop", in the valve cover was due to :

- butadiene stagnation : the valve, which was closed at the time of the accident, constitutes an abandoned channel, with no circulation of the product
- the ambient temperature
- the absence of an inhibitor (tert-butyl cathecol): the tank did not contain any, as the butadiene is derived from a recondensed gaseous phase and the inhibitor is eliminated during this operation.

The increase in volume during polymerisation caused the internal pressure to rise sharply, thus causing the brittle fracture of the cast iron valve, the cover of which was torn off.



## ACTIONS TAKEN

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Over and above the analysis of the accident, the department of the DRIRE (French regional inspectorate for industry, research and the environment) that is responsible for the inspection of classified installations requested a plan of action from the operator, in order to prevent the same type of accident from occurring again.

The measures are as follows:

🔗 Enumeration of similar configurations throughout unit U400, based on the following criteria:

- 🔗 Presence of dry or wet butadiene without inhibitor
- 🔗 Development of pop favoured by temperature

- ✚ Development of pop favoured by the presence of a gas phase

- ✚ Development of pop favoured if the output is low or nil ("abandoned" channel, upper taps of tanks in the gas phase, valves and fittings, etc.)

- ✚ Cast iron valves and fittings

👂 Analysis of the risks of the installations based on the following criteria:

- ✚ Output conveyed

- ✚ Nominal diameter

- ✚ Line or tank pressure

- ✚ Volume involved in case of confinement

- ✚ Isolability: is there a means of insulating the critical point, is it accessible in the case of a leak?

👂 Site inventory and analysis: machine checks, verification of the upstream/downstream pressure levels of identified points, manoeuvrability tests of valves and fittings at risk.

- ✚ Similar configurations have either been removed for verification of the absence of pop, cleaning where necessary and replacement in certain cases, or a manoeuvre test has been carried out on the valves and fittings, allowing seizing or pop to be detected. In the case of a negative test, the valves/fittings were removed and cleaned.

- ✚ The [quarter-turn] valve in question has been replaced by a steel ball valve, pending a detailed study of the problem with the by-pass. Two other cast iron valves have been replaced.

- ✚ The offending valve was not referenced as critical. At the request of the DRIRE, a "critical valves/fittings" inspection plan has been completed by valves and taps which could present a risk of blocking by pop.

👂 In addition, the following preventive measures have been taken:

- ✚ Surveillance rounds (visual control, pressure and output controls) and a 2<sup>nd</sup> level control performed by the company's inspection department

- ✚ Biannual manoeuvrability tests while in operation

- ✚ Removal for biannual internal examination at the time of the two annual shutdowns. These last two points are staggered, in order to ensure maximum cover of the valves at risk

- ✚ Replacement of critical gate valves and cast iron valves by steel valves, at the time of the July 2001 order

- ✚ A study of each abandoned channel that has been enumerated, in order to carry out modifications to reduce the risk of pop, at the time of the July 2001 order

At the request of the Inspection des Installations Classées, the classified installations inspectorate, a study on the atmospheric dispersion of the butadiene cloud was carried out, in order to determine whether the cloud that was dispersed towards the south/south-west could have caused an explosion

exterior to the site, and to evaluate whether the populations exposed to the passing cloud could suffer irreversible damage to their health.

1,3-butadiene is a highly inflammable gas that can form peroxides. The explosivity of the vapours in air ranges between 2% (LEL) and 12% (upper explosive limit, or UEL).

It is an anaesthetic gas if inhaled in strong concentrations. Weak concentrations in the air (1%, or 10,000 ppm) do not have any noticeable effect on breathing, but this kind of exposure can cause quickening of the pulse or sensations of stinging or dryness in the nose and mouth. Inhalation at strong concentrations first cause eyesight problems, nausea and irritation of the eyes, followed by progressive anaesthesia. Respiration of an atmosphere containing 25% volume of butadiene for more than 20 minutes can be fatal. The recommended maximum allowable concentration of butadiene in the atmosphere of industrial premises, which allows for 8 hours' exposure per day, 5 days a week, with no detectable effect for most individuals, is 2 ppm. The IDLH (Immediately Dangerous to Life and Health) is a concentration value which was defined by the National Institute for Occupational Safety and Health (NIOSH) in the mid-1970s. It represents the threshold for irreversible effects after 30 minutes' exposure. For butadiene, it was set at 20,000 ppm. This value was reduced to 2,000 ppm in 1994. In addition, different studies have shown that 1,3-butadiene is a carcinogen.

Lastly, this gas has a density of 1.9. Heavier than air, it forms clouds which are then dispersed more or less rapidly, depending on the weather conditions.

This study concludes that the explosive area does not come out of the site's limits. Concerning the irreversible effect area (IDLH), it slightly comes out the site but does not impact outside residences.

## LESSONS LEARNED

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In terms of feedback, the phenomenon of spontaneous, uncontrolled polymerisation of butadiene is a reality which must be taken into account and is a scenario that must be analysed, particularly in valves that serve as a by-pass.





This accident revealed problems in the organisation and indeed in the culture of safety that are currently being analysed, and of which the analysis should result in an additional order within the framework of the order of May 10<sup>th</sup>, 2000 (SEVESO II), drawing conclusions in particular about:

- ✚ The failure to react, on the part of the personnel, at the time of the leak, and the failure to intervene on a manual valve located between the tank and the offending valve, which could have considerably reduced the quantity emitted into the atmosphere

- ✚ The absence of analysis of this scenario in the studies of the dangers, leading to a lack of training and practice on the part of the personnel and a doubt concerning the risk of explosion in the area around the site (culminating in the closure of the Paris-Bordeaux TGV line)

- ✚ The location of the operator control unit which could have been inside the butadiene cloud



-  The anxiousness of some residents concerning the smell of butadiene, due to lack of information
-  The ill-defined limit between P.O.I and P.P.I. depending on the drift of the gas in changing winds
-  Improvement of crisis management (decisions taken after some delay)
-  Interface of instructions with the SNCF (French national railway company).

## 6 - Fire in a glue factory. Haguenau (67). December, the 08<sup>th</sup>, 2000

### THE INSTALLATIONS IN QUESTION

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#### The site and its history :

The company in question operates a glue and sealant factory in Haguenau, under the authority of a prefectorial order dated February 14<sup>th</sup>, 1990. Since the order was issued, the company has progressively altered its production and is now mainly engaged in the production of polyurethane prepolymers (including polyurethane sealant for the automobile industry).

On May 9<sup>th</sup>, 1995, in conjunction with the reorganisation of its production, the company declared a stock of MDI (diphenylmethane-4,4'-diisocyanate) in excess of 20 t. Following an inspection of the establishment on July 1<sup>st</sup>, 1996, the operator was asked to file for extended regularisation authorisation. The first application was filed in September, 1999. It was not accepted, and was reworked and filed again on November 8<sup>th</sup>, 2000. At the time of the fire, the installations were being operated without the necessary authorisation.

### THE ACCIDENT, ITS BEHAVIOUR AND ITS CONSEQUENCES

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#### The accident

The fire broke out around 10 o'clock, while an employee was engaged in pumping a sealant from a 1,000-litre container to a 25-litre drum by means of an explosion-proof pump and an antistatic rubber hose in an area that was protected by halon explosion suppressant. The employee saw sparks jump out, followed by flashover. Despite the rapid intervention of the personnel, the fire quickly spread to the central workshop, as the fire door between the workshop and the solvent area had been left open, and then spread to the finished products storage area. These two areas were insulated by a fire door, but the fire spread through the roof (melting of the sky-dome type light fixture).



Photo Media

The emergency services intervened rapidly.

A sizeable black smoke plume was released and reached the community of Haguenau. As the atmospheric conditions were against the smoke plume rising and dispersing, the emergency services advised the population to remain indoors. The event was widely reported in the media, via the broadcasting of confinement instructions on local radio stations. Three schools that were located in line with the smoke plume were evacuated. The fire was brought under control after 2 hours and 30

minutes. The confinement measures were lifted around 1.30 p.m., as the fire had been put out. The emergency services maintained surveillance measures for the whole day.

### The consequences :

The effects on the environment were slight: analysis of the fumes up to 100m from, the fire revealed 4 ppm of hydrochloric acid and 100 ppm of benzene at the site closest to the fire. The medical enquiry revealed no cases of intoxication. As there was no containment capacity, some of the waters (1,800 m<sup>3</sup>) flowed into the wastewater system without causing any malfunctioning of the treatment plant, which had been warned in time. The results of the analysis of the soil and the waters did not reveal any significant pollution.

The material damage, in the order of 70 million French francs, was considerable: plastic materials, mostly PVC, solvents (toluene et xylene) and finished products (polyurethane sealants and prepacked glue) formed the largest part of the materials affected by the fire. The MDI storage area and the drums being produced, which were protected by the fire walls, were not affected.



Photo media



## THE ORIGIN, THE CAUSES ET CIRCUMSTANCES OF THE ACCIDENT

The fire was probably caused by an electrostatic discharge during the solvent transfer operation. There was no continuity between the pallet truck and the floor, and the operator was not wearing anti-static footwear. There was therefore a break in ground continuity. The fact that the operator started to panic and the fire spread very rapidly prevented the employees from reacting in any way, and they left the workshop after a few minutes.

## ACTIONS TAKEN

Once the fire was extinguished, a series of measures were taken to ensure that the situation was followed up:

### **Provisional measures:**


-  Inspection of the entire installation and checking of the on-site operating conditions (administrative and regulatory situation),
-  A prefectorial order prohibiting the restart of activity and laying down measures for pollution management, storage and waste disposal to be implemented.


### **Medical measures:**




### **Statements from 360 doctors concerning the medical effects of exposure to smoke.**


#### **Environmental** measures:


 Analysis of the soil and plants in the area concerned,


 Analysis of the monitoring of the effluents from the fire-fighting waters and those of the treatment plant.

#### Results obtained:

 The impact was low regarding health and the environment.

 At the time of the incident, the company was operating in anticipation of the required authorisations (particularly the increase in the amount of MDI that was being stored)

 The inspection of the installations revealed the absence of a fire-fighting water containment facility, the insufficiency of the flow of extinguishing waters available for fire fighting, storage of waste in an unconfined area and in the open air, and the existence of an incomplete file for regularisation.

 The activities of the units concerned by the accident and irregular ones were stopped.

## **LESSONS LEARNED**

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### technical

The fire walls and the intervention of the emergency services allowed the emergency to be dealt with efficiently, although the sky-dome, which was placed too close to the fire wall, rendered the firewall ineffective. It is important to take into account the risk of flashover of elements that are meltable by under the effects of heat, thus rendering protection devices such as the fire walls inoperative.

Moreover, for the transfer operation of a low point solvent, it is a good practice to use a security drum instead of a bucket. Equipotential balance must be taken into account. This link has to be installed before any transfer of product.

In danger studies, it is important to describe the degradation products in the case of fire, and to evaluate the consequences, in order to adapt the measures for prevention, protection and intervention.

### Administrative

Requests for authorisation for installations that are already operating must be subject to notice, in accordance with article L514-2 of the environmental code.

### Crisis management.

The incident was widely covered by the media, due to the broadcasting of confinement instructions, a message that was then taken up by the national radio stations. A large number of press organisations immediately sent reporting teams to the site, and they arrived on the premises before there was even time to take stock of the situation, and even before a real operational control post could be organised. This almost instantaneous mediatization of the incident resulted in strong pressure being brought to bear on all those taking part in the operations as regards the demand for information, even before the

setting up of co-ordination structures and the collection of reliable information about the incident and its consequences not reported in the danger studies.

## 7 - Outbreak of fire in the supply duct of a chemical reactor.

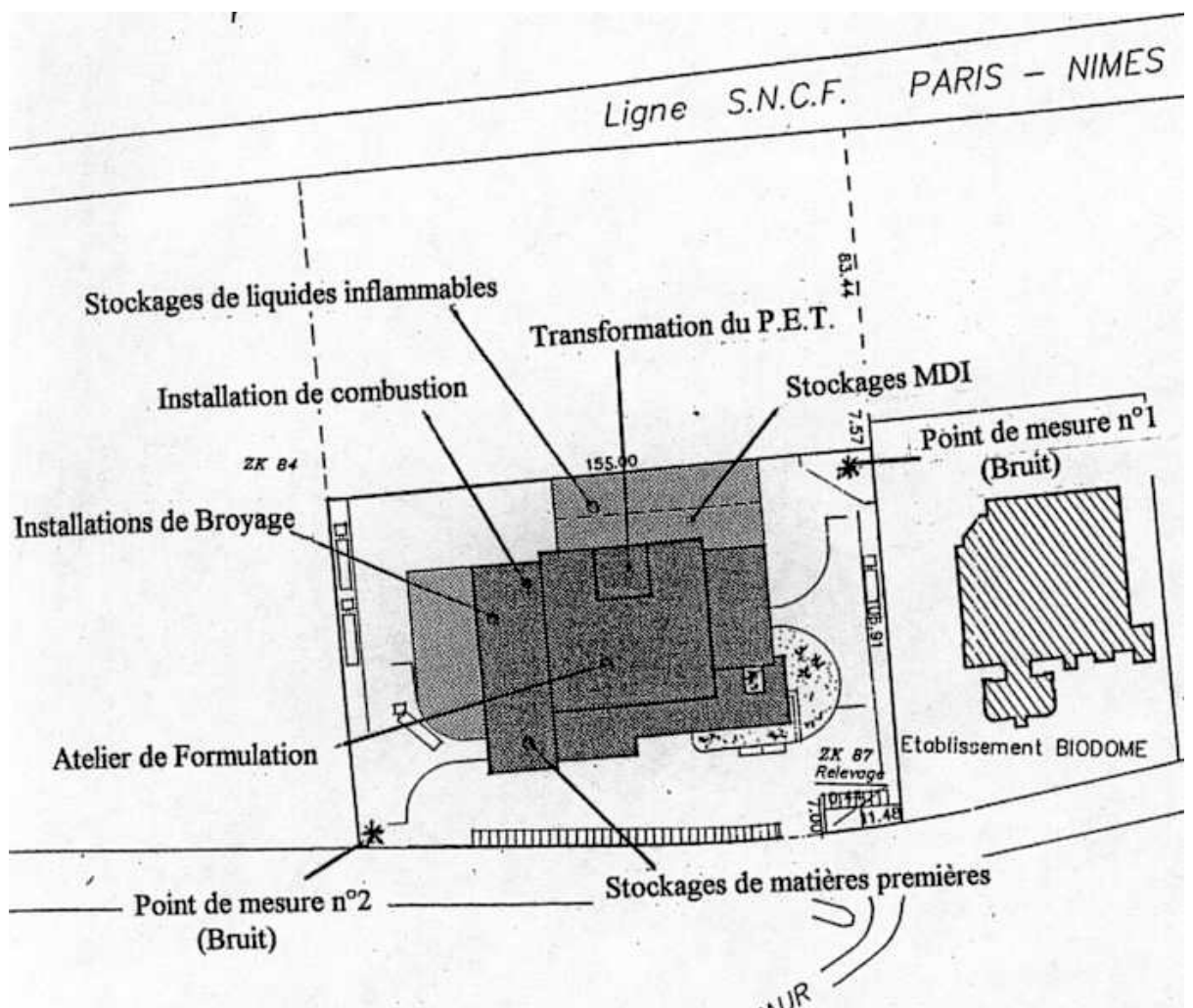
Issoire (63).

May, the 20<sup>th</sup>, 2000

### THE INSTALLATIONS IN QUESTION

#### The site :

The company, located in a recently created industrial zone in Issoire, France, specialises in the manufacture of polyurethane foam derived from recycled food-grade bottles made of polyethylene terephthalate (PET), for use in building construction applications. The PET is reclaimed by chemical transformation in order to produce polyols/polyester.



The manufacture of polyesterol comprises three main stages:

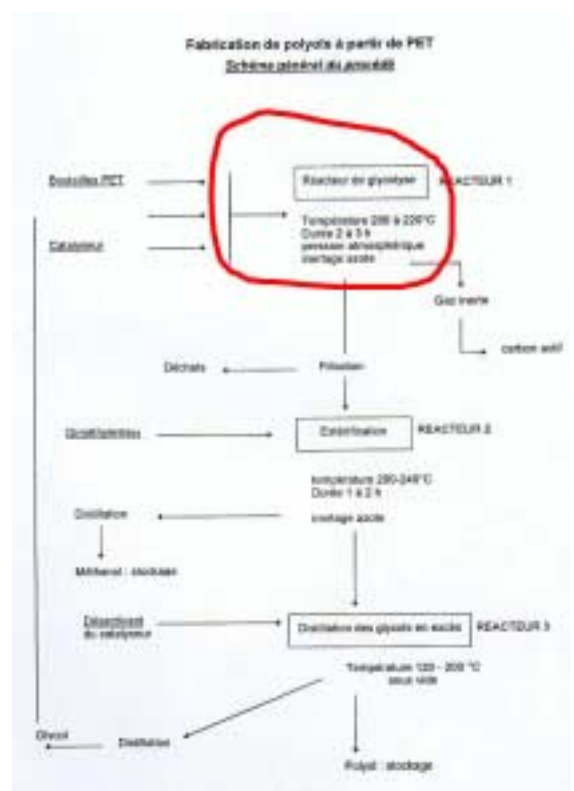
🔗 **Glycolysis reaction of the PET:** The PET bottles, which have been pre-ground, and the catalyst are introduced into a reactor containing the mix of glycols. Glycolysis takes place at 210°C-225°C for approximately 3 hours in an inert atmosphere.



🔗 **Interesterification reaction:** the glycolysat is filtered and then transferred to a second reactor, where interesterification takes place by a mixing of diesters at a temperature of 205°C. Methanol forms during this reaction. It is distilled, separated and stocked for use as a fuel in the boiler that provides heat energy for the operation of the installation.

🔗 **Distillation of free glycols:** the excess glycol is eliminated by vacuum distillation at a temperature gradient between 130°C and 175°C.

The company operates using a patented process. Start-up of the unit firstly involved lengthy laboratory studies which were carried out at the "Ecole Centrale", followed by the construction of a micro-pilot (150 kg capacity). This first pilot facility allowed the laboratory tests to be reproduced with no apparent deviation. A half-scale industrial pilot facility (1,000 kg capacity) was then constructed and operated for 2 years without incident. The large amount of data collected was used in the dimensioning of the industrial unit.



The establishment received authorisation by prefectorial order dated July 7<sup>th</sup>, 1998, in particular for the storage of diphenylmethane diisocyanate, plastic materials (PET bottles, polyols and raw materials in tanks) and the manufacture or regeneration of plastic materials.

## THE ACCIDENT, ITS BEHAVIOUR AND CONSEQUENCES

### The accident

The accident occurred on Saturday, May 20<sup>th</sup>, during the first tests of reactor R1. The company's technical manager and chemical engineer were present, as well as representatives of the Contracting Authority and the Main Contractor. A Saturday had been chosen to allow the tests to be carried out without any environmental or safety constraints (work sites in progress, etc.).

When the accident occurred, only the principal reactor (R1), which is used for glycolysis, was operating. The steam plant and the cold water production station were operating normally. Reactor R1 had been loaded normally, with 12 t of a precise mixture of 3 glycols and its temperature was 223°C, for a temperature control programmed at 215 °C. The reactor was under an inert atmosphere and under constant N-flux, the vent on the condenser outlet was open. In normal operation, monitoring and control appeared correct and no operating anomaly was indicated.

The protocol of the test procedure called for repeated manipulations, in order to check the functioning of the commands in manual and automatic mode, particularly the PET supply.



The inlet valve being open, the catalyst was inserted through the branch connection installed on the reactor. Following insertion of the catalyst and before initialisation of the insertion of the bottles, a fire started in the inlet duct. It immediately spread to the duct's acoustic liner. The liner, which was combustible, spread the fire, and "deflagrated", producing blazing droplets. Two dry chemical extinguishers were immediately used to put out the fire, which proved difficult to reach. The guillotine valve was locked and the N-flux in the reactor was sharply increased.

Over and above these measures, and faced with increasing flames on the duct liner, the operator decided to call the fire brigade and emergency services. When they arrived, however, they could see only persistent smoke. In order to make the site safe, they "flooded" the reactor in a multipurpose dry chemical, using a high-power nozzle. A water curtain was set up between the outer facade of the building and the methanol storage tanks, in order to protect the tanks from the consequences of any subsequent re-ignition of the fire.

### The consequences :

The damages caused by the fire itself are as follows:

- 🚒 Destruction of the supply duct,
- 🚒 Destruction of the separator and damage to all sensors and electrovalves,
- 🚒 Partial destruction of the guillotine valve,
- 🚒 Destruction of the thermal insulation and all electrical, computer and pneumatic cabling on the upper zone of reactor R1,
- 🚒 Structural damage to the building, mainly to the roofing and the structure situated near the fire.

The damage caused by the fire required extensive cleaning, repair of the electrical cabinets and circuits, the replacement of robots and electronic equipment (such as pressure and temperature sensors), as well as the replacement of all the unprotected thermal insulation in place. As the water used on the outside had damaged a series of sensors and electrovalves on the methanol tanks, the safety devices were replaced. A methanol pump was also destroyed by the water. The materials contained in the reactor were subject to stresses rendering them unusable and will be removed by a specialist company.

The cost of the damage, which was mainly caused by the extinction methods used, is estimated to be 3 million French francs, 2 million francs of which will result from operating losses. The cost of strengthening the safety systems amounts to approximately 400,000 French francs.

## THE ORIGINE, THE CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

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A fire broke out in the supply duct, which immediately heated up. The outer acoustic liner deteriorated, caught fire, spread the fire, melted and formed "droplets". Two types of fire occurred:

- 🔗 The initial fire, which was caused by spontaneous ignition and the combustion of glycol vapours and condensed glycol,
- 🔗 An induced fire that spread, due to combustion of the acoustic liner.

The fire broke out for the following reasons:

- 🔗 The presence of condensed glycols and glycol vapour in the PET supply duct and the presence of oxygen in the supply duct,
- 🔗 The temperature of the mix of glycols in the reactor, which was too close to the temperature of spontaneous combustion of diethylene glycol. The temperature in the reactor was 223°C and the temperature of the vapours was 220°C (the point of spontaneous combustion of DEG being 232°C),
- 🔗 Aggravating factors such as:

- 🔗 The possible presence of traces of catalyst in the supply duct, which would favour combustion,
- 🔗 The absence of ground straps linking the different metal parts of the supply duct, even though the connections were made without splices and the supply duct was earthed (the absence of ground straps could explain a spark of static electricity),
- 🔗 A discharge flow that may have been too weak, thus favouring the return of glycol vapours back into the supply duct,
- 🔗 The ease with which the protective liner caught fire (possible hypothesis of combustible gas forming in the supply duct, being gas resulting from the decomposition of the liner or its mounting adhesive).

## ACTIONS TAKEN

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Considering certain non-modifiable parameters, particularly the nature of the products and the temperature of the reactions, the operator has decided to:

- 🔗 Eliminate the oxidant by high-pressure injection of nitrogen in the PET supply duct, to prevent combustion from occurring,
- 🔗 Eliminate the presence of glycol vapours in the supply duct by strengthening the extraction at the condenser outlet, in order to prevent combustion,
- 🔗 Stay as far below the temperature of spontaneous combustion of diethyleneglycol as possible, by maintaining the temperature of the mix at 205°C during the entire duration of the insertion of the PET, by controlling the thermal inertia coupled with the weight of the equipment, products and the influence of the thermal insulation,



- 🔗 Prevent the presence of catalyst in the supply duct: the catalyst, which is extremely soluble in cold glycol, will now be introduced in the form of a solution, by a dosage pump, via an unused tap of the reactor in a completely closed cycle,
- 🔗 Prevent any sparks caused by static electricity by connecting the components of the supply duct using a bonding jumper and earthing,
- 🔗 Prevent the spread of fire caused by combustion of the liner, by removing the liner,
- 🔗 Install a powerful exhaust fan above reactor R1 and at the level of the separator, in addition to the natural ventilation already existing on the upper part of the roofing,
- 🔗 Install the control room high in an elevated position, and in the immediate vicinity of the emergency exits, in order to ensure the safety of personnel located too close to the zones in which the reactions take place,
- 🔗 Replace the current system for inserting the bottles by a continuous and hermetic procedure, in order to prevent oxygen from accumulating in the PET supply duct, with installation of a dry chemical extinguisher system inside the supply duct itself.

## LESSONS LEARNED

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The fire occurred during the systems testing and validation phase, and the operator cannot be blamed in this respect, as that is the reason for carrying out these tests. It does demonstrate, however, the difficulties of transposing a correctly functioning pilot unit to the industrial phase. The sole reproach that can be made to the operator was his failure to immediately contact the inspectorate of classified installations.

A synthesis report concerning this accident was sent to the inspectorate of classified installations by representatives of the company on June 5, 2000, in accordance with article 38 of decree No. 77-1133 of September 21<sup>st</sup>, 1977. The causes and consequences of the fire, in addition to the measures foreseen or already in place to prevent any further incident, have been analysed.

## 8 – Successive accidents on a chemical platform in 2000

Chalempé (68).


March, the 20<sup>th</sup> 2000, August, the 23<sup>rd</sup> 2000, September, the 29<sup>th</sup> 2000 and October the 18<sup>th</sup> 2000.


### PREAMBULE


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#### The platform :

The Chalampé (68) platform includes 4 chemical plants:


**P**  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, and section 150 (flammable liquids under special conditions for the fabrication of Olone), 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 prefectural 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.

 The two entities (C and D) which have the same general manager, place products, goods and various services at mutual disposal: one produces hydrogen for the companies of the site, the other produces the nitrogen and oxygen for the companies and various external 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 prefectural 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 :

- ✚ The first on March 29th, 2000 in the hydrocyanic acid workshop of plant B,
- ✚ The second on August 23<sup>rd</sup>, 2000 in the installations producing adipic acid in the plant A,
- ✚ The third on September 29th, 2000 in the adiponitrile workshop of plant B,
- ✚ The last, on October 18<sup>th</sup>, 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 INSTALLATIONS IN QUESTION

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### 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 and adiponitrile acid (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),
- P 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.





Liquid ammonia (NH<sub>3</sub>) 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** (TGN) purification shop 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<sub>2</sub>) 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<sub>2</sub> then into CO<sub>2</sub> and CH<sub>4</sub> before being cooled.


 **Methanation-cooling**: the reforming gas is treated by H<sub>2</sub>; the CO<sub>2</sub> and the CO are transformed into CH<sub>4</sub> with the production of water.


 **HCN synthesis**: the reaction produces a temperature between 1,100 and 1,200°C, ammonia, natural gas and air coming into contact with the catalyst (Pt). The synthesis gases (HCN, water, excess NH<sub>3</sub> 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 NH<sub>3</sub> and 2% of the HCN are absorbed. The gases cleansed of the NH<sub>3</sub> are sent to the HCN purification/recovery section.

 **Recovery of NH<sub>3</sub>** (NH<sub>3</sub> train): the phosphate solution is sent to a HCN-phosphate stripping tower. The HCN vapours are sent back to the gas input of the NH<sub>3</sub> absorption tower and the liquid is sent to the NH<sub>3</sub> stripping tower. The stripping of NH<sub>3</sub> takes place using steam; after condensation, the NH<sub>3</sub>/water vapours are sent to an enrichment tower. In the tower, NH<sub>3</sub> 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 NH<sub>3</sub> by counter-current spraying with a H<sub>2</sub>SO<sub>4</sub> 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 tanks which supply the ADN workshop.


## THE ACCIDENTS, THEIR BEHAVIOUR AND CONSEQUENCES


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### [✈ The accident of March 29th, 2000](#)

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 CNIM 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 CNIM 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. 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 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 tower H2241 at 5.30 p.m. Only the Toxguard 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 cm<sup>2</sup>. 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 took place Monday the 10th through Thursday the 13th of April, 2000.

### ✳ The other chemical platform accidents : The accident of August 23rd, 2000 - Emission of nitrogen oxides :

A TRICONEX 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 (HNO<sub>3</sub>). The resulting nitrous vapours (N<sub>2</sub>O and NO<sub>x</sub>) are drawn in by a compressor and sent under pressure into an RVN oxidation reactor where the nitrogen dioxide (NO<sub>2</sub>) is transformed into HNO<sub>3</sub>.

🌀 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 20m 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.

### ✳ The other chemical platform accidents : The accident of September 29th, 2000- Emission of « pentenes nitriles »

According to the operator, 150kg 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.

### † The other chemical platform accidents : The accident of October 18th, 2000 - : $\text{PCI}_3$ accident

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). No consequences were noted outside the site. 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.

## THE ORIGINE, THE CAUSES AND THE CIRCUMSTANCES OF THE ACCIDENT

### Accident of March, 29<sup>th</sup>, 2000:

The analysis of the accident was conducted by an interdisciplinary work group. Its 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 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

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### [✈ The accident of March 29th, 2000](#)

#### **Actions correctives initially proposed by the operator:**

- ✈ Immediate modification of the shutdown procedure,
- ✈ Immediate 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.
- P 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 CNIM boiler installed during the next major shutdown of the installations,
  - 👥 The operating procedure is modified for phases after the drainage of the HCN train:
    - P Stripping started using nitrogen to lower the HCN concentration in the liquid as in the gaseous phase and to remain below the LEL,
    - P Shift to air stripping below 0.7%,


- P Lowering of the alarm threshold and installation of a safety device acting on the recirculation output of the liquid phase,
- P 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):

- P Examination of 2 possible worst case scenarios of the incident of March 29th, 2000:
  - P **Non closure of valves:** the release would have continued to 1 t/h of N<sub>2</sub> at 2.6% HCN → release of 26 kg/h and ZOLEM of less than 50 m.
  - P **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 from now until late 2001.

#### The accident of August 23rd, 2000 :





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 NO<sub>x</sub> released into the atmosphere, as well as the risks for the neighbouring villages,
-  Study the possibilities of preventing NO<sub>x</sub> 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,
- P 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:

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 :

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

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### The accident of March 29th, 2000

#### **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...).

## 9 - Release of sulphur dichloride for the first use of a batch process

Castleford (United Kingdom).

January, the 20<sup>th</sup>, 2000

### THE INSTALLATIONS IN QUESTION

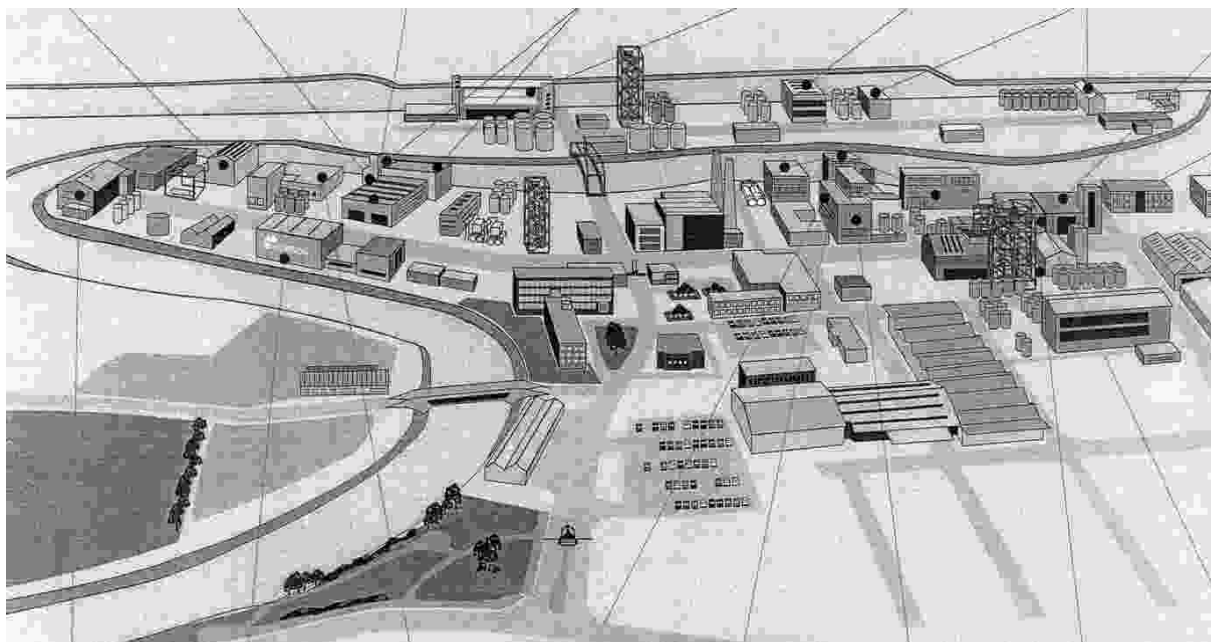
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#### The site and its history :

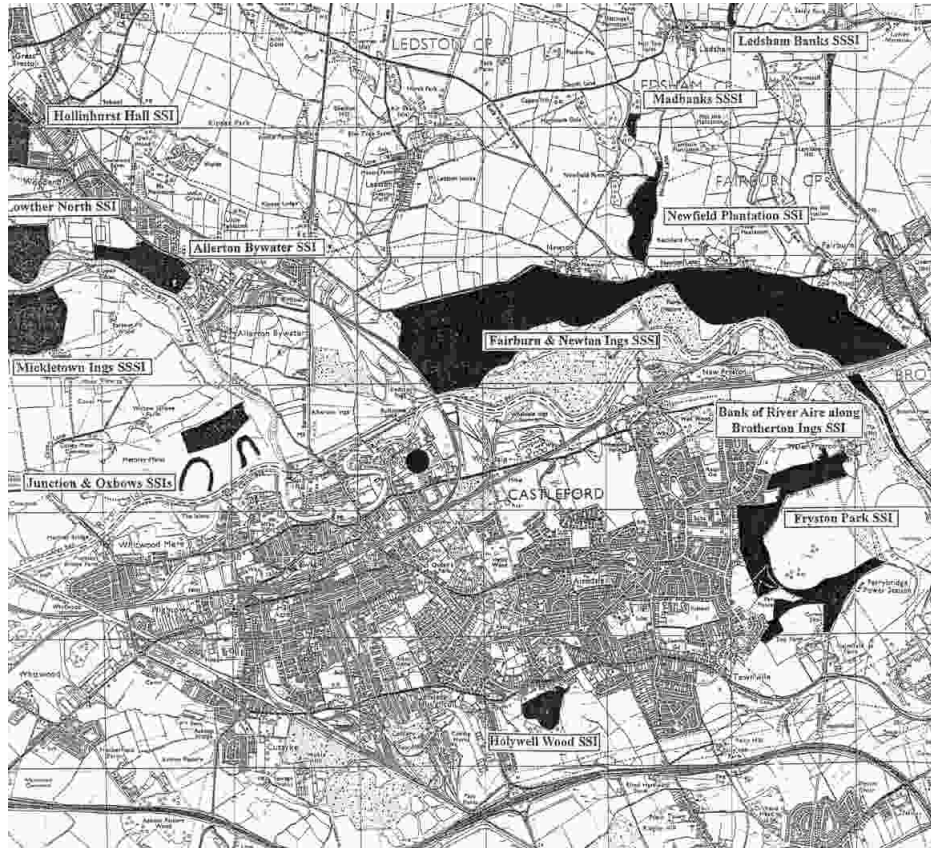
The company in question is a major chemical site handling a wide range of chemicals that bring it under the COMAH regulations. Using the COMAH aggregation rules and the quantities of materials declared to the Local Planning Authority (Wakefield Metropolitan District Council – MDC) under the Planning (COMAH) regulations 1999, in October 1999, the site had a total of 39,5 times the qualifying quantity for the top-tier COMAH status on the toxic test and 3,3 times the quantity on the flammable test.

The site carries out a wide variety of chemical transformations, mainly but not exclusively using batch processes. These processes use a wide variety of toxic and flammable chemicals as raw materials. Both the wanted products and the waste materials produced can themselves be toxic, flammable or dangerous to the environment.

The site has been in continuous use for chemical manufacture since 1915 when a factory was constructed at the direction of the War Office. The factory manufactured TNT for use in munitions during the First World War. The original site was 6 acres beside the River Aire giving frontage for quays of some 650 feet and offering facilities for railway sidings direct on the London and North Eastern Railway direct from its Castleford station. The land had previously been used mainly as a cricket field and as allotments. The site has grown since then and now covers 75 ha (175 acres).







The ten named substances used on the site in significant quantities are as follows. The declared site maximum inventory for each substance is the quantity that was used when applying for Hazardous Substances Planning Consent. It is possible that this quantity may be held on the site.

No other named substances are used on the site. Before the addition of any new named substance to the site inventory, notification will be made under the Planning Regulations in addition to notification under the COMAH regulations. The different substance involved in the process or stored on the site, according to the inventory, are the following ones : Arsenic (V) oxide and salts (0,4 t), chlorine (70 t), hydrogen (1,8 t), Hydrogen Chloride – liquefied gas- (20 t), LPG (100 t), Methanol (260 t), Oxygen (25 t), Phosgene (0,7 t), Sulphur dichloride (<1 t), sulphur trioxide (75 t).

The location of the site between an urban area and important waterways near a number of areas of special scientific interest make substance and accident control especially important issues in the operation of this plant.

**The installation :**

The part of the plant involved is the sulphur dichloride unit (called SDC in the following part of the document and whose formulation is  $SCl_2$ ). The following diagram shows the materials involved in the process, the main ones are the following ones : weight system and container venting line, transfer line with its pump, measure pot (T34). In the main lines, SDC, used in the process, is transferred in the ensuing unit from a dedicated vessel : a purpose designed pressurised steel container with nitrogen blanketing in the ullage space. This capacity is connected via a flexible to a transfer system composed with : a capacity located at the top of the reactor and equipped with its own scrubber and venting system. A pump pushes the product through the flexible to the capacity. At this time, it was the first start of this installation, adapted for SDC use. Previously, the part of the line concerned had been flushed with MCB, a solvent and still contained a part of it.



## THE ACCIDENT, ITS BEHAVIOUR AND CONSEQUENCES

### The accident

It happens on the 20th of January, 2000, in unit 280, for the first transfer operation since the repair of the product suction line. Indeed, previous attempts to start the transfer earlier in the day had been unsuccessful, and it had been found that there was a minor leak, leading to loss of suction on the suction line from the transfer pump to the portable container.

The leak had been repaired, and the transfer at 20.20 was the first after the repair

had been effected. Three attempts were made to transfer the contents by starting the transfer pump and opening the valves : these attempts were unsuccessful.



At 20.20. on the evening, an attempt was made to transfer the contents of a transportable container of Sulphur dichoride to a measure pot (vessel T34).

The SDC container has connected to it, a supply of gaseous nitrogen which has a supply pressure limited to 500 mbar. This nitrogen supply was opened up to assist in priming the pump (as designed). The pump then successfully primed, and SDC was noted to begin transferring to T34 as evidenced by the increase of recorded weight from the load cells upon which T34 is stationed. The weight in T34 was seen to rapidly rise to in excess of 200 kg by the operatives in attendance. As this was the first transfer of the material after repair of the suction line to the pump, the operatives in attendance « walked » the length of this line to determine whether any further leaks had developed.

Within 5 minutes of the transfer starting, fumes were seen to be emitted to the atmosphere, from the pressure relief valve system situated on top of T34.

The transfer pump was immediately stopped, and almost immediately, the emission of fumes from the relief valve ceased. As the operatives re-entered the main plant from the annex where the container offloading station is situated, there was a loud “thud” which was followed by a cloud of fumes being emitted into the plant area, emanating from the gas scrubbing system area for the process.

The site main control office was contacted by the area personnel and the on site « toxic gas » alarm was raised and the works fire team assembled. No assistance was requested from the off site emergency services.

At this time, the level of fumes within the plant area was low. The operator team was then instructed to evacuate the plant facility after making the other plant equipment safe (this entailed closing down the adjacent T36 vessel distillation). By this time, the fume density within the plant had increased, but was such that the opposite wall of the plant (about 30 meters away) was still visible. The on site fire team closed the valves on the SDC container. The fire team entered the plant to ensure that all personnel had been evacuated and that no problem was evident.

🚨 A “water curtain” was deployed to the east of the plant to mitigate any downstream effect of the gas cloud.

🚨 The fumes had abated by this time, and technical personnel to ascertain the damage to the equipment then entered the plant. It was quickly noted the main scrubber vessel lid had been displaced during the incident, and some further damage to pipelines in the vicinity of the scrubber lid had been damages. A low level of fuming was seen being emitted from a leak on a flexible line connecting the SDC transfer line to the top of the measure pot T34. An inspection of the plant at 9.30 PM identified that the T34 measure pot contents were approximately 50°C (close to the boiling point of SDC).

### The consequences :

No personnel on site was injured and an inspection of the roof of the plant immediately below the pressure relief valve found evidence of a very small degree of contamination from material being emitted from the relief valve vent. The estimation of lost SDC quantity is about 71 kg, the mass of SDC transferred was 206 kg (container weights) and the quantity on site at the moment of the incident was 400 kg.

On the material level, the top of the scrubber column is ruptured, together with other materials in connection with it.



The cost is not available but the accident losses cover the following operations :

- 🚧 Engineering re-installation of the process,
- 🚧 Lost materials (cf. photos).
- 🚧 Response teams operation costs,
- 🚧 Clean up of the installations,
- 🚧 Post-accident investigations : both for internal and external investigation inquiries.

On another hand, this kind of accident may involve problems with public confidence as well as on the company reputation with its customers.

The adjacent sports centre to the works was informed of the accident at this time. There has been no further interest shown from the occupants of the sports centre. There has similarly been no interest shown by any media representatives either local or national.

## THE ORIGINE, THE CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

The liberation of HCl and sulphur dioxide gases is the result of a reaction of SDC with water. This reaction occurred in the T34 measure pot as evidenced by the relatively high temperature detected in the measure pot after the incident.

As a result of the investigations, three potential sources of water were determined from the configuration of the plant. The balance of the evidence is strongly in favour of the contaminated drum of MCB being likely source of the water, as described below :

✚ Subsequent investigations into the drums used for the cleaning process showed that one drum of MCB still contained a significant quantity of free water (analysed at 35 % water content, but this only of the sample taken- MCB and water are immiscible). No other drums used were found to contain free water. A structural inspection of the drum containing water showed evidence of internal corrosion suggesting a long-term contact with water. Other drums inspected showed no evidence of this corrosion.

✚ Unfortunately, the MCB used in the washing out procedure is transferred as part of the operation into solvent recovery vessel to be used later in the process. This is a continuing integral part of the process as MCB is a solvent for the later part of the process. The wash out MCB had already been distilled free of water as part of the start up process and therefore it cannot be confirmed that the material was wet when in the measure pot.

## THE ACTIONS TAKEN

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The restart of the unit is submitted to the relevant authority agreement, after the operator showed them technical elements they asked for : analysis of the accident, actions taken.

## LESSONS LEARNED

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Lessons to be learned cover very different fields :

**As far as Security management, on a general level, is concerned**, the main points are the following ones :

- 🔗 Increase emphasis on Hazop studies,
- 🔗 Management of change procedures are crucial,
- 🔗 Pay particular attention to reducing inventories of dangerous substances in process to limit maximum losses.

Apart from the general methods, it is possible to focus on a few elements concerning **the practices** :

- 🔗 The check of the quality of materials, particularly of raw ones, must be taken in account and adapt according to the installation risk. In the case of this accident, the reaction with water was well-known. In spite of that, the operator did not carried out special checks on this point.
- 🔗 Commission must be carried out during normal working hours and in daylight.

Lessons are to learned for **the design** operations too :

- 🔗 The equipment is not dedicated to one product : this increases the risk of accident.
- 🔗 Control rooms should normally be manned to allow immediate shutdown action to commence after an instrument indication of a problem. Acting on visual observation is second best.

If we consider **the studies**, it is necessary to underline that a completed COMAH Safety report would not have prevented this accident. But it is seen as useful in identifying adjacent and possible knock-on hazards and plant preparedness for emergencies.

## 10 - Explosion for a mixing operation in a multi-purpose plant

Wuppertal (Allemagne).

June, the 8<sup>th</sup>, 1999

### THE INSTALLATIONS IN QUESTION

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#### The site :

The incident took place in an installation producing a variety of products for crop protection in a small quantity of 10 – 30 tons per months and proving new products and new operating procedures. It showed typical characteristics of a multi-purpose plant. All components could be interconnected any way and used for several productions.

The plant was subject to license according to German Federal Immission Control Act. Due to the quantities of hazardous substances at the installation in amounts that exceeded upper tier threshold limits the extended obligations of German Ordinance on Incidents had to be fulfilled by the operator. A safety report has been drawn up. The establishment is located in a valley amidst a residential district and crossed by a public means of conveyance, strictly speaking a suspension railway.





### Part of the plant involved :

The installation was lodged in a stone structure building. In June 1999, three productions were planned to be carried out at the same time. At the moment the incident occurred two productions were still working. The third one as origin of the incident was in the state of start up and should produce a commodity chemical of an active ingredient for chicken food industry.

Because some of the following information come from confidential documents, these elements had been changed into an anonymous form.

The process that should be carried out consisted of the following steps:

- ✚ Filling of a definite amount of potash into a stirring reactor
- ✚ Metered addition of a crystalline reactant A solved in solvent
- ✚ Activation of the stirrer and heating for several hours
- ✚ Metered addition of reactant B
- ✚ After a reaction time of several hours, draining of the make-up, further heating and removing of the solvent by distillation
- ✚ Discharging of the product to further work up.

In the process no hazardous substances listed in annex II of German Ordinance on Incident (1991) were handled. Therefore the incident described in the following was not notifiable due to this Ordinance.

## THE ACCIDENT, ITS BEHAVIOUR AND CONSEQUENCES

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### The accident

On the 8<sup>th</sup> of June, 1999, 500 kg potash was filled into a 4 m<sup>3</sup> stirring reactor. After that reactant A solved in a solvent (together 1.600 kg) was added in a metered form. After activating the stirrer the content of the reactor was heated up to 90°C.

At 16:30, two employees standing not far from the reactor suddenly heard a loud hiss and alarmed by this immediately ran away in the direction of the fire door.

At the same moment the reactor exploded. The pressure wave grasped the two employees who were injured considerably. In the following of the explosion a fire occurred.





### The consequences :

The two employees staying in the room where the explosion occurred suffered heavy injuries especially the drumheads bursted. Four other employees of the multi-purpose plant, three employees of other departments and two members of the establishment fire brigade were injured respectively had to be investigated providently at the hospital.

The first two employees had to stay in the hospital for several weeks. Three of the injured employees were attended ambulatory and the six others were dismissed after check-up.

Outside the establishment 91 persons were notified with complaints concerning breathing passages or injuries by glass fragments and had to be attended ambulatory.

A lot of dwelling houses suffered partly considerable damages especially because a lot of windows were smashed by the blast. The establishment was devastated in a circuit of 200 m around the place of explosion. A contact line of the railway was pulled down.



## THE ORIGINE, THE CAUSES ET CIRCUMSTANCES OF THE ACCIDENT

Two expert bureaus got the job to find out the reasons of the accident. A few days later due to the evaluation of circumstances and interviews with the employees the reason was found out. It was a substance confusion during feeding the reactor. Instead of potash the employee had filled potassium-hydroxide into the reactor.

The ordered packing drums with potash were provided correctly. An employee by mistake took a stillage of potassium-hydroxide from supply area and brought it to the reactor. Maybe the similarity of the labels „potash“ and „potassium-hydroxide“ on the drums in foreign language was the reason. The employee who had to fill the content of the packing drum into the reactor by using the man hole recognized the mistake. He told his foreman that something was wrong with the packing drum but the foreman ordered him to fill in the packing drum as planned.

The evaluation of operation recordings showed that after activating the stirrer and beginning of heating there were no remarkability ascertainable over a longer period. Then suddenly the temperature was rising in such a steep manner that after a few seconds the reactor failed. The speed of the runaway reaction was so high that the plant personnel could not interfere effectively. Furthermore, the opening of the safety valve was too slow.

## ACTIONS TAKEN

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The establishments fire brigade arrived immediately at the location where the explosion had taken place. At 6.45 p.m. the fire was under control and at 7.23 p.m. it was extinguished.

The laboratory truck of North Rhine-Westphalia State Environment Agency arrived at 6.20 p.m. and started immission control measurements in respect of hazardous substances. Only for chloric acid gas there were higher values of 0,5 ppm which were distinctly below the German MAK-value of 5 ppm (MAK = German Occupational Health and Safety Threshold Limit). As a result no hazard for the public due to hazardous substances had been recognized.

After the explosion the public in the neighbourhood was called to close the windows. Due to broken windows, not everyone was able to comply with this advice. For several hours the operator was not able to determine the substances released.

## LESSONS LEARNED

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The destroyed plant wasn't rebuilt. So the incident didn't entail consequences to this plant. The consequences of the accident led to the company's decision to displace the production of corp protection products to another location far away from any residential districts (> 1000 m).

Meanwhile the competent authorities began to consider the problem of substance and product confusion in multi purpose plants intensively and to reflect upon the measures necessary from a new point of view.



The company itself planned a complex multi purpose plant for corp protection products at another location where the residential districts are so far away that in case of an accident no consequences for the public could occur.

Therefore obviously the competent authorities paid attention to lessons learnt from this accident in the license procedure of that new plant.

Up to the day of the accident the operator only applied house-keeping measures to fight the problem of substance and product confusion. From his point of view after the accident there was no reason to change this procedure on principle. Only better house keeping measures as a non-hierarchical 4-eye-principle was taken into account. The competent authorities are convinced that only house keeping measures to prevent substance and product confusion do not correspond with the state of the art in safety technology. From the competent authorities point of view additional a technical identification system like a barcode system for example with technical interlock has to be installed. In this case each packing drum will get a plain machine readable code. The code on the packing drum shall be read automatically immediately before filling the substance into the reactor.

The feeding devices as metering valves, metering screws and so on should be interlocked by process control system in a way that feeding is only possible after reading the expected code. The competent authorities are sure that the accident presented above would not have taken place, if such a technical identification system like that described above had been used.

During the lapse of the licensing procedure a lot of controversy discussions between the operator and the authorities concerned had taken place. As a final result the new plant will get a technical identification system without interlock in addition to the improved house keeping measures suggested by the operator.



# 11 - Explosion in a cracking unit on a refinery site.

Gonfreville l'Orcher (76)

September, the 3<sup>rd</sup>, 2000

## THE INSTALLATIONS IN QUESTION

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### The site:

The refinery is located in the industrial port zone of Le Havre, in the district of Gonfreville l'Orcher and Rogerville.

The unit in which the accident of September 3<sup>rd</sup>, 2001 occurred is known as "cracker no. 7", and is a catalytic reforming unit that produces high-octane gasoline fractions. The unit can treat up to 4,200 t per day of product, following the successive phases described below:

#### **1 – Desulfurization-hydroprocessing Section:**

The load is mixed upstream of the heating and hydrogen reaction section. Following the reaction, the various reaction products (water, H<sub>2</sub>S, gas etc.) are separated and the gases are condensed.

#### **2 – Catalytic reforming Section:**

The catalytic reforming operation is designed to transform normal paraffins and naphthenes into aromatics, allowing the production of high-octane gasoline fractions.

The reaction is performed at a high temperature (~500°C) and at a pressure of around 14 to 20 bar. It is an endothermic reaction and produces a fluxing medium that is rich in hydrogen and is used, in particular, in the xylene isomerization section.

#### **3 – Fractionation Section:**

This section comprises the separation of the different fractions formed during the catalytic reforming reaction. The reformate separated from the light fractions is sent to storage, with a view to the preparation of fuels by mixing.

On an administrative level, the unit was initially authorised by a prefectorial order dated November 30<sup>th</sup>, 1967, and was made subject to complementary provisions on March 12<sup>th</sup>, 1997, following a danger study.

## THE ACCIDENT, ITS BEHAVIOUR AND CONSEQUENCES

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### The accident

A fire with muted explosions broke out at the refinery in Gonfreville l'Orcher on September 3<sup>rd</sup>, 2001, around 9.15 p.m., on the desulfurization section of the cracker 7 unit. The fire burned actively until 3.15.p.m. on September 4<sup>th</sup>. The chronology of the accident is as follows:



9.12 p.m.: rupture of a ¾ inch connection on the suction line of pump P3B,

9.12 and 30 seconds p.m.: flash-up of the cloud (approximately 200kg of product) and creation of a fed torch-type fire,

9.13 p.m.: rupture of a 3 inch naphta line that was exposed to the torch, which created another, larger flaming jet,

9.18 p.m.: through a domino effect, rupture of the manifold of a cooling tower and flash-up of the leak that was caused,

9 22p.m.:

- through a domino effect, rupture of the header (8 inch diameter) of tube V3, and flash-up of the leak,
- through a domino effect, rupture of the valve manifold of tube V3, which is connected to the site's flare-stack network, and flash-up of the gas leak. This led to a partial venting of the flare-stack network.



From 10 p.m. onwards: the burning leaks continued to burn until the rest of the unit was consumed and the flare-stack network could be isolated without danger, which was on September 4<sup>th</sup>, around 3 12 p.m.

#### Combating of the emergency:

The emergency was combated by means of the refinery's fire-fighting equipment and the firemen of Le Havre.

The strategy for fighting the fire consisted in limiting the dangers of the fire spreading and cooling the superstructures that were exposed to heat fluxes, in order to prevent collapse. However, at the height of the fire, extremely high flow rates of water were used (in the order of 2300 m<sup>3</sup>/h, at 7 to 8 bar, taken from the site's fire system).

#### Consequences:

The fire had no significant impact on the environment, and the fire protection water was stored in a 60,000 m<sup>3</sup> buffer storage tank designed for that purpose.

## ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

The accident originated at the level of a pump and steam turbine unit (reference no. P3B). In fact, the accident was provoked during a phase of periodic testing of the equipment, which is in fact a backup unit of pump P3A.

The various analyses carried out following the accident allowed the identification of several factors that together provoked the accident:

- The presence of condensates in the turbine (discharge valve closed),
- • Faulty fixing of the frame to the base,
- • Insufficient lubrication of the pump bearing,
- • Pump design with an overhung rotor,
- • Cavitation phenomena on the pump, due to insufficient suction.

This led to:

- strong vibrations on the pump, which caused the rupture of a ¾ inch connection located just above the pump, through fatigue stressing,
- a misalignment of the turbine/pump, which caused a rupture of the shaft and deterioration of the connection.

An aggravating event has been identified: the abnormal delay in closing the supply line's shut-off valve on pump P3B (approximately 10 min). Indeed, if the closing of this valve, which was ordered by the programmable safety controller had been carried out within the time anticipated (approximately one minute), the domino effects on the other piping could have been prevented and the gravity of the accident would have been vastly reduced.

## ACTION TAKEN

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Following the accident, an emergency measures order was signed on September 4<sup>th</sup>, 2000, requiring the operator to provide:

- • A list of the installations affected by the accident,
- • A report of the accident and details of the measures designed to prevent the re-occurrence of such an accident,
- • A report concerning the operating condition of the equipment.

The order also specified that the restart of the installations was subject to preliminary authorisation from the Prefect of the Seine Maritime district.

The emergency measures order gave rise to several exchanges of communication with the operator. In particular, two letters were sent by the DRIRE (Direction Régionale de l'Industrie, de la Recherche et de l' Environnement), the regional board of industry, research and the environment, to the operator on October 6<sup>th</sup>, 2000. These two letters were requests for:

- Recourse to a third-party expert who would examine the accident report drawn up by the operator,
- Implementation of a systematic, methodical inspection plan to assess the condition of the equipment.

Following examination of the neighbouring equipment, the operator advised the Prefect that only the "cracker no. 7" unit was considerably affected.



### Condition of the equipment:

As regards this point, the following method was decided upon:

➤ In the first instance, **an inspection plan** (methodical and systematic) was established. The plan was approved by an expert also used by the insurance companies.

✳ The inspection plan was implemented for **the totality of the equipment** which could have been affected by the accident.

✚ Implementation of the inspection plan allowed **classification of the equipment** according to its serviceability (category A, B or C).

Taking these factors into account, the DRIRE notified, by mail, the respective classifications given to each piece of equipment as a result of implementation of the inspection plan, and also sent a reminder that the various construction and repair operations to be performed on the equipment should be carried out in accordance with recognised trade practices and the strict adherence to the regulations concerning the matter.

### Corrective and preventive measures:

The operator proposed the following corrective measures:

🔧 Modification of the type of pump and the vertical positioning of the tube, to prevent cavitation phenomena.

🔧 Replacement of the motorised suction valves of pumps P3A and B, in order to obtain a quicker closing time, with the objective retained by the operator being closure in less than 30 seconds.

🔧 Modification of the speed regulation device of the turbine, in order to obtain an "isochronous" governor,

🔧 Replacement of the ¾ inch connections of the pumps concerned by 1 inch connections fitted with reinforcement gussets.

🔧 Modification of the purge system of the turbines concerned,

🔧 Implementation of an awareness campaign concerning the strict application of the operating procedures for turbines in the process of heating.

These recommendations were approved by the third expert, who drew up some supplementary regulations in parallel.

In the light of these different expert reports, the Prefect authorised the restart of the unit, on the condition that the operator respect the complementary provisions (complementary order dated March 27, 2001).

Following the accident, the unit was shutdown for around 7 months. The amount of the damage is in the order of 90 million French francs for rehabilitation and 450 million French francs in operating losses.

## LESSONS LEARNED

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As is generally the case, this accident is a clear illustration of how the simultaneous occurrence of several causal events which, if taken separately, can appear of secondary importance, and can have extremely serious consequences. The difficulty in the closing of the supply line's shut-off valve is also a perfect illustration of the theme of the aggravating factor.

This accident also reminds us that in the case of this type of activity, given the rapid development of the incident, everything hangs on the first few minutes following the occurrence of the accident.

As a result of the expert report ordered by the operator, the chronology of the accident was able to be reconstituted. This chronology was confirmed by the analysis performed by the third expert. However, in the context of its analysis, the third expert confirmed the great difficulty in treating the theme of the domino effects between units on this type of petrol installation. This observation is of concern as regards the revision of danger studies.

Lastly, it is important to remember that this accident could have had serious consequences in terms of human life if one or more operators had been located at the site where the leak occurred.

## 12 - Explosion for maintenance operation in petrochemical plant, after a propylene leak Port of Antwerp (Belgium). October, the 6<sup>th</sup>, 2000

### THE INSTALLATIONS IN QUESTION

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#### The site :

The plant where the accident happened is situated in the port of Antwerp, Belgium. It concerns a plant for the production of olefins. The plant is subject to the Seveso II Directive because of the presence of:

- toxic substances 23 206 t high threshold : 200 t
- liquefied extremely flammable gases (including LPG) and natural gas high threshold 200 t
  - 5 636 t of n-butane
  - 1 254 t of iso-butane
  - 306 t of 1,3 -butadiene
  - 10 550 t of propylene
  - 21 600 t of ethylene

The plant is a strongly integrated unit and consists of:

- 📍 5 process units
  - 🏭 Two Ethylene unit (1 and 2 ) each composed with a naphta cracker and a cracked petrol hydrogenation unit
  - 🏭 Aromatics unit
  - 🏭 C<sub>4</sub> hydrogenation unit
  - 🏭 Cyclohexane unit
- 📍 Storage depots
- 📍 Loading and unloading facilities
- 📍 Pipelines,
- 📍 General services.

### The installation :

The accident happened in the naphtha cracker 2 unit. In this unit, naphtha, LPG and recycled ethane are heated in 11 furnaces and converted to a number of products through a change of structure. After the cooling, the cracked product is conveyed through the first separation tower where the first precipitation takes place. The light gases go overtop; they are compressed and subsequently conveyed to various reactors and distillation columns. The cracked petrol is precipitated as a liquid in the middle. At the bottom we find the fuel oil. The main product of the naphtha cracker 2-unit is ethylene, the by-products are propylene, a C<sub>4</sub> mixture, cracked petrol and fuel oil.

The propylene leaves the plant as a liquid through a pipeline under pressures of 55 and 60 bar. It is also transported by ship, train and truck.

## **THE ACCIDENT, ITS BEHAVIOUR AND CONSEQUENCES**

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### The accident :

On 6 October 2000 at 00:27, an employee of the plant tried to replace a manometer on the outlet side of the pump that pumps propylene out of a holder into the depropanizer tower and into a separation tower. The pump is located at the edge of the production unit and is adjacent to an open space. The working pressure of this pump is 20 bar. The employee tried to unscrew the manometer by means of a pipe wrench. During this manoeuvre the pipe nipple broke off on the screw thread at the first shut-off valve. The shut-off valve on the press of the pump was closed. The shut-off valve which makes that there is no pressure in the manometer set-up was opened.



Propylene was released in the direction of the employee and away from the production unit. A cloud of gas was formed in the open space next to the production unit, which got ignited very fast. The ignition was accompanied by a muffled bang followed by a fireball with a diameter of about twenty metres.

After that, the fire was reduced to a jetfire, which went on for a couple of minutes until the propylene leak was stopped. Calculations have shown that the estimated flow-rate of propylene was 16 tons/hour. The actual amount of released propylene is estimated at 1 ton.

### The consequences :

The consequences for the employee were very serious. The victim's clothes caught fire and he suffered third-degree burns especially in the face and on arms and legs. The victim was wearing the required safety outfit (among other things, clothes in Kermell viscose).

The consequences for the installation were rather limited. Near the pump there was fire damage to the installations (pump destroyed, lighting melted). A pipe-rack at the opposite side of the open space was damaged by the jetfire.

## THE ORIGIN, THE CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

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The reconstruction of the accident and the intervention were executed by the plant on the basis of found evidence and the various statements that were made. The research team, consisting of 6 persons, interrogated 24 persons in total. In order to determine the cause, they made an appeal to a team of external experts. The findings of the research team are indicated below.

### 🔗 Manipulation of the manometer set-up

🔗 No written instruction was given to replace the manometer. The plant regards this kind of manipulation as a standard activity that can be carried out by employees themselves. The decision to replace the manometer is taken by the person who checks it. Replacing a manometer is part of the 'wider functions' training, which was followed by the victim 2 years ago.

🔗 After inspection of the part that broke off and based on the victim's statement, it was concluded that the victim followed the correct procedure for replacing the manometer.

### 🔗 Fracture of the manometer set-up

🔗 The set-up concerned is a 1/2" connection to a 4" pipe. The specification indicates that for such a set-up a "schedule 80" pipe must be used. This implies a **wall thickness** of 3.734 mm.

🔗 It appears from the wall thickness (2.5 to 2.7 mm) measured that a pipe with specification "schedule 40" was used; the specification indicates a wall thickness of 2.769 mm for this.



🔗 According to the specification, the coupling between the valve and the pipe must be a welded joint (type "Socket Weld"). On the concerned part the connection was made by means of a screw thread.


🔗 Calculations have shown that the built set-up has a moment of fracture which is five times smaller than a set-up that would be built in accordance with the specifications and that a fracture in a manipulation under these circumstances is not unusual. Therefore, the direct cause of the accident is the realisation of a non-conformal set-up.


🔗 The installation was built in 1972. No deficiencies were found in the design dossier, so the defect has arisen during the stage of construction or repair.


🔗 The investigation could not establish when the defects mentioned first occurred.


🔗 The following system causes were identified:


🔗 Deficiencies in the QA/QC system for constructional works (verification of the wall thickness is not provided)

 The absence of a QA/QC system for repair or modification works.

 Ignition of the gas cloud

 No ignition sources were found in the immediate vicinity of the gas cloud. The estimated outlet flow-rate of propylene was 16 tons/hour. Considering the physical properties of propylene and the high exit velocity, it is assumed that the gas cloud has been ignited through a discharge of static electricity. The creation of static electricity is a normal phenomenon under these circumstances.


 Operation of the emergency plan


 The investigation has not shown any malfunctions in the operation of the emergency plan.


## ACTIONS TAKEN


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### The intervention :

 Another employee noticed the ignition of the gas cloud and immediately sounded the fire alarm. After that, some colleagues brought the victim to the nearest emergency shower. Afterwards, the victim was brought to a burns unit in Antwerp by the emergency services.


 A water screen was set up at once to protect the cableway and the pipe-rack on the opposite side of the open space from the fire.


 At 00:29 (2 minutes after the ignition) the members of the intervention team of the shift started to release the pressure from the pump by closing the valves on the suction and outlet sides of the pump.


 At 00:31 (4 minutes after the ignition) the fire brigade arrived. Some seats of fire above the pump were put out by means of dry chemical fire extinguishers.


 At 00:50 the fire alarm was called off.

### The inspection :

 At 3:30 a fax was sent to the Environment Inspection Section of the Ministry of the Flemish Community to inform them about the accident that had happened at the plant.

 After the inspection by the Environment Inspection Section, the plant received the following letters of formal notice:

 To carry out an investigation into the accident by 22 November 2000; this investigation has to describe at least: the circumstances of the accident; the dangerous substances involved (nature and quantity); the data available on the basis of which the effects of the accident on man and environment could be assessed; the emergency measures taken; the chronology of the accident; the combined direct and underlying causes; the circumstances that have influenced the (possible) consequences; the direct consequences; the safety measures taken (technically and organisationally) and the possible failure thereof; the people present and their function; the instructions given and the work permits; the person in charge of supervising the executed works; the explanation and evaluation with regard to the operation of the emergency plan; the indication of the means used to control the fire.

 To identify and make an inventory of places in the plant where a similar release could take place.



- ✚ To examine what different kinds of scenarios could lead to a similar release.
- ✚ To examine what different kinds of scenarios could develop with effects beyond the boundaries of the establishment in case of a similar release
- ✚ To examine what preventive and mitigating measures should be taken for these scenarios and to draw up a planning for the execution of these measures.

### Corrective actions :

🔗 The plant has (temporarily) prohibited all employees from executing manipulations on similar installations under pressure.

🔗 An extensive control and repair programme was started for smaller branches that are frequently used and are risky. The other small branches will be included in a periodical inspection programme. Set-ups that do not meet the required criteria (according to the new construction specification for small branches, see below), will be provided with a red identification tag, which means that they may not be manipulated when the installation is working.



🔗 The implementation of the control and repair programme has shown that different construction specifications are used for small branches. A new construction specification for small branches is being developed. This specification is based on international practices.

🔗 The verification of the wall thickness will be included in the QA/QC system for constructional works.

🔗 A QA/QC system is being developed for repair or modification works.

## **LESSONS LEARNED**

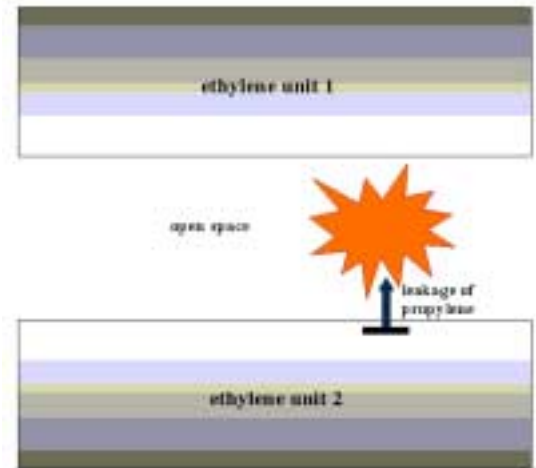
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🔗 An efficient quality system for constructional works as well as repair or modification works is essential in order to avoid similar accidents; verification of the wall thickness in case of constructions/repairs/modifications is indispensable.

🔗 Small branches should have sufficient wall thickness and welded joints should get preference to screwed joints.

🔗 The plant's internal emergency plan has functioned properly and has contributed to the fact that the effects and consequences of the accident stayed within the boundaries of the establishment.

🔗 The manometer set-up was rather coincidental. As a result, the gas cloud was formed in the open space next to the production installation after the pipe nipple had broken off. The question what would have been the effects for and impact on man and environment if the leak had started in the other direction and if the gas cloud had been ignited in the production unit remains unanswered for the time being. Currently, the plant is looking into this at the request of the Environment Inspection Section.



## **13 - Explosion of an unconfined cloud of vapour coming from a tank storing drain water mixed with hydrocarbons (Italy). 1999**




### **THE INSTALLATIONS IN QUESTION**

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#### **The site :**

The accident took place in an Italian hydrocarbon tank farm, in 1999. The plant is under the condition of Safety Report presentation, due to the Italian decree implementing the "Seveso II" European directive.

The storage activities concern the reception, storage and distribution of liquid petroleum products and LPG by pipelines and tankcars. The storage capacities are shown as follows :

 Essence :	200 000 t
 Gazole :	360 000 t
 GPL :	4 300 t

#### **The installation :**

The accident took place in the plant unit consisting in the temporary storage of drain water from gasoline and gas-oil tanks (water with some hydrocarbons).

The drain water from the storage tanks is directly sent to a sump tank by gravity and from here pumped to the drain water tank. Before joining the process water and being fed to water treatment plant, the drain water is sent to an air stripper, in order to remove the MTBE. The water treatment plant is intended to remove the oil content and to enable the water to be discharged in the sewage system. Before feeding the water treatment plant, the oily waters are sent to a settler and a water storage tank.

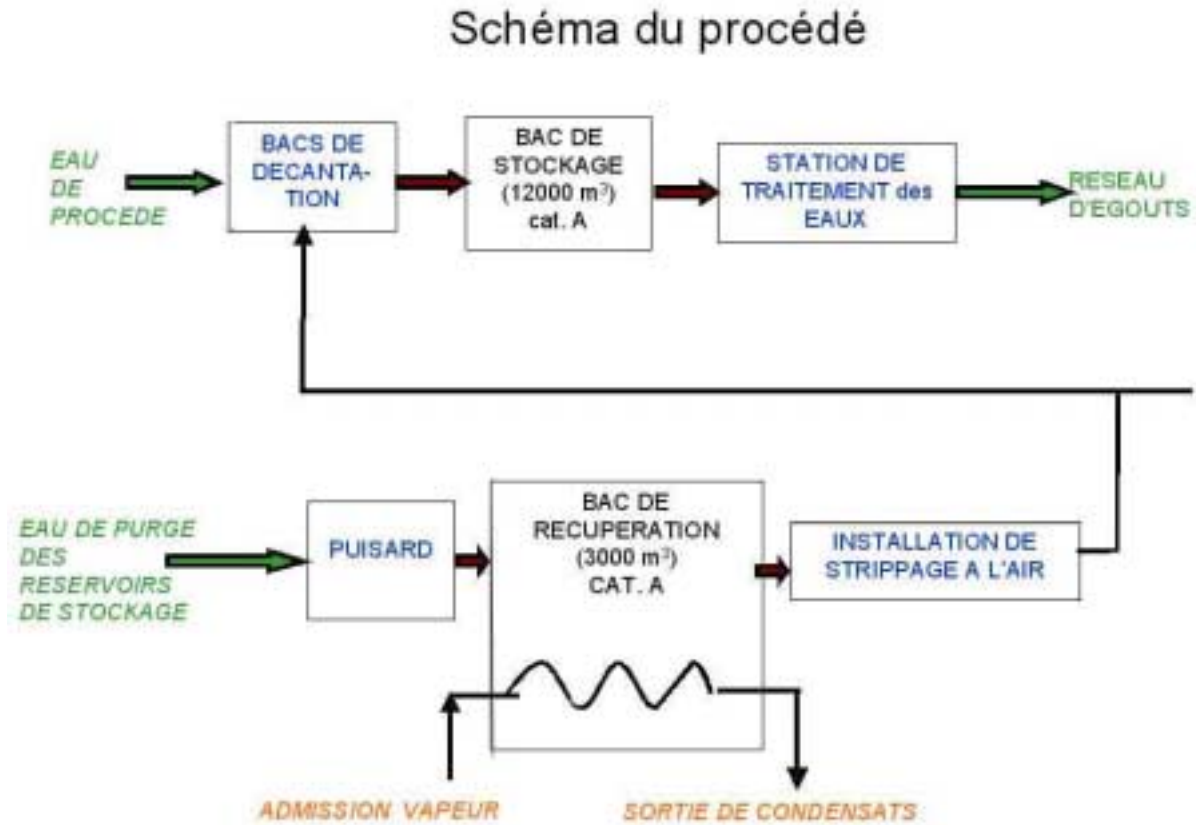
The following equipments were in operation in the storage plant when the accident took place. The following figure describes the process and the different equipments: unleaded gasoline tank, sump tank ; drain water tank ; air stripping treatment plant; settling tank; water treatment feed tank ; waste water treatment plant; sewage system.

The draining operation is performed manually by an operator. For this purpose, the following valves are open, in sequence:

- on the sump tank inlet pipe
- on the pump discharge
- on the pump suction
- on the outlet from the water pot at gasoline tank bottom.

The operation is stopped by closing this last valve when the operator can realize that gasoline is flowing to the sump tank, instead of water.

A high level signal on the sump tank starts automatically the relevant draw off pump, in order to let the water to be forwarded to the drain water tank.



The drain water tank is floating roof type, with the following geometrical characteristics: its maximum capacity is 3 000 m<sup>3</sup>, its diameter is 16 m, it is 14,5 m-high, its maximum roof height is 12 m. The tank is not diked, being the surrounding area just soil and gravel, without any impermeabilization. The tank is equipped with an internal steam heating coil, positioned at the bottom, in order to provide the proper winterising and to optimise the following air stripping operation.

A TV monitoring system is provided in order to watch over the actual height of the floating roof, with indication reported in the control room. Two high level alarms are provided, set at 11 and 12 m (operational conditions) and two block systems are provided, set at 13 m, with automatic stop of the feeding pump.

Furthermore, the tank is provided with all the fire fighting equipment normally provided for this type of tanks.

## THE ACCIDENT, ITS BEHAVIOUR AND CONSEQUENCES

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### The accident

At the moment of the accident, the liquid level in the water drain tank was 3.4 m high, corresponding to about 680 m<sup>3</sup> of hold-up. The amount of hydrocarbons contained was about 20 m<sup>3</sup>, since it was estimated a depth of the upper layer about 10 cm. The drainage of the unleaded gasoline tank has been just started, by sending the drain water to the sump tank.

The waste water treatment plant was not running continuously, as in normal operation.



About 20 m<sup>3</sup> of hydrocarbons were released by the safety vent of the drain water tank on the floating roof and, from here, flowed through the roof draining pipe to the ground. A pool of hydrocarbons was formed near the tank. A vapour cloud was formed by the hydrocarbons evaporating from the pools on the tank roof and on the ground, reaching the neighbouring road, located about 60 m away.

The meteorological conditions were characterized by clear sky and absence of wind.

A UVCE occurred, due to the ignition of the cloud, probably caused by two lorries passing along the road.

The UVCE was followed by two other explosions, taking place after few seconds. The flashback flame ignited the hydrocarbon pools, with the engulfment of the drain water tank and the following involvement of the nearby settler.

### The consequences :

Fortunately, the damages to people have been quite limited: only the drivers of the two lorries have been affected because of light burns and recovered in 7 and 15 days.

The material consequences have been more significant, due to severe damages to the drain water tank and the settler, some minor damage to a nearby building and damages to the two lorries and another vehicle at the works.

The economical consequences are quantifiable in 500,000 euros, due to direct material damages, and 350,000 euros, due to response, restoration and clean-up.



## THE ORIGINE, THE CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

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The tank was equipped with an internal steam heating coil, positioned at the bottom of the tank, in order to keep the temperature at 20-30°C for winterizing and for a slight preheating, to improve the following air stripping.

Live steam entered in the tank, due to a failure of the coil, probably caused by corrosion. The inner temperature of the tank raised up to 60°C at least, causing the quick evaporation of light end of hydrocarbons to start. The internal overpressure caused the opening of the safety vent on the floating roof with an outflow of the upper hydrocarbon layer.

Furthermore, the effects of the explosion and the duration of the fire make reasonable to suppose that the quantity of hydrocarbons contained in the tank was much more than the design one. This circumstance is much more probable, as the end of the drainage was decided by the operator only on subjective basis, without any instrumental aid.




The tank was not provided by indication of the inner temperature and of the upper layer depth.

## ACTIONS TAKEN

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The internal emergency plan has been immediately started. An emergency shut-down of the plant has been carried out and the fixed firewater cooling systems activated. The fire fighting has been carried out in the initial phase by the internal emergency team. In the meanwhile, the alarm has been given to fire brigades, first aid and police.

In 15 minutes the external intervention was carried out by:

-  Fire brigades starting to fight the fire (extinguished after one hour and a half)
-  Police controlling the local traffic, blocking the nearby road and coordinating the precautional evacuation of houses and workshops nearby the place of the accident
-  Ambulances arrived for first aid and transfer of injured people to the hospital.

## LESSONS LEARNED


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The most part of the lessons to be learned are leading rather to managerial features, than to physical and more direct causes. The identification of the first ones is often much more difficult, but in any case much more effective: a possibility is given to have an effect on the real root causes of the events, not just to act on the contingent facts.

For this reason and consistently with the principles stated in “Seveso II”, a specific approach has been developed and applied in Italy to perform the analysis of accidents with the main scope to point out the faults in the Safety Management System (SMS), directly connected to the accident itself or anyhow shown by the events and circumstances related to the accident.

Reference is made to the check list of the SMS elements considered, consistent with the main articulation given for the SMS by the “Seveso II” directive.

An analysis of the actual accident pointed out the faults in SMS :

-  A risk analysis could put on evidence the possibility of a presence of an excessive quantity of hydrocarbons and of a severe overheating of the tank possibly due to live steam input.



- 👂 Lack of instrumentation to indicate anomalies and/or dangerous situations.
- 👂 Maintenance procedures should have taken into account the periodic inspection and the eventual repair or substitution of the coil.
- 👂 The realization of technical-plant modifications should have taken into account:
  - Spotting of dangers and the evaluation of relevant accident risks;
  - Verify the compliance with safety requirements and criteria.
  - Final validation of design modifications.
- 👂 Safety audit aimed to evaluation of conformity to regulations of SMS and of its efficacy should have put on evidence the above mentioned management faults.



# 14 - Explosion of an alcohol-tank in a sugar factory/distillery

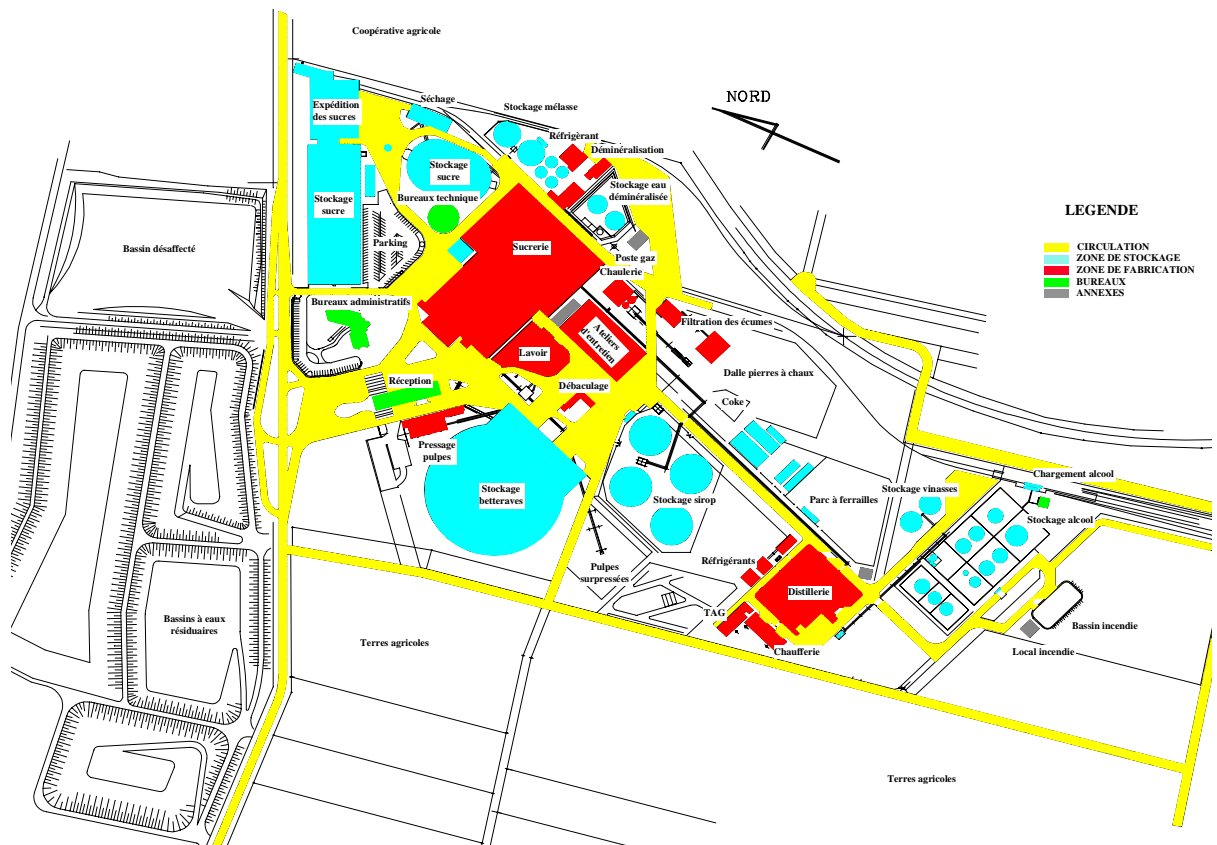
## Villette-sur-Aube (10).

### July, the 24<sup>th</sup>, 2000

#### THE INSTALLATIONS IN QUESTION

The factory / distillery is located in Villette sur Aube (10), France and is classed SEVESO. The sugar factory operates, amongst other things, a workshop that produces alcohol by distillation and an alcohol rectification workshop that has a capacity of 1,600 hl per day.

Since 1984, it has had a category 1 inflammable liquid storage capacity of 24,000 m<sup>3</sup>, consisting of 10 tanks of volumes ranging from 1,000 m<sup>3</sup> to 5,000 m<sup>3</sup>. It is therefore an upper threshold SEVESO storage facility.



## THE ACCIDENT, ITS BEHAVIOUR AND CONSEQUENCES

### The accident

On July 24th, as the weather was stormy, the company had stopped loading the trucks and an operator had closed the valve at the base of the tank at around 4.35 p.m.

Ten minutes later, the roof of one of the alcohol storage tanks, tank no. 211, was struck by lightning. The tank, which has a capacity of 5,000 m<sup>3</sup>, contained 1,000 m<sup>3</sup> of 96% absolute ethanol.

The lightning provoked an explosion, the roof blew off and fell into the tank, and a fire broke out. The tank shell remained intact and the fire was confined to the inside of the tank, but the valve at the base of the tank cracked as a result of the impact.

*Photo DRIRE Champagne-Ardenne*



Various tanks were sprayed down until 11 p.m., at which time the fire brigade were called off. The on-site storage of 23,000 litres of foam concentrates was sufficient to extinguish the fire. The extinguishing water was retained in the retention pits.

*Photo DRIRE Champagne-Ardenne*



Foam concentrates were poured on, thus preventing the tank from catching fire. The tanks located nearby were sprayed down, in order to cool them down. The fire was considered to be extinguished around 7.45 p.m.



*Photo DRIRE Champagne-Ardenne*

### The consequences :

The damage caused as a result of the accident is estimated to be more than 15 million French francs.

No one was injured.



*Photo DRIRE Champagne-Ardenne*

## **THE ORIGINE, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT**

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The accident was caused by lightning that struck the tank, but the exact causes and circumstances have yet to be evaluated by experts.

It should be noted that the tank was not fitted with flame arrestors on the vents.

In addition, as the tank was 4/5 empty, and given the outside temperature, the gaseous atmosphere must have been considerable.

## **ACTIONS TAKEN**

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The fire protection water tank was filled up during the course of the evening, by pumping water from the Aube river which is located approximately 500m from the site. New foam concentrates were ordered.

As the installation was classified as at-risk, the factory / distillery was covered by the provisions of the ministerial order dated January 28th, 1993 concerning lightning protection for certain installations that are classified for the protection of the environment (an obligation that is also provided for in article 1.8 of the prefectorial order pertaining to the site).

Article 2 of the ministerial order specifies that the lightning protection devices must be in conformity with French standard C 17-100, and in article 6 it provides for a 6-year time limit for existing installations to comply with these conformity regulations.

Memorandum No. 93-17 dated January 28th, 1993 provides for a preliminary study concerning lightning protection to be supplied by the manufacturer.

The study for this installation was carried out on December 9th, 1998. The recommendations included the installation of fire resistors on the vents and breather valves for the various alcohol storage tanks. These fire resistor devices had not been installed. The inspectorate of classified installations recorded the facts. In addition, an order was issued on 10th August giving the operator notice to install these devices within one month.

In order to take into account all possible effects of the fire on the totality of the storage facilities, an emergency order was issued on 10th August, requiring:

- 🚒 checking of the soundness of the tanks (as the 3 tanks of 2,500 m<sup>3</sup> capacity that were next to the damaged tank had been subjected to a high amount of thermal radiation, it was therefore necessary to check that the soundness of the tanks, (hermetic seal, strength) had not been affected)



Photo DRIRE Champagne-Ardenne

- 🚒 checking of the electrical installations for the entire storage facilities, by a qualified agency before the restart of any activity.

The quality of the water table was monitored daily over a period of 7 days, then weekly for a period of 3 weeks. There was no evidence of any impact on the water table.

The extinguishing waters, of around 1,500 m<sup>3</sup>, were transferred into one of the company's leakproof retaining pools.

## LESSONS LEARNED

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The operator had previously, during the month of May, carried out a POI ("Plan d'Organisation Interne", internal contingency plan drill), in which the scenario was that of a fire on one of the alcohol tanks. The fire and emergency services therefore knew the site well, and the means of intervention were able to be put rapidly and calmly into operation.

The administration made no particular comment on the way in which the operations were carried out.

Direct protection devices designed to attract the lightning (lightning rods) had been installed, but the channelling of the currents of atmospheric discharge (equipotential connections between the different tanks and the grounding terminals) at pre-determined points, in such a way as to spare the protected zones from the lightning, was perhaps insufficient.

The absence of fire resistor devices was another factor which contributed to the causing of the explosion.

In addition, according to witnesses' accounts, it would appear that lightning first struck near an overhead electrical power supply pylon a few moments previously. The energy which was brought to the earth certainly resulted in a modification of the ground in the area nearby.

A detailed analysis of this information is needed, in order for the phenomenon to be better understood, and for the appropriate lessons to be learned.

Lastly, it should be noted that 23,000 litres of foam concentrates and 7,000 m<sup>3</sup> of water were used during this accident.





*Photo DRIRE Champagne-Ardenne*



## 15 - The appearance of legionella in the cooling system of a sugar refinery.

Sillery (51)

November, the 30<sup>th</sup> , 2000

### THE INSTALLATIONS IN QUESTION

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The closest housing, which is occupied by the personnel, is located 150 m from the cooling towers, while the nearest off-site housing is located approximately 400 m away.

The sugar refinery is subject to authorisation, while the refrigeration facilities are subject only to declaration.



As regards the regulations, the memorandum of 23 April, 1999 requested that specific provisions concerning prevention of the risk of legionella be required by a supplementary order of the prefect for establishments subject to authorisation that come under the heading of installations classed 2920 (compression-refrigeration installations), and cooling towers in particular, that are located in heavily populated areas or close to sensitive establishments (hospitals, day care facilities, etc.). As the Sillery site does not fall within this configuration, no specific provisions had been made by supplementary order of the prefect.

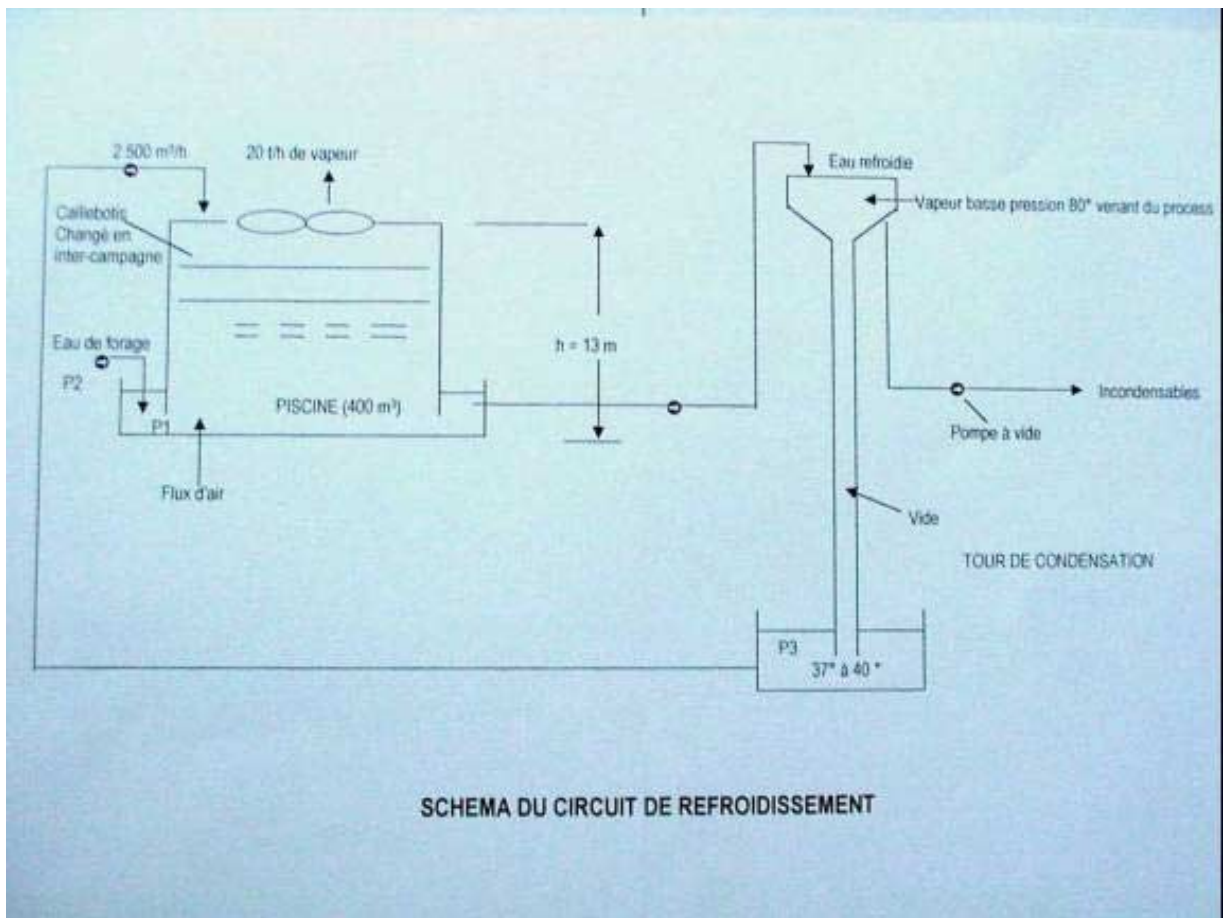
## THE ACCIDENT, ITS BEHAVIOUR AND CONSEQUENCES

### The accident

Within the framework of an internal procedure of the group, the operator of the Sillery site ordered that a legionella analysis be conducted in the cooling system (performed by the CHROMOSOME regional hospital complex in Reims). On October 26<sup>th</sup>, 2000, samples taken on October 19<sup>th</sup>, 2000 revealed that there was no legionella present in the system. On November 24<sup>th</sup>, 2000, analysis of further samples taken on November 16<sup>th</sup>, 2000 revealed the presence of bacteria of more than 10<sup>6</sup> CFU/1 (colony-forming units per litre).

The DDASS (the French department of health and social services) learned of the incident through the press, who had been informed by someone who worked on the site. The DDASS notified the DRIRE (the French regional inspectorate for industry, research and the environment), and a meeting was held on-site that evening, in the presence of labour inspectors, the occupational health physician, the DDASS, secretaries of the establishment-level works council and the CHSCT (the committee for hygiene, safety and work conditions), the site managers and the DRIRE.

As soon as the results of the analysis became known, the manufacturer decided to initiate treatment of the cooling system as soon as possible. These operations began on November 29<sup>th</sup>, 2000 at 6 p.m. The treatment consisted of cleaning the system with a dispersing agent and a biocide for 48 hours, at a rate of 1-3 "shock" treatments per day (at a concentration of 100 ppm), a complete purge of the system and constant disinfection with a biocide over a period of 18 hours (at a concentration of 400 ppm). It should be noted that the water in this system is not used by the personnel.



The area around the cooling towers was marked out during the day, including the building in which the vacuum and circulating pumps were located. An internal memo from the management prohibited access to this area, as of December 1<sup>st</sup>, for all persons not wearing a respirator designed to protect against biological risks. If it became necessary to intervene on the cooling system network, such operations were only to be carried out by trained personnel wearing personal respiratory protective devices: the head of the establishment issued specific instructions to that effect on the same day.

As of December 1<sup>st</sup>, 2000, the industrial medical officer informed the personnel of the risks involved, the actions that should be taken if they suffered a health problem, and the tests and treatment necessary. He also personally interviewed an individual suffering from asthma. The labour inspectorate informed the refinery manager and the CHSCT of the specific instructions to be applied as regards the entire body of on-site personnel (during the sugar harvest period, 140 seasonal employees work on the site) and as regards agents using respiratory protective devices. Analyses on the points of circuit P1 (in the pool at the foot of the cooling towers), P2 (on the makeup underground water inlet) and P3 (in the tank at the foot of the condensation tower) after decontamination (Saturday, December 2<sup>nd</sup>, 2000) were requested by the DDASS and DRIRE departments. The tests revealed that treatment had been effective.

## **THE ORIGIN, THE CAUSES AND CIRCUMSTANCES OF THE ACCIDENT**

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The legionella bacteria is found in weak concentrations in its natural state, in lakes and rivers. The ideal temperature for it to develop is between 25°C and 42°C. Legionella is caused by inhaling water contaminated by the bacteria which is diffused in a spray (steam, showers, air-conditioning, hot water systems, etc.). Contamination takes place via the respiratory routes. Factors which favour contamination are warm water at a temperature greater than 20°C, the surface conditions of the systems (scale, corrosion, algae, etc.) which allow a biofilm (an organic slime) to form, the presence of deposits, abandoned legs in the piping, the presence of amoebae whose cysts can carry the bacteria. It is an accepted fact that below 10<sup>5</sup> CFU/l, the bacteria can cause disease in man.

The temperature of the water in the cooling towers was between 37°C and 40°C. The cooling towers therefore formed an ideal environment in which the bacteria could develop.

## **ACTIONS TAKEN**

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As regards the regulations governing classified installations, applicable as of the beginning of the 2001 sugar harvest and subsequent harvests, a proposal for the systematic implementation of the provisions concerning the prevention of legionella, as provided for in the memo cited above, was presented to the departmental hygiene board of January 2001. A supplementary order of the prefect, taken in the framework of article 18 of decree 77-1133 of September 21<sup>st</sup>, 1977 retranscribed these provisions. It should be noted that they have been modified, at the request of the DDASS, the frequency of the analyses during the period in which the cooling towers are in operation becoming monthly, and not only at the time of cooling system restart. On a regional level, the inspectors responsible for supervising sugar refineries and distilleries have been requested to do likewise.

## **LESSONS LEARNED**

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The personnel's lack of information concerning the risks involving legionella led to extreme anxiety amongst the employees. It became necessary to provide all personnel with clear information on the subject, and any individual requesting a personal meeting with the industrial officer was granted one.

As the temperature of the water in the cooling towers corresponds to the optimal temperature at which the bacterium develops, it is necessary to monitor the cooling tower systems and to perform regular analyses. The personnel are advised to wear a respiratory mask when approaching high-risk zones.

## 16 - Management of a legionella epidemic in a densely populated urban area

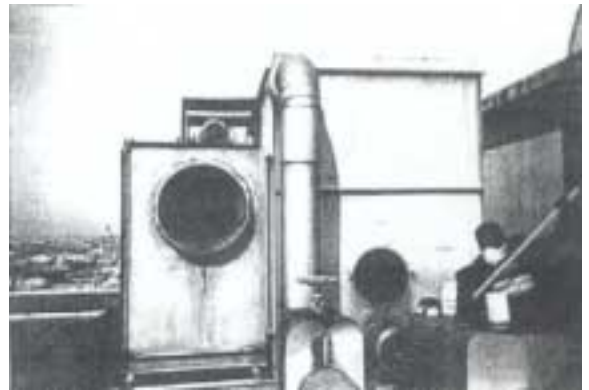
Paris XV (75)

August, the 8<sup>th</sup>, 1999

### THE INSTALLATIONS IN QUESTION

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The installations in question are cooling towers connected to cooling systems and covered by the legislation governing classified installations.



#### History of the issue

Legionella is disease requiring compulsory notification. The DGS (Directions Générales Sectorielles) industry sector branches memorandum No. 97/311 dated April 24<sup>th</sup>, 1997 concerning monitoring and prevention of legionella specifies that where there are 2 or more cases of legionella, the health authority must conduct an epidemiological study with the aim of identifying a common source of infection (domestic hot water, cooling towers, etc.), in order that suitable preventive measures can be taken. An environmental study is then conducted on the basis of the information supplied by the patients. Water samples are taken from "suspect" installations, in order to determine their concentration of legionella and if a strain from patients is available, the environmental and clinical strains must be compared.

A first epidemic of legionella that occurred in Paris in 1998, during the Football World Cup (19 cases, in 4 of which the patients died), called into question a classified cooling installation. The consequence of this epidemic was a rising of the collective consciousness of the risk of legionella (a risk that was judged to be unacceptable by the chief of police) and it highlighted the necessity for the prevention of legionella to be taken into account in the regulations covering classified installations. This concerns, in particular, installations that have spray-type cooling towers and risks of emission into the environment of aerosols contaminated by legionella. Moreover, taking into account the health risk posed by installations now forms part of the priorities defined by the Ministère de l'Aménagement du Territoire et de l'Environnement (MATE) (the French Ministry of the Regional Planning and the Environment).

In order to take rapid action, the Service Technique Interdépartemental d'Inspection des Installations Classées (STIIC), the interdepartmental technical department of the Classified Installations Inspectorate initially proposed completing the standard order and the authorisation orders with the following provisions :

*"Disinfection of the water used in the cooling towers must be instigated, in order to prevent the development of bacteria that could affect human health. The efficiency of this disinfecting must be checked regularly, and the analyses must be sent to the inspector of classified installations"*

A work group from the DASS 75 (the local French department of health and social services) was set up in order to draw up complementary regulations. The most difficult problem was that of determining an action threshold (concentration of legionella). The thresholds were established empirically:

- 📍 below  $10^3$  CFU/l: maintenance and follow-up
- 📍 between  $10^3$  and  $10^5$  CFU/l: alert level → implementation of the measures required in order to bring down the concentration to below  $10^3$  CFU/l
- 📍 above  $10^5$  CFU/l: action level → shutdown of operation of the cooling system, informing of the classified installations inspectorate and the DDASS, emptying, cleaning and disinfecting before restart of activity.

The standard order, drawn up by the STIIC, was signed by the chief of police on April 27<sup>th</sup>, 1999. Information concerning the order and a questionnaire designed to identify "at risk" towers were sent by the STIIC to all operators declared under the heading 2920 that applies to cooling installations. This procedure was designed to make it possible to compile a list that can be used in crisis management and to allow a trend chart for each *département* to be established. There was only partial feed back on the questionnaires, and it had to be followed up by a telephone reminder.

## THE ACCIDENT, ITS BEHAVIOUR AND CONSEQUENCES

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### The accident

The first symptoms of legionella were identified on August 8<sup>th</sup>, 1999. The appearance of group cases was detected on September 1<sup>st</sup>, 1999 (the DASS 75 informed the STIIC by telephone on the same day). In total, 8 cases of legionella were recorded, one of which included a foreign tourist who had stayed in a hotel. The patients had all been in or around the 15<sup>th</sup> district in Paris, one of them will die. Pressure from the media was immediately brought to bear.

The results of the epidemiological study that was conducted as of 1<sup>st</sup> September, apart from domestic hot water, prompted the search to be directed towards an environmental source of contamination (common geographical area and simultaneous appearance of the first symptoms). Once again, the cooling towers came under suspicion.

The environmental enquiry was conducted by STIIC in parallel with the epidemiological enquiry. It was decided that an enquiry perimeter would be set up within a radius of 500m on both sides of the areas in which the patients had been. The place that they all had in common was the 15<sup>th</sup> district, and the enquiry was therefore confined to this district alone. Within the perimeter that was established, 20 establishments were listed (9 authorisations/11 declarations).

The information that was collected on the basis of the list compiled from the results of the questionnaire allowed the identification of 6 "at risk" sites. The person who died was working on a flat roof close to the cooling towers of one of these sites (the towers were operating, which *a posteriori* justified the mandatory wearing of a mask, as per the order concerning legionella). Naturally, this was the first site to be visited.

The first series of analyses began on September 8<sup>th</sup>, 1999 (7 days after the group cases were identified, and 1 month after the appearance of the first symptoms). Samples were then taken on September 10<sup>th</sup> and 13<sup>th</sup>, 1999. Of the 6 sites, 20 cooling towers were listed as being on flat roofs. Nine



samples (each of which corresponded to an independent circuit, according to the information provided by the on-site operators) were carried out, with a view to testing for the presence of legionella.

It was noted that 4 out of 6 sites had at least one tower contaminated by Legionella. One of the contaminated sites had a strain that matched that of the patients. There were 8 towers on that site. In two of these towers, the concentration of legionella was between  $10^3$  CFU/l and  $10^5$  CFU/l.

In light of information later supplied by the operator, the two offending towers were supplied with make-up water from 2 common water tanks of 100 m<sup>3</sup> that were located in the basement with the cooling systems and the water treatment plant. These tanks were also used to maintain the supply of water to the fire alarm circuit and all the buildings. In this case, a high-rise building that was constructed at the beginning of the 70s, and the water supply system is the original one. Both towers are located on the same premises, but they belong to different owners, which accounts for their different maintenance and use.

## **THE ORIGINE, THE CAUSES AND CIRCUMSTANCES OF THE ACCIDENT**

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The site that matched the patient strains has existed for 30 years. For this reason, the circuits of the cooling towers are no longer well-known. In addition, access to the towers for maintenance purposes is difficult, which has led to a build up of considerable scale. Moreover, the site is complex (there are several owners and 8 towers that correspond to 4 different circuits).

Biocide treatments were carried out on May 21<sup>st</sup> and July 20<sup>th</sup>. In July, the operator had called in a society that specialises in the provision for legionella risks. At the end of July, however, a malfunctioning of the deconcentration system occurred, which probably led to the concentration of bacteria.

All of these facts taken together would explain the proliferation of legionella.

It should be noted that only 6 of the 20 sites at risk were visited, and the analyses were performed after the actual epidemic took place.

## **ACTIONS TAKEN**

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### [Action taken by the Paris Chief of Police as regards the owners of the cooling towers:](#)

*Note: In Paris, the regulations concerning ICPE (installations classified for protection of the environment) legislation are issued by the Chief of Police, and those concerning the Public Health code are issued by the Paris Prefect.*

On the basis of a legal analysis performed for the DASS in 1998, following the first legionella epidemic, an order was issued on September 15<sup>th</sup>, 1999 by the Paris Prefect, based on article L 17 of the Public Health Code. It required the owners of "at risk" towers located within the perimeter to proceed with emptying, cleaning and disinfecting of the water circuits without delay. Specific provisions were laid down for the installations that could not be shutdown (with documentary evidence). The owners had a time limit of 15 days within which they had to report to the DASS75 on the action taken. The DASS 75 was instructed to supervise the applying of the order. In parallel, a press release was published by the DGS on September 20<sup>th</sup>, 1999.

The operator of the 2 towers that were suspected of being the cause of the environmental contamination received the order of the Paris Prefect on September 24<sup>th</sup>, 1999. The towers were subjected to cleaning and disinfecting procedures as of October 1<sup>st</sup>, 1999. A preventive treatment was initiated (using a quaternary ammonium-type biocide), as well as monitoring of water consumption and physical-chemical parameters.

No sanction was imposed on the operator, as he had called in a water treatment firm at the beginning of July in order to safeguard against the risk of legionella, and had shown complete co-operation during the enquiry.

A total of 23 sites were affected by the order. An evaluation of the application of the order was made on 24<sup>th</sup> November, 1999 by the DASS 75: 7 owners had not replied, 3 sites turned out to be located the area concerned (errors in the addresses), 4 notifications were returned (marked "Not known at this address"), 2 owners replied that the towers were not "at risk" (dry system) and 7 sites were subject to disinfecting procedures. It should be noted that the order of the Paris Prefect was not founded on the regulations covering classified installations.

#### Post-crisis management:

The STIIC decided to launch a systematic campaign for all the classified installations inside the perimeter of the epidemic, taking local interests into account (densely populated urban area). The aim of the campaign was to check the technical specifications for the classified installations that are subject to declaration (AT 2920 modified and submitted), and to carry out visits, with the aim of drawing up complementary orders for classified installations subject to authorisation. In all cases, the aim was to raise the operator's awareness of the "legionella" risk.

The campaign took place from 5<sup>th</sup> to 22<sup>nd</sup> October, 1999: 16 sites in the 15<sup>th</sup> district were subjected to at least one visit (the list was completed during the campaign). The 4 sites in the 15<sup>th</sup> district that had been identified as being contaminated during the epidemic were subjected to reinforced monitoring (knowledge of the networks, the water treatment procedures in the cooling circuits, analytical follow-up available, etc.).






The site on which the towers suspected of being the cause of the environmental contamination were located was subjected to several follow-up visits. Analyses of legionella were carried out monthly. A complementary prefectorial order was issued on October 19<sup>th</sup>, 2000. An audit of the installation was requested, taking into account the complexity of the site. Following the audit, the operator made numerous modifications (in particular, removal of abandoned channels that were the cause of the re-contamination of the installation). The preventive treatment, which was carried out in an empirical fashion, *in situ*, was validated using the analyses of the legionella. The considerable scale of the networks delayed the implementation of an efficient treatment for several months.


## LESSONS LEARNED

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Management of the crisis and post-crisis period brought to light the following points :

#### On a technical level:

-  The almost non-existent training and knowledge of the operators
-  Passive that requires management in the existing towers: circuit design, existing air intakes or passage zones, scale build-up of circuits, random water treatment procedures, access to difficult towers
-  An audit is necessary in some cases
-  The need for a detailed visit of "at risk" installations
-  Analysis of legionella: in cases where the concentration is greater than 10<sup>5</sup> CFU/l, it is essential that the operator be required to furnish an explanation and a new analysis must be carried out 3 weeks after the decontamination, in order to verify that there has been no recontamination of the circuit. In the case of unsatisfactory results, an audit must be requested and a new decontamination must be carried out.

 A maintenance book must be established: this ensures traceability as regards the actions carried out by the operator and any failure in the installations.

## 17 - Pollution following a leak of sulphuric acid

Le Thillot (88)

May, the 26<sup>th</sup>, 2000

### THE INSTALLATIONS IN QUESTION

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#### The site:

The commune of Le Thillot is located in the Moselle Valley, in the south of the "Vosges" department along the Epinal – Mulhouse highway route. In 1864, the company was founded at the same location as the current site, next to the Couard Brook, for the necessary water supply. The current company produces full-grain, rectified full-grain, nubuck and flesh split leather from French bull skins.

The breakdown of the company's markets is as follows in 65% shoes, 25% leathercraft and watchbands and 10% belts. With a workforce of 80 plus roughly an average of ten temporary staff, the company handles 2,630 tonnes of raw material per year and has a turnover of 80 MFF.

On May 26th, 2000, a sulphuric acid leak polluted the natural environment and a fish farming operation. It could have disturbed the operation of the communal treatment plant located 2 km further down the valley.

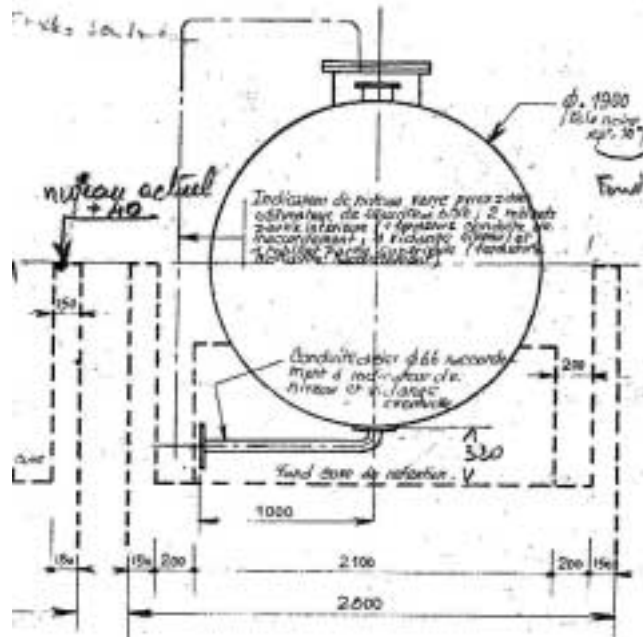
The treatment plant, created in the early 1980s by the multiple-trade union with the industrialist's participation, was designed to treat urban wastewater and effluent from the tannery by biological purification. The tanner's effluents undergo an initial treatment consisting of a lime slurry and ferrous sulphate (pH control and precipitation of the sulphides) prior to entering the domestic effluent in the aeration tank.

A supply channel of a micro-power station also supplying the pools of a fish farming operation was also tainted by the direct pollution of the Couard Brook. Ten brook trout spawners of the 30 present were killed by the pollution.

#### The plant:

**The sulphuric acid storage tank** was designed in 1967 by the tannery's engineering office. As early as the design phase, the general provisions of standard order 31 were not taken into consideration which requires that the lower drainage not be constantly under load and stipulates that an interior plug be able to block the drainage line.

The sizing of this tank took transport costs into account and originally limited the number of deliveries. At present, with 16,000 litres in stock and consumption of 37,000 litres in 1999, only 2 to 3 deliveries per year are required. This is not in line with economical logic which attempts to limit the amount of outstanding stock which is a source of carrying charges, on the one hand, and environmental protection logic which tends to reduce the quantities of dangerous materials stocked, on the other hand.



The storage facility is located near the tanning workshop where the acid is used for the pickling operation. As the tank is under pressure (2 bar), the acid is sent directly to the workshop via an overhead line.

The pickling operation prepares the skins for tanning on a kicker machine in the presence of sodium chloride and strong acids. The pH must be reduced from 12 to 8.

The associated concrete catchpit, as well as the general condition of the tank, was last inspected 1994. Although the auditing agency issued a favourable report regarding the storage tank's soundness, it recommended that the heavily corroded access gangway be replaced and the cracked and chipped retention pit be refurbished.

## THE ACCIDENT, ITS BEHAVIOUR AND CONSÉQUENCES

### The accident

The chronology of events is summarised below:

- 26.05.2000 5h00 :** Discovery of the leak by workers (suspicious odours)
- 6h15 :** As the maintenance worker could not control the leak, he informed the director and shut off the tank's excess pressure
- 7h15 :** The director arrived at the site
- 7h30 :** Alert by the treatment station operations supervisor of the arrival of highly acidic effluent, which proves that the catchpit drain valve was open.
- 7h30 :** Shutdown of the settling tank pump, drainage of the acid still contained in the tank into 1,000-litre containers and closure of the catchpit drainage valve.
- 8h00 :** Leakage from the catchpit

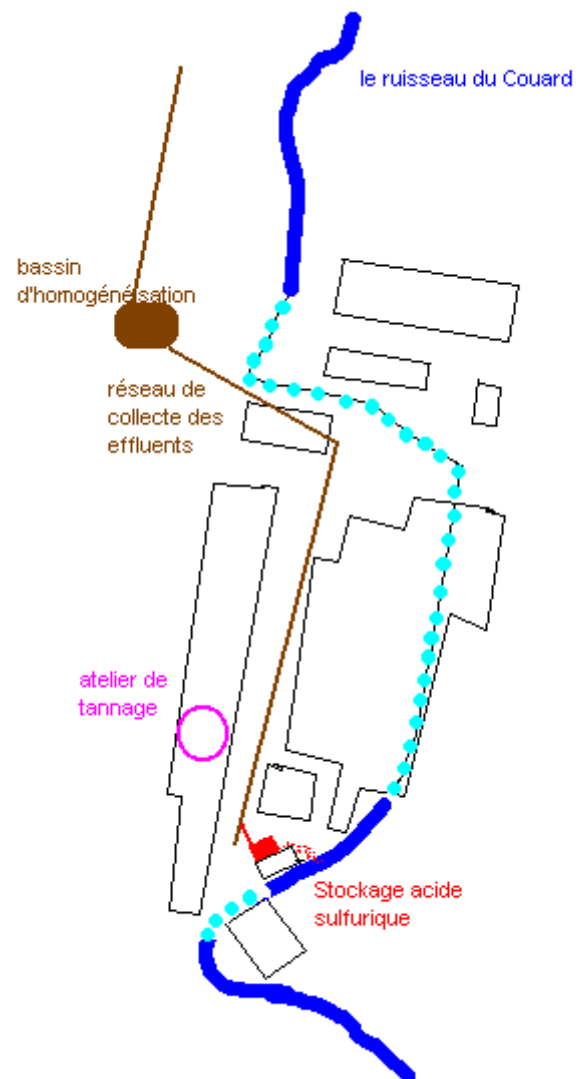
- 8h15 :** Call made to the fire brigade, the gendarmerie, the town hall, and the prefecture
- 9h00 :** Arrival of specialised firemen in the pollution in order to control the leak on the drainage line
- 14h30:** A specialised company arrives to pump to 500 litres of acid still in the catchpit
- 17h30 :** Emergency prefectorial order prohibiting the operator from releasing all effluents toward the treatment station whose pH may jeopardise the biological balance of the station
- 29.05.2000 15h00 :** Consultant services provided by an independent laboratory regarding the implementation of treatment designed to raise the pH of the settling tank and control of this parameter prior to release to the station
- 02.06.2000** Retour à la normale pour les conditions de rejets des effluents vers la station d'épuration

### The consequences :

The existence of the two routes of contamination taken by the sulphuric acid should be noted :

🚰 6,000 litres directly into the site's settling tank threatening the treatment plant

🚰 500 litres directly into the Couard brook then the Moselle and a supply channel, destroying the piscifauna in the fish farming operation.





## ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

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The direct and obvious origin of this type of accident is the lack maintenance performed on the storage facilities and particularly the catchpit designed to retain any pollution.

The location of the leak on the elbow of the interior drainage line which was always in contact with the acid and under pressure, attests to the faulty design of this storage container, which does not respect the provisions of standard order 31 "bis" concerning sulphuric acid storage facilities.

The faulty maintenance, inspection and design of the storage installations were the cause of this accident. The pressurisation of the gas in the tank is an extraction method which aggravates the consequences in the case of a leak.



## ACTIONS TAKEN

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### Measures taken by the industrialist at the time of the accident

As the series events following the discovery of the leak show, the industrialist did not have any leeway for action as the concrete catchpit was unserviceable.

The measures taken by the industrialist in the heat of the moment, including the transfer of the acid still present in the tank, shutdown of the overpressure and confinement of the largest flow into the settling tank, partial neutralisation of the acid still present in the catchpit using sodium carbonate, allowed the consequences of the accident on the environment to be limited as much as possible.

### Les actions de l'administration

The "Conseil Supérieur de la Pêche" (supreme council for fishing) reported harm to the natural environment and to the piscifauna. The inspection by the ICPE ("Installations Classées pour la Protection de l'environnement", installations classed for the protection of the environment) observed that the technical requirements were not respected.

Faced with the danger of destroying the bacterial fauna of the treatment plant by the massive arrival of a highly acidic effluent, the industrial no wanting to shutdown their production, the Classified Installation Inspectorate proposed the Vosges Prefect **an emergency order** based on the following two principles:

🔗 The protection of the biological balance of the station: to ensure the compatibility of the contents of the homogenisation tank with the correct operation of the biological treatment process under the control of a laboratory certified by the French Ministry of the Environment for the water analysis,

🔔 The prohibition to engage in activities which may lead to the production of residual effluents as long as the homogenisation tank has not been treated.

The emergency prefectorial order was transmitted by the gendarmerie to the operator at 5.30 p.m., May 26th, 2000 and was effective immediately.

In order to prevent the operator from continuing to use the acid storage facility prior to a complete overhaul and in compliance with standard order No. 31 "bis", a **formal prefectorial order** was issued July 5th, 2000.

Prior to return to operation, the order required that the tank be subjected to an internal and external inspection, the backfitting of the drainage device, and the installation of a leakproof containment device or the refurbishing of the catchpit.

Given the cost of such measures, the operator decided not to return the defective storage facility to service. The operator uses 1,000-litre containers directly on a retention pit inside the tannery workshop. There is now only a maximum of 2,000 litres on the site which are on a retention pit. The containers are in a zone where, even in the case of a mishap during installation or handling, all spills cannot enter the natural environment and will be directed toward the homogenisation tank.



## LESSONS LEARNED

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The operator learned two major lessons:

🔔 The essential role of the homogenisation tank is to confine all pollution on the site, with the risk of having to stop production the time necessary to treat the pollution.

🔔 The problem of correctly sizing the storage tanks. It is necessary to stock 16,000 litres for an annual consumption of 40,000 litres, knowing that the supplier makes several deliveries throughout the year? It is regrettable that the solution of reducing the stock to just 2,000 litres is only the consequence of excessively expensive refurbishing and not a voluntary and preventive action by the industrialist.

## 18 - Explosion in a furnace in a metal alloy production plant.

Feurs (42).

February the 21<sup>st</sup>, 2000

### THE INSTALLATIONS IN QUESTION

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#### The plant :

The Feurs site employs 650 people and includes 3 units:

- ✚ a unit producing cast steel,
- ✚ a unit producing wear parts particularly for public works equipment,
- ✚ a unit created in late 1997 specialises in the conversion of industrial co-products and complex metallic composites (batteries, dusts and iron scales from foundries, catalysts derived from the petrochemical or chemical industry, milling sludge,..) through pyrolysis (drying, calcination, fusion). The plant had a turnover of 18 MFF in 1998, and has a workforce of 35.

By virtue of the prefectorial order of April 14th, 1997, the company is authorised to operate metal waste processing (fusion) installations, as well as ferrous alloy production and non-ferrous alloy and metal foundry installations.

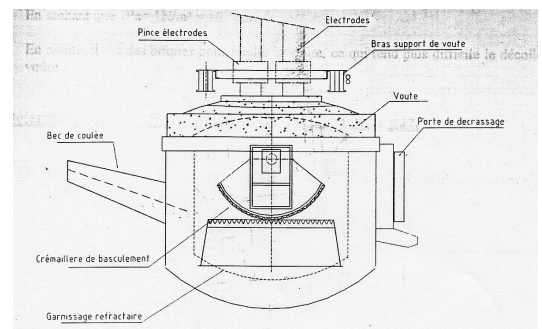
In 2000, using a 5-tonne light-arc furnace, the plant processed:

- ✚ 700 t of metal slag and dusts
- ✚ 800 t of nickel, cobalt, molybdenum and iron alloys
- ✚ 1300 t of batteries.

The furnace is hooded, and the fumes are drawn off (50,000 m<sup>3</sup>/h) and filtered. The following parameters are recorded continuously: output, temperature, dusts, COT, CO, CO<sub>2</sub>, O<sub>2</sub>

The processing operation underway at the time of the accident was the fusion of a mineral and metal load in order to produce alloy ingots. The load was consisted of the following elements:

- ✚ 836 kg of sand, essentially comprised of alumina, silica and nickel oxide,
- ✚ 6690 kg of Fe - Mo - Co - Ni-alloy into 350kg-ingots,
- ✚ 540 kg ordinary structural steel,
- ✚ 240 kg lime.



The normal sequence of events for this processing operation is as follows:

- 🚮 The prepared load is introduced into the furnace all at once;
- 🚮 The electric arc, electrodes above the load, melts it,
- 🚮 Gaseous oxygen is blown into the bath through a nozzle, for refining purposes,
- 🚮 The electric arc is shut off, the refining operation continues,
- 🚮 The furnace tips, the floating slag is removed, and the metal is then poured into ingots.

## THE ACCIDENT, ITS BEHAVIOUR AND CONSEQUENCES

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### The accident

The light-arc furnace started at 7.35 a.m. with the melting of metal scraps containing essentially iron, molybdenum and cobalt (3,210 kg) and scrap metal (1,080 kg).

The process took place without incident and at 12.40 the liquid metal was poured into ingots of approximately 800 kg.

The furnace was entirely emptied of its liquid metal. An inspection of the furnace was performed by the furnaceman. No anomaly was reported (no water leak, or refractory damage).

### **Loading of the furnace : chronology**

**13 h 20 / 13 h 25:** Introduction into the furnace of 836 kg of sand contained in a big-bag and consisting essentially of nickel oxide, silica and alumina. The sand is distributed in a homogenous manner at the bottom of the furnace to a height of approximately 20 to 25 cm.

**13 h 35 :** Introduction into the furnace of the metal load and lime using the loading basket :

- 🚮 metal ingots weighing approximately 350 kg, Fe - Mo - Co - Ni (6,690 kg),
- 🚮 Fe- Ni-Ti metal alloy (210 kg),
- 🚮 "classic" metal scrap (540 kg),
- 🚮 lime (240 kg).

**13 h 45 :** closure of furnace arch and ignition of electric arcs.

### **Melting process :**

The main operation are the following ones :

- 🚮 0 to 1,000 kWh: electric arc only.

🔧 1,000 to 1,552 kWh (around 14 h 20): electric arcs + introduction of gaseous oxygen into the metal bath

🔧 At 1,552 kWh (around 14 h 40): shut-down of the electric arc. The temperature of the metal in contact with the thermocouple is 1,530° C, and the blowing of gaseous oxygen into the bath continues.

🔧 At roughly 15.15, the accident occurred. Approximately 10 minutes prior to the accident, the furnaceman reported that the metal in contact with the temperature reading thermocouple was 1,575° C.

#### Events at the time of the accident :

Metal and slag were ejected by the furnace's slag door. A few seconds or fractions of seconds after the metal and slag were ejected, the arch collapsed into the furnace; Incandescent particles were thrown with a muffled rumbling noise and an intense blast; an excessive amount of dust swept across the workshop. The event was not accompanied by an explosive blast noise.

#### The consequences :

Of the six individuals hospitalised, 3 of which were released the same evening, 2 persons who were seriously burned were transported to a specialised hospital in Lyons, 1 was just slightly injured. These individuals were injured by molten metal, incandescent dust and flames.

## ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

The main factual data relative to the circumstances gathered follow :

- 🔧 The level of the metal bath was abnormally high. The furnaceman had to raise the level of the dam and slightly incline the furnace spout.
- 🔧 Solid products came to the surface of the metal bath when oxygen was being blown in.
- 🔧 The furnaceman noted unmelted parts in the bottom of the furnace (by testing with a metal rod) a few minutes before the accident.
- 🔧 There were no unmelted elements attached to the sides of the furnace.
- 🔧 The average thickness of the arch bricks was measured at 180mm. The new brick is 250mm thick.
- 🔧 A few bricks of the arch's outer row were found on the periphery of the arch's metal ring.
- 🔧 A sample of metal ejected by the furnace door was analysed .:

Element	C	Mn	Si	S	P	Ni	Mo	Co
%	0,35	0,05	0,83	0,061	0,252	2,38	16,43	6,22

🔗 The examination of the off-gas recorder on the stack outlet highlights the rapid increase of CO content at the time of the accident.

Time	15h00	15h05	15h10	15h15	15h20	15h25
Concentration expr. mg/m <sup>3</sup>	32,0	83,3	393,0	291,0	114,0	66,3

🔗 No water leak was reported on the cooling systems and the refractory material of the hearth was in very good condition.

🔗 While the load remaining in the furnace was melting after the accident, melting difficulties and rapid temperature increases to 1,700° C followed by abrupt drops to 1,550° C were noted. The temperature rise/drop phenomenon was noted 2 to 3 times. This phenomenon is interpreted by the dissolution of unmelted products in the bottom of the furnace and their rise to the top.

Based on testimony by the personnel, reconstitution of the previous casting operation through to just after the accident, and post-accident investigations, some hypothesis relative to the phenomenon observed were presented. After analysis, some of them were finally rejected (Water leak inside the furnace, presence of a hollow body, collapse of the arch, collapse of unmelted elements attached to the side of the furnace, water present in the slag tank).

On the opposite, the following **causes had been retained** :

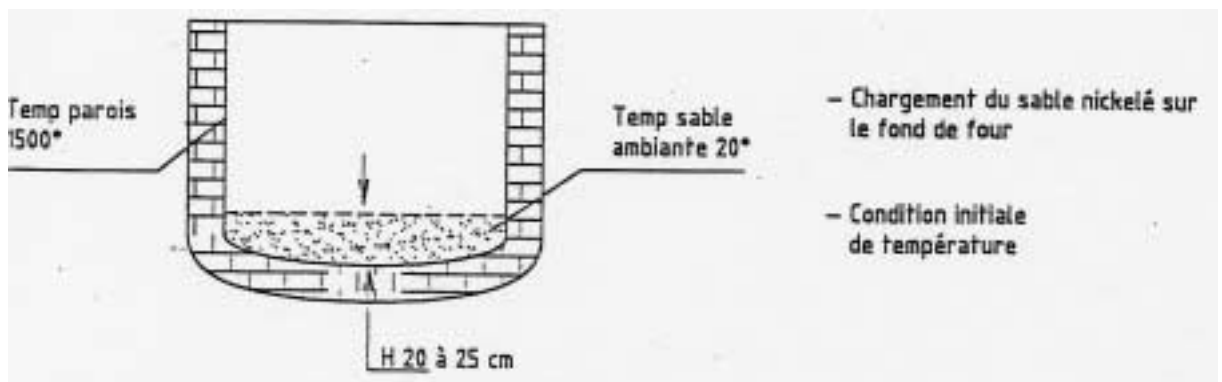
🔗 The nickeled sand in the bottom of the furnace did not melt completely; the intense mixing of the metal by the injection of gaseous oxygen helped the nickeled sand rise to the surface. The nickel oxide was deoxidised by passing through the metal; the oxygen thus released combined with the carbon present in the bath and produced large quantities of CO and CO<sub>2</sub> very rapidly. This hypothesis is substantiated by the recording of the gas analysers; a calculation shows that this reaction produces 73 m<sup>3</sup> of CO in a few seconds.

🔗 The unmelted nickel sand in the bottom of the furnace contained a certain quantity of water and gas, held under pressure by a layer of pasty metal. The blast would have been due to the release of these gases; a calculation shows that this phenomenon generates 8 m<sup>3</sup> of steam.

🔗 The analysis of the causes concludes that the loading method (nickeled sand in the bottom of the furnace) which was the origin of the accident.

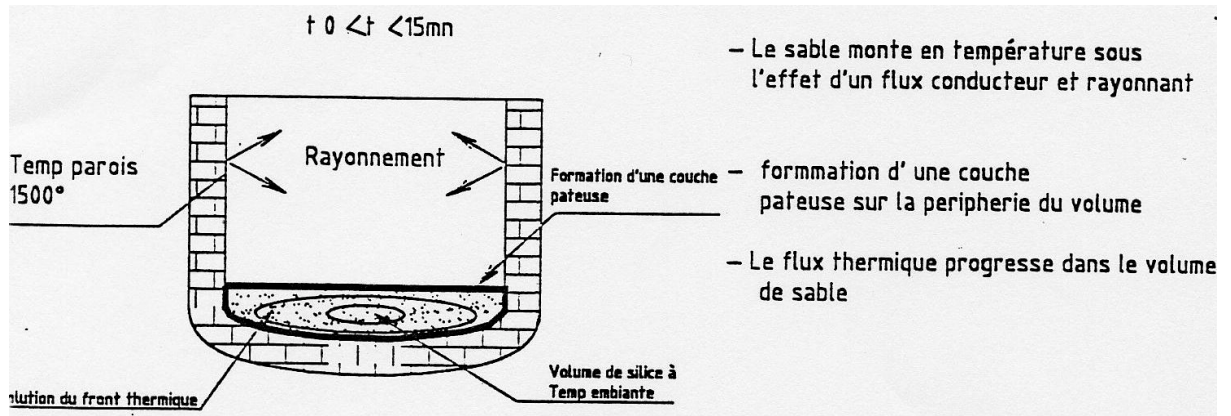
The presence of personnel not necessarily required around the furnace during the fusion operation was an aggravating factor in the number of people injured.

**Possible development of the accident :**



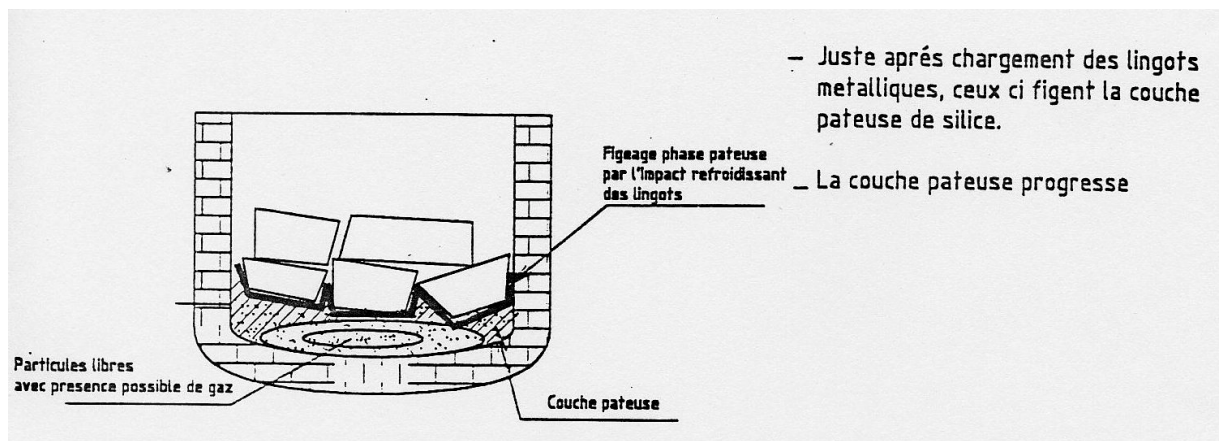


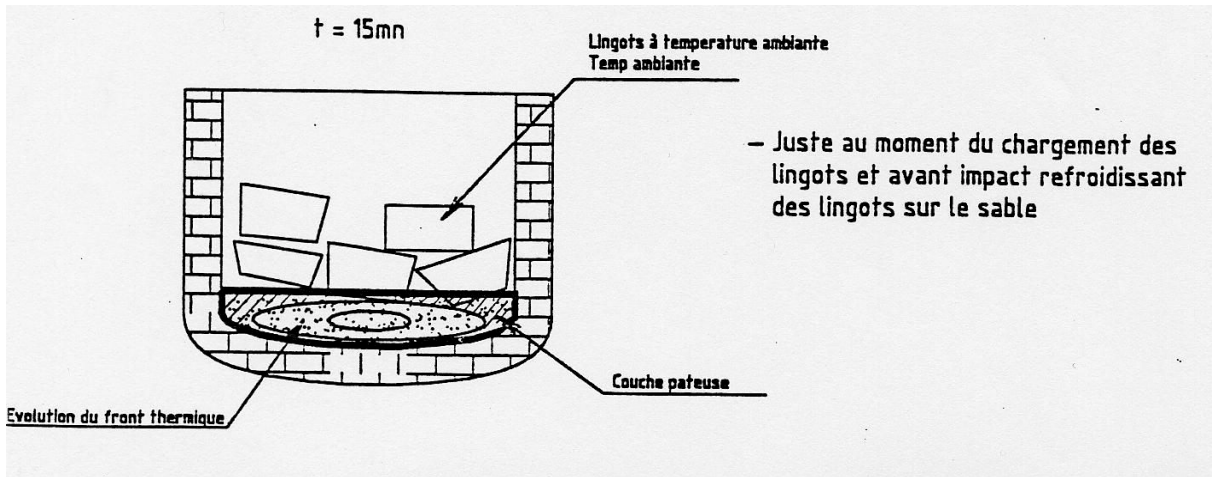
Start of the operations : t=0



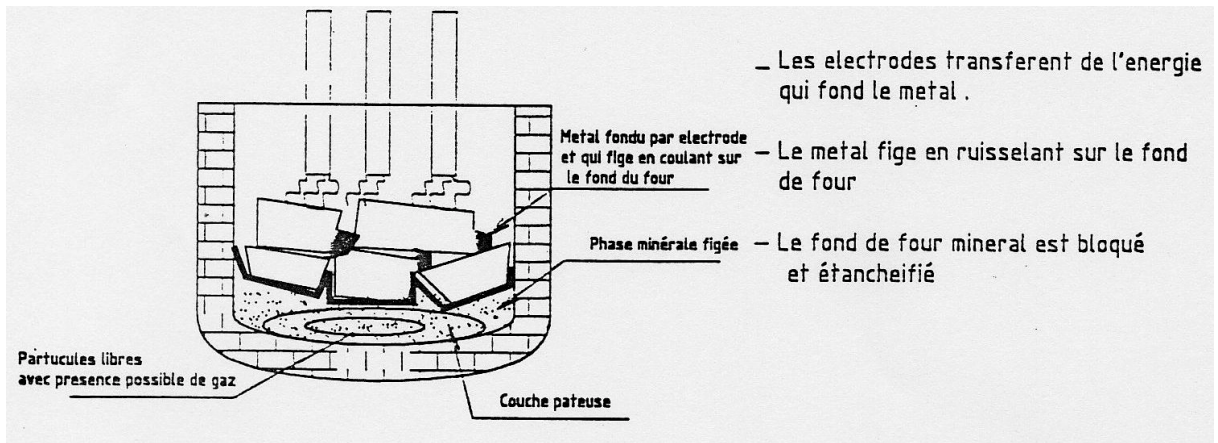
Intermediate period before the loading of the ingots t<15 min

Loading of the ingots moment t

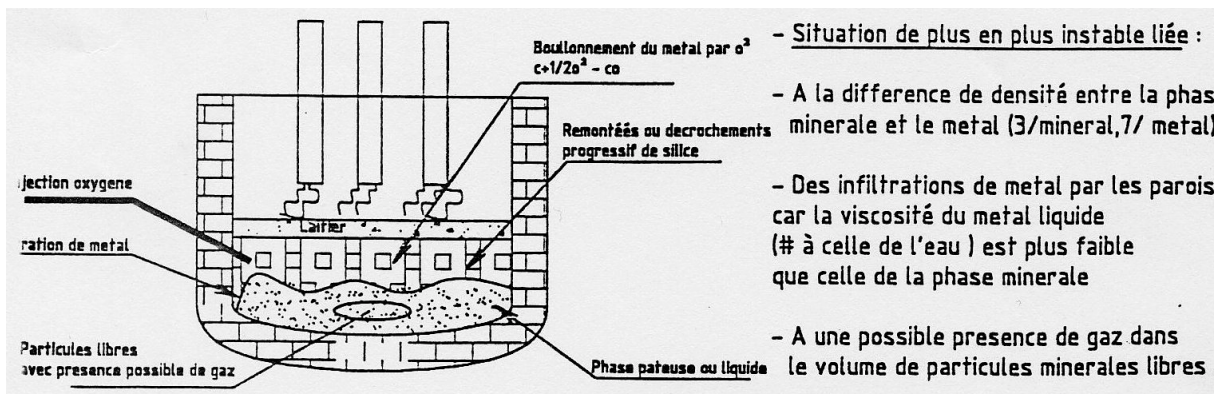




Thermal impact of the loading of the metal ingots



Fusion start of the metal ingots  $t=15min+x$



Furnace situation, melted metal ( $t+15min +40min$  : injection d'oxygène et  $t+15min+45min$  : metal fusion)

## ACTIONS TAKEN




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At the time of the accident, the operators called the emergency rescue services, disconnected the electrical power and oxygen supply.

The furnace was rebuilt a week later; the metal remaining in the bottom was melted and poured.

An "emergency" prefectorial order was put into effect on February 28th, 2000, subjecting the recommissioning of furnace No. 2 to the understanding of the causes, consequences and the implementation of solutions to remedy the problems...

The letter by the DRIRE, dated March 10th, 2000 stipulates which responses were expected in terms of the prefectorial order of February 28th, 2000, namely:

-  the probable causes of the accident,
-  accidentology of the activity sector and the reasons which lead to retaining the probable causes identified,
-  the types of loads or pouring operations for which a restart is required, argued by the risk analysis and counterbalancing procedures.

For these three points, an evaluation by a specialised organisation independent from the operator was requested. The IRSID ("Institut de Recherche en Sidérurgie", a USINOR group) was retained.

In response, the operator produced a file on March 24th, 2000; completed by the expert's report of March 27th, 2000.




The prefectorial order of April 7th, 2000 authorised furnace No. 2 to return to operation for the fusion of 3 product families, according to the procedures validated by the IRSID expert; the order also stipulated that a modelisation study be conducted concerning the phenomena which lead to the accident as well as an update of the danger study (last version: September 1996).

The modelisation study was conducted by the Laboratoire de Thermodynamique et de Physico-Chimie Métallurgique at the Institut National Polytechnique of Grenoble, France. Based on small-scale tests (200g of sand, 1kg of cast iron), the study confirmed the scenario of a sudden release of gas due to the deoxidation of the nickel oxide contained in the sand.



## LESSONS LEARNED

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The **main lessons** to learn from this accident may be summarised as follows :

-  The unexpected and uncontrolled reaction in the furnace is the origin of the accident.
-  The presence of people near the furnace at the time of the accident increased the human toll.
-  Adequate operating procedures are sufficient to prevent the occurrence of this kind of accidents.

As a result, the operator had to take **measures** :

-  Modification of the area surrounding the furnace: protective panels for observation purposes and certain operations, the creation of circulation zones, regulated access near the furnace...,
-  Revision of all of the operating procedures, safety instructions (individual protective equipment ..),

 Recruitment of a safety engineer for the site.

The accident reminded the industrialist that basic precautions are required around a metallurgical furnace; in this instance, the routine, the poor understanding of the risks by the management and the operators allowed individuals to get into a dangerous situation.

# | Other documents

[Sheet presenting BARPI's website](#)

## Presentation of ARIA website

The wide distribution of information reflecting the lessons learned through the analysis of industrial accidents is an essential element in developing the mechanism aimed at preventing technological risks.

Since 1992, an office of the *Ministère de l'Aménagement du Territoire et de l'Environnement*, the "*Bureau d'Analyse des Risques et Pollutions Industrielles*" (the Office of Industrial Pollution and Risk Analysis), located in Lyons, France, has been tasked with distributing data on industrial accidentology.

A team of technicians gather, analyse and edit the data before it is entered into the A.R.I.A. (Analyse, Research and Information on Accidents) database. The database currently contains more than 20,000 accidents or incidents primarily concerning industrial installations, although it also includes the transport of dangerous materials.

During 2000, nearly 1,800 accidents or incidents were recorded in France. The increase in the number of events recorded (+15%) can be interpreted by enhanced reporting of accident information and the greater awareness of operators and society in general concerning the prevention of risks.

The main sources of information are governmental bodies (Fire and Rescue Services, Civil Defence, the Classified Installations Inspectorate, "Water Police"), the press and insurance companies.

The information in the ARIA database is used to create customised studies conducted by the B.A.R.P.I. at the request of industrialists, engineering offices, insurance companies, training organisation or administrative services.

Throughout 2000, nearly 1,100 technical responses (+20%) were established, the majority being for industrialists and engineering offices, or industrialists establishing danger studies concerning classified installations.

The other services offered by the B.A.R.P.I. may include participation in colloquiums, continuing or initial training sessions, as well as ministerial publications or articles in the specialised press. In June 2001, in order to further complete the mechanism, the B.A.R.P.I. will put all the technical information concerning industrial accidentology on line at the following address:

[www.aria.environnement.gouv.fr](http://www.aria.environnement.gouv.fr)



**INVENTAIRE DES ACCIDENTS TECHNOLOGIQUES ET INDUSTRIELS**

**Ministère de l'Aménagement du Territoire et de l'Environnement**

**Accidents technologiques et industriels**

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- Analyse des accidents par secteur industriel
- Analyse des accidents par thème
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Tappez les mots de votre recherche

Recherche avancée

Près de 1 000 accidents industriels de gravité variable ont été répertoriés au titre de l'année 2000 dans la banque de données ARIA. Pour l'essentiel, ces événements résultent de l'activité d'usines, ateliers, dépôts, chantiers, carrières, élevages, et du transport de matières dangereuses. Ces accidents, dont le recensement ne peut être considéré comme exhaustif, ont été à l'origine de 50 décès et de plus d'un millier de blessés. Le recueil et la diffusion des enseignements tirés de l'analyse des accidents contribuent à l'amélioration du dispositif de prévention des risques.

This information will supplement the Internet site of the *Ministère de l'aménagement du territoire et de l'environnement*, primarily in the following areas:

- Initially, an inventory of industrial accidents recorded over the last three years (6,000 events),
- Detailed analysis sheets about specific accidents or accidentology implicating industrial sectors or specific themes,
- Technical recommendations.

This mechanism allows us to take yet another step forward in making available a certain amount of information to both public and private players allowing them to improve risk prevention.

# | Conclusions

## **Closing speech**

**IMPEL seminar June, 12<sup>th</sup> and 13<sup>th</sup>, 2001**