Fire on an elastomer storage site
January 20, 2000
Clermont-Ferrand (63)
France

Rubber
Rosin
Cobalt hydroxide
Vulcanox
Fire
Explosion
Dangerous releases
Difficulties of intervention
Organisational anomalies
Human failure
Victims
Pollution
Environmental analyses
Appraisals

THE INSTALLATIONS CONCERNED

The site:

The plant was subject to authorisation under the terms governing installations classified as being installations principally used for combustion. The damaged building, built in 1958 and called O24 was classified by virtue of its long existence for the storage of rubber derived materials (receipt of declaration of 18th May 1987) It had been used as a tire manufacturing plant for civil engineering equipment until the early nineties.

Photo DRIRE Auvergne

The fire involved a building with a ground surface area of 16 000 m². Mainly unused, but in the course of re-development this building served principally for the storage in the basement of raw synthetic gum. In the West of the building there was a machine, known as MAC BU, which served for the preparation of the mixtures for the gum.

Roughly 2 500 tonnes of gum were stored in the basement, this gum included:

- ✓ « PB » gum (polybutadiene)
- ✓ « SBR » gum (copolymer of butadiene and of styrene)
- ✓ « Extended SBR » gum (copolymer of butadiene and extended styrene with petroleum oils).

Various toxic products in transit were located on the ground floor of the building in smaller quantities. They were mainly stored around the MAC BU machine and were not affected by the incident (flames or extinguishing water), with the exception of 5.8 t of colophane (rosin), 0.9 t of cobalt hydroxide and 59 t of a vulcanising component were stored in the burned out part.

THE ACCIDENT, THE SEQUENCE OF EVENTS AND THE CONSEQUENCES

The accident :

On the 20th January, 2000 at 16h40, an employee of an outside company undertaking work on the ground floor, detected the presence of smoke in the basement of the building.

A first attack on the fire, organised as from 16h55 by the on-site firemen, proved to no avail and the town fire brigade intervened at 17h41.

The site of the fire was difficult to approach and the fire rapidly spread, then the disaster extended over a few hours to the major part of the building. It took two days until the Saturday 22nd January in the middle of the day for the fire to be brought under control by the emergency services.

In all likelihood, and subject to the conclusions of a judicial enquiry, the fire appeared to have been initiated accidentally by thermal cutting work undertaken by the outside company.

A major fire, linked to the ignition of the various stored products or those formed during the incident (hot gases…) can create several risks:

- ✓ An extension of the accident with explosions, back-draft and the associated physical consequences (major thermal flows, sources of burns, compression shock waves),
- ✓ A release to the air of toxic components produced or released during the fire,
- ✓ A pollution of the natural environment by extinguishing water when this can not be contained.

Although, during the fire and the succeeding weeks, media attention was, above all, focused on the smoke cloud observed during the fire-fighting, the intervention of the public authorities including the DRIRE (Regional Directorate for Industry, Research and the Environment) naturally took into account all three categories of risk, from the outset of the incident.

It should however be noted that the installation presented no factor giving any one of these risks a major importance (absence of large-scale storage of toxic products, or easily inflammable or explosive products…)

Chronology

- 20.01. 2000:

16h50: the heat alarm for the zone 51 of the building activated, then the in-house firemen confirmed a major emission of smoke 7 minutes later,

17h35: the town firemen were called in reinforcement for a rubber fire, the fire-brigade arrived on site at 17h41,

18h12: a sprinkler system of the “flooding” type in the basement was partially activated (protecting about 1/3 of the surface area of the basement). For the remaining part, the valves were inaccessible. Attempts to reach them resulted in injury to 5 firemen, in two cases serious, by explosions at 18 h and 19h30.

From this point the town firemen took charge of operations:

- the affected area was some 3 000 m² ; 1 300 to 1 400 t of gum was on fire, but 1 100 t of gum was protected by the sprinkling,

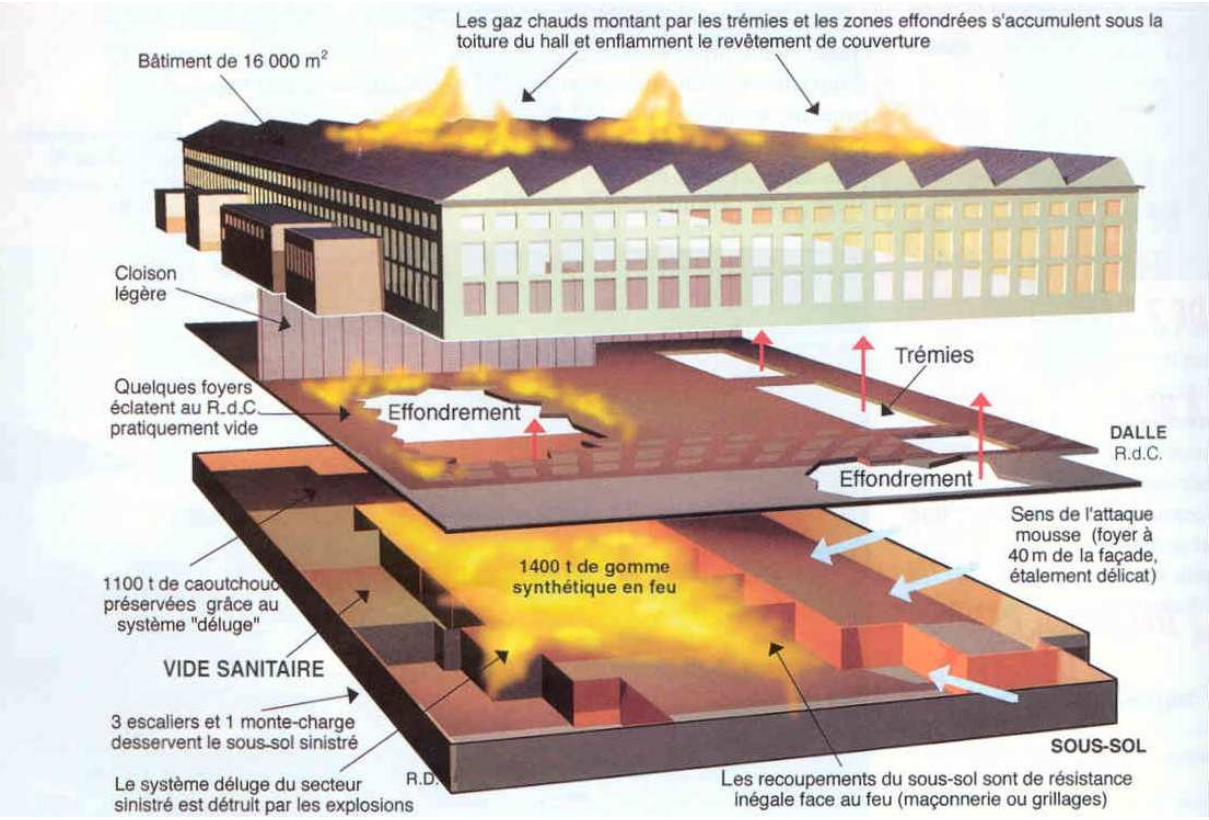
- a thick layer of smoke rose to considerable altitude before being dispersed.

21h15: the Director of the DRIRE and an inspector of classified installations arrived on the site.

21h30: reinforcement firemen were requested from neighbouring districts. Nearly 500 firemen were involved in all with a maximum of 130 in simultaneous operation. The gum continued to burn until the evening of Friday 21st January when its intensity diminished visibly around 19 h.

22.01: around mid day, the fire was declared to be extinguished.

Illustration by René Dosne (Face au Risque n° 364 June-July 2000)



Human and material consequences:

9 people were injured: 6 in-house firemen, 3 outside firemen (of whom one while withdrawing equipment after the extinction of the fire).

The disaster was confined to building O 24, the action of the firemen having immediately and successfully sought to prevent any extension of the fire to the neighbouring buildings (laboratory, oil and solvent storage, electrical transformer…).

Photo DRIRE Auvergne

Photo DRIRE Auvergne

Material damage was serious. Most of the damaged building had to be torn down; 1 415 t of gum had been affected by the fire. The only important machine in the building, an automatic dosage weighing device (MAC BU), separated from the fire by a wall, was protected by the firemen and was not affected. This was also the case for the major part of the chemical products.

Economic consequences were limited. Only the “buffer” stocks of raw materials and a large part of building O24 were destroyed. No essential installation was affected. No technical layoffs were envisaged and the MAC BU machine was rapidly returned to service.

Impact on the environment: air pollution

As from the origin of the incident, the nature of the materials involved in the fire permitted the assumption that there would normally be little risk of release of toxic fumes; on the other hand the large size of the fire and incomplete combustion would generate a spectacular smoke cloud, heavy with unburned residues (soot).

The firemen took several elementary measurements of the air quality, close to the fire, without revealing any evidence of toxic components.

The ATMO Auvergne network (note: this is an association which concerns itself with air quality) detected no spectacular rise in the pollutants surveyed. The air quality remained good throughout the urban area. On the other hand numerous requests for information were received. Real-time measurements were communicated as from 21st January 2000, the installation of a mobile laboratory from the network in the axis of the cloud and complementary measurements, by an accredited organisation, of fallout of dust and particulates, prolonged during the following weeks, confirmed that at the peak of the pollution, concentrations of dust in the ambient air outside the cloud remained far below the W.H.O. recommendations as regards the daily average.

All measurements gathered subsequently confirmed that the cloud had caused some moderate and temporary increases in dust and sulphur dioxide levels. The fallout of particulates remained very localised. These increases remained inferior to levels reached during meteorological conditions unfavourable to the dispersion of pollutants – thermal inversion, anticyclonic period.

Impact on the environment: water pollution

No major impact was measured during or after the fire (die-off of fish or vegetation…). Later, serious evaluation and analysis work was conducted on invisible effects. The results of these are described in the section “Measures Taken”.

Long and complex analyses were also undertaken on the sediments in the Bedat and the Morge rivers.

EUROPEAN SCALE OF INDUSTRIAL ACCIDENTS

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

The accident at Clermont-Ferrand is characterised by the following indices:

The parameters comprising these indices are available at the following address: http://www.aria.ecologie.gouv.fr

The effects of the explosions not having been characterised and the evaluation of the distances for broken windows being less than 330 m, parameter Q2 is scored at 1. During the intervention, 5 firemen were injured, of whom two seriously, this explaining the index relating to human and social consequences of 2 (see. parameter H4). The results of samples taken in the rivers into which flowed the extinction water confirmed a non-negligeable quantity of Vulcanox in the sediment of the rivers Bedat and Morge. This pollution of the surface water leads to an index relating to environmental consequences of 1 (see. parameter Env).

THE ORIGIN, THE CAUSES AND THE CIRCUMSTANCES OF THE ACCIDENT

The probable cause of this fire was a fire source following the ignition and slow combustion, with pyrolysis, of the gum present in the basement.

An outside company, with a fire permit, was undertaking maintenance operations involving the mounting and dismounting of metallic components using blow-torch cutting and welding. The hypothesis is that a lump of molten metal initiated a slow combustion of the gum present on palettes for an indeterminate period of time prior to the fire.

Favourable conditions for smoke dispersion and the absence of strong winds facilitated the intervention of the firemen, in particular by allowing for the protection of the surrounding buildings in immediate proximity to the fire. Indeed, a large assembly workshop and research laboratories had great importance for the activities of the site and the company.

The company management, the fire-brigade and the local authorities very quickly acquired a clear view of the situation:

- ✓ A large and spectacular, but not specially dangerous incident but without great danger nor serious economic consequences provided that its extension could be prevented,
- ✓ A fire which was difficult to extinguish before almost complete combustion of the materials which were directly involved.

Photo DRIRE Auvergne

On the other hand, knowing the difficulties of extinguishing a generalised fire in gum, it would appear, with hindsight, that the fire could probably have been better contained and then beaten back if the in-house firemen, intervening with inadequate means, had called for assistance from the town fire brigade earlier.

The decision to soak ("flood") the storage seems to have been taken tardily (1h20). The absence of an automatic device showed that it was impossible to operate manually the equipment present because this was inaccessible, close to the flames and not on the outside. Wherever the sprinkler valves could be opened rapidly, the stores were protected and the fire prevented.

The fire fighting mobilised large stocks of foam from beyond the Auvergne region (100 000 litres of which 80 000 were used). Analysis of the water consumption showed that 90 000 m³ were used to extinguish the fire of which 1/3 consumed by the protective sprinkler installations.

The incapacity to contain the extinction water, even if today it appears that this had little consequence, became the subject of deep reflection to find a remedy. This one will be subsequently extended to the other sites belonging to the company.

THE MEASURES TAKEN

No fault or culpable negligence having been attributed to the management of the installations, there were no administrative penal sanctions taken against them.

In the light of the results of the technical enquiry conducted after the incident, corrective measures were ordered. In a general manner, evaluation of risks and of preventative measures were undertaken (updating of the risk evaluation and examination of possible domino effects, possible third party appraisals…).

The risk of pollution of water and of the natural environment by the vector of water was the subject of an **in-depth evaluation**: as from the moment of his arrival on the site, on January 20th, the inspectorate of classified installations made enquiries concerning the retention of extinguishing water. Taking into account the small capacity available (1 000 m³) and of the possibility of extension of the fire to the test laboratory containing toxic products, this capacity was set aside and finally not used.

Indeed, during the fire, little risk had been identified. The company management had declared a stock of 1 300 t of synthetic gum (in fact there were 2 531 t, even though only 1 415 t were affected by the fire) and the presence of a few tonnes of chemical products close to a machine protected by a wall and by the sprinkling of the damaged building. At first glance, no major pollution problem seemed likely to arise.

An inspection made on January 25th confirmed that the products close to the protected machine had indeed not been reached by the fire or by the extinguishing water. On the other hand, according to information provided by the management, "a few big bags" (several tonnes of products packed in bulk in large bags of roughly 1 or 2 m^3) which were stored in the part of the building destroyed by the fire, were irrecoverable.

However, on February 4th, 2000, the inspectorate of classified installations received complementary information concerning the presence of quantities, which had been revised upwards, of chemical compounds in the area affected by the fire:

- ✓ 60 t of a vulcanising compound, Vulcanox,
- ✓ 900 kg of cobalt hydroxide,
- ✓ 5.8 t of colophane (rosin),

Taking into account the potential pollution risks relating to certain of these compounds, **major impact analysis and evaluation work** were undertaken at the initiative of the principal private and public authorities.

The attention of the inspectorate was rapidly drawn to the Vulcanox, taking into account the quantities and the nature of the missing products. Indeed:

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

- ✓ The colophane (purified pine resin) probably burned during the fire, given its high degree of inflammability and its insolubility in water,

The Vulcanox could have been destroyed by the fire, drawn away by the extinguishing water or, partly, remain in the rubble of the basement of the building to which access was difficult. It was therefore important to establish a balance sheet, as precise as possible of the quantities found in the rubble or in the natural environment and to learn the impact and future evolution of this chemical product in the environment.

Vulcanox is composed of N-(1.3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD) which has anti-oxidant properties. Although it is identified as being "very toxic for aquatic organisms and having very harmful long term effects on the environment" according to the file of the manufacturer, it is very little soluble in water and very little bio-degradable, while being very sensitive to photo-chemical oxidation.

The evaluation of potential pollution and possible effects :

As from the outset of the fire, on the evening of 20th January, the operator took samples of the extinguishing water at regular intervals in the canal leaving the factory. These samples were analysed by the company laboratory and by a regional laboratory.

The analysis covered the usual parameters (DCO, or Chemical requirement of oxygen and MES or Material in Suspension). The results appeared not to present any special level of danger given the context (maximum MES of 983 mg/l and maximum DCO of 739 mg/l). Some samples were taken in parallel by an outside laboratory without the company being informed.

On January 25th 2000, as soon as the problem linked to the "few" big-bags of Vulcanox surfaced, the inspectorate requeseted additional analyses concerning this compound in the samples taken by the operator, of which certain had to be undertaken by one or several outside laboratories coordinated by the regional laboratory mentioned above.

When the missing quantities had been better evaluated, the inspectorate of classified installations officially requested of the operator, by fax dated February 14th, confirmed by a detailed letter dated February 23rd, to take **samples of water and sediment** in the watercourses downstream from the site of the incident with a view to the detection and evaluation of possible pollution following the drifting out of toxic compounds on the extinction water:

- × 2 samples of sediment were therefore taken on February 21st in the Bedat and the Morge in the presence of the inspectorate of classified installations. In parallel, samples were requested on February 25th by fax to measure the biological impact of possible pollution on the watercourses into which the extinction water had flowed: Tiretaine, Bedat and Morge (a watercourse of mediocre biological quality).

- × 3 were subsequently taken in the presence of the inspectorate on February 29th to determine the number of oligochaetes (small worms living in the sediment) of which the taxonomic distribution provides a criterion for assessing and characterising local pollution.

From the results of these measurements received on March 7th and date from the file on the fire handed to the inspectorate by the plant operator on March 8th, it emerged that pollution of chemical origin was detectable but without a clear link to the fire.

The quantity of Vulcanox present at the time of the fire was moreover evaluated at precisely 59 t in this file. A meeting on March 13th between the inspectorate and the industrialist was centered on the following actions to be taken as regarded the ongoing investigations.

On March 17th the works and analyses to be conducted were presented in detailed form to 2 members of the executive committee of the group, by the Prefect of the region, assisted by the Director of the DRIRE.

These elements were accepted and confirmed in a letter dated 10th April 2000 from the Director of the DRIRE to the company, setting the framework for the **complementary investigations and research to be conducted:**

- ✓ Precise balances for the various compounds and metals,

- ✓ Complementary samples and analyses,

- ✓ Measures for conservation to be taken on the site of the fire,

✓ Theoretical and experimental studies on the degradation of Vulcanox in the environment and the possible toxicity of the compounds formed by the degradation.

On April 6th and 7th, some thirty samples were simultaneously taken of the water and the fine sediment covering 25 km of the watercourses downstream from the plant, in the presence of the operator, the inspectorate of classified installations and a representative of a municipal laboratory.

The agreed analytical programme, for which the coordination was delegated to the regional laboratory, had the objective of observing the geographical distribution of the possible Vulcanox pollution and also of pollution by possible products of degradation, either from this compound or resulting from the combustion of elastomers or other products present during the fire.

The first results, officially announced on June 8th to the inspectorate, showed a confirmed non-negligeable presence of Vulcanox in the sediments of the rivers Bedat and Morge.

On June 15th, the inspectorate received a file from the plant operator detailing the quantities and the disposition of the Vulcanox which had not been destroyed during the fire; 46 t of this compound at the most had been carried away by the extinguishing water.

The **official synthesis of the Regional Laboratory** on the programme of analyses was produced on June 22nd. Its conclusions were as follows:

× There had indeed been a considerable spread of raw materials containing 6PPD into the natural environment caused by the carrying away of this by the extinguishing water,

× Other pollutants (metals, mainly lead and zinc) were detectable,

× A degradation, of the biotic index downstream from the plant was measurable, but its origin remained to be determined (Vulcanox and/or metals, or other cause independent of the incident).

Following a proposal of the inspectorate of classified installations, the Prefect of the department requested or confirmed on June 23rd further investigations to be conducted by the plant operator:

× Evaluation of the extent of the pollution by a new campaign of sampling and of biological indices,

× Theoretical and experimental study of the biodegradability of Vulcanox in the environment (degradation processes, toxicity and solubility of resulting products), with the establishment of a committee of experts,

× Research into possible observable toxic effects,

× Proposals to remedy the pollution (de-pollution operations which could prove necessary).

The expert committee, selected in agreement with the inspectorate of classified installations, met for the first time on June 6th 2000.

Conclusions of the investigations :

The work of the experts and all the available date led to the following conclusions:

Metals:

While not being considered as being a major problem, metal pollution was the subject of precise evaluation:

× The lead in the water probably originated in old radiology rooms used in particular for checking tires for civil engineering equipment on the site of the destroyed building. The plant operator indicated that these installations did not contain any sources of radioactivity. It should be noted that the risk of lead pollution does not seem to have been envisaged by anybody at the time of the fire, it was only revealed by in-depth analyses.

× The zinc could have come from the roofing, of which a part was covered with this material.

Polycyclic aromatic hydrocarbons (or PAH):

Analyses of the water undertaken by an outside laboratory revealed measurable traces of certain polycyclic aromatic hydrocarbons without these presenting any risk for the water quality. The presence of these compounds was surprising because they were neither present in the gum nor the Vulcanox and their conditions of synthesis do not correspond to those present at the time of the fire. The search for these compounds was moreover undertaken originally for scientific and verification purpose. The likely origin was a layer of tar present on the roofing of the destroyed building.

Vulcanox :

The Vulcanox content of the sediments was demonstrable in July for all the watercourses concerned as far as the Allier, but at levels which were lower than during the first sampling campaign in April 2000, except in a zone of 8 km at the confluence of the Bedat and the Morge.

The comparison made between April and July showed a diminution, doubtless accompanied by a displacement of the pollution following the violent storms which had occurred during the springtime. Thus the samples taken in April indicated quantities 2 t of 6PPD while in July, the samples indicated only a quantity of around 0.5 t. The difference can be explained by the dispersion of this chemical substance.

Even taking into account major uncertainties, inherent in the calculations and the sampling, the quantities present in the sediment, between 0.5 and 1 t, are very far from the 46 t which disappeared during the fire. Maximum concentrations were of the order of 200 to 400 mg/kg of dry sediment. The solubility in water had been revised downwards from 1 to 0.2 mg/l at 20 °C. Taking into account the temperature of the water, this should not have displaced a quantity of Vulcanox of over 2.6 t within 6 months.

The absence of Vulcanox “lumps” in the sediments, the storage of 59 t of this compound close to one of the two chimneys of the fire (zone where the concrete slab had collapsed as a result of the fire) and the low apparent content of 6PPD in the sediments and the mud in the basement of the building outside certain well defined zones, made plausible the idea that a large quantity had been vaporised or burnt. This hypothesis is reinforced by several arguments from the plant operator.

- ✓ Heavy metallic elements in steel had been distorted under under the action of the temperature close to the “chimneys” of the fire, confirming that temperatures of the order of 800 to 1 000 °C had been reached,
- ✓ A roller door in PVC and polyester (strengthener) had disappeared, however polyester starts to destruct as from 280 °C and the stocks of 6PPD, colophane and cobalt hydroxide were between this door and the first chimney of the fire,
- ✓ A plaque of 6PPD, melted then solidified, was found covering 150 m² confirming that part of the product had been liquefied by the heat (the melting point at atmospheric pressure is around 50 °C),
- ✓ No trace of the packaging (big-bags) of the products was found apart from a few fragments of pallets, whereas this packaging is destroyed at around 250-300 °C,
- ✓ A laboratory study consisting of placing some 6PPD beneath an air flow at rising temperatures showed that the 6PPD starts to disappear at around 220-230 °C, the disappearance (evaporation or decomposition) accelerates suddenly at around 290-300 °C and is to tal at 350 °C.

Photo DRIRE Auvergne

Biotoc indices measured in February and particularly in June at 10 points along the watercourses, of which 6 were measured in the polluted zone, showed that the receiving environment had been subject to a toxic aggression, but that this had not been lethal (presence of oligochaetes – in the mud – in all samples). The comparison between the analyses effected in February and in July suggest that there was a certain improvement in the environment. On the Allier below the confluence with the Morge, there was no sign of toxic impact on the environment.

There was therefore no major harmful effect detected in the natural environment, this seems to be confirmed by the absence of mortality among the fish populations. This point was raised during the work with the administrative departments concerned, (agriculture, fisheries) associated with the last sampling campaigns in the milieu.

Analyses undertaken under the supervision of the sanitary service concerned did not show any degradation of the quality of water taken from the Allier or in its aquifer, below the confluence with the Morge.

Bibliographic references available, in particular chemical and toxicological works, underline the high degree of photo-oxidability of 6PPD in an aqueous milieu and relativise its toxicity. This compound should therefore biodegrade slowly and in a natural manner.

The expert committee met on 27/04/2001 to complete the study of the results of the analyses and the experiments, especially in the light of the theoretical data. In particular, experimental studies in microcosms (suitably equipped aquaria reproducing in model form the natural environment) were requested from a specialised laboratory. Naturally, a further campaign of measurements will be undertaken on the sediments of the contaminated watercourses in 2001 and if necessary later, to check on the disapprearance of the 6PPD pollution. The company will draft a report summarising all the information gathered and the analyses undertaken, and this will be submitted to the expert committee and validated by the inspectorate of classified installations.

The company will contact specialised companies to undertake, where required, de-pollution work.

LESSONS LEARNED

Attention must be given to dangerous products (distribution, storage and traceability), to the capacities for rapid and automatic reaction in the event of accidents, to the positioning of reserves of foam, to the improvement of retention basins of correct dimensions to recover the totality of extinction water in the event of fire.

Special attention should be given to the state of buried pipelines: these have been susceptible to being damaged by the movements of the ground (dilation of the slabs resulting from the thermal effects of the fire).

An initial report of the synthesis, duly completed and updated, was presented to the inspectorate of classified installations by the representatives of the company in early March 2000, in conformity with article 38 of decree n° 77-1133 dated 21st September 1977. This allowed the inspectorate to keep informed the members of the departmental hygiene council of Puy-de-Dôme by reports submitted on 13th March and 6th September 2000.

Photo DRIRE Auvergne