Welcome address

Romain LAUNAY

Industrial Environment Regional Head

DRIRE ILE-DE-FRANCE (the Regional French Authority on Industry, Research and Environment)

Ladies and Gentleman,

I have the honour and privilege to welcome you today in Paris to exchange our views and bring our ideas together on the occasion of this seminar organised by the French Ministry of Ecology and Sustainable Development and especially by the Bureau for Analysis of Industrial Risk and Pollution (BARPI) in Lyon.

May I first of all excuse Mr. Philippe LEDENVIC, the Chairman of DRIRE Ile-de-France, the Regional French Authority on Industry, Research and Environment, who was called by the Minister and thus cannot join us this morning. I am pleased to welcome you on his behalf.

After having visited four regions renowned for their wines and local products (Champagne, Bordelais, Bourgogne and Normandie), you have this time selected Paris and the Ile-de-France region to share your experience in managing industrial risks.

The Ile-de-France region, due to its other features is not naturally associated with the industrial sector. However, despite its small size, it is France's leading region in terms of industrial jobs. For instance, how many people know that the Ile-de-France region surpasses Toulouse and the Midi-Pyrénées region in the aviation sector?

With its 5,000 industrial installations awaiting permits and 80 SEVESO sites, the stakes are high in the Il-de-France region. The expertise gained by inspecting installations classified under the inflammable liquid depots category has led the French Ministry of Environment to entrust DRIRE Ile-de-France with the management of a working group on regulatory affairs. With over 200 "top-tier" SEVESO sites, in France, it is a matter of great responsibility. May I assure you that the accident that took place in December 2005 in Buncefield in the United Kingdom, which will be discussed during this seminar, has caught our attention. It reminds us that zero risk, even if it is our ultimate objective, does not exist, and teaches us that one can never be too safe.

The industrial fabric of Ile-de-France is the fruit of a long history. Located within or on the outskirts of one of the biggest European metropolitan areas, these industries have long required vigilance on the part of the authorities, making Paris a pioneer city in managing polluting or high-risk activities.

In the beginning of the 19th century, Paris was involved in the industrial revolution that witnessed the development of factories, tanneries, breweries, distilleries, various chemical plants along with urban habitat in the same zone. In modern times, it is difficult to imagine the host of problems ranging from a mere nuisance to a serious health hazard that could rise from such a degree of proximity.

The proposed solutions were until recently based on random individual decisions devoid of any genuine framework that on the one hand leave conditions that are unacceptable and even dangerous for residents unchanged, and on the other expose operators to radical and unpredictable solutions that do not guarantee the legal safety required for an optimal development of economic activity.

In 1806, the Police Commissioner, through the judicial decree dated 15 February laid the foundations of a modern approach in controlling polluting or hazardous activities by making permits mandatory for workshops, factories and unusual or dangerous laboratories and dividing them into two categories to determine their distance from urban habitat. Ever since, what is known today as town planning has been used as a vital tool in managing nuisance and hazards. Consulting with and taking into account the opinion of residents to grant operating permits was also a key feature. The judicial decree dated 12 February 1806 provided for an administrative enquiry designed to survey all parties in the neighbourhood before giving permit to start a planned operation.

Completed and applied throughout France by the imperial decree dated 15 October 1810, this provision still serves as the basis for French regulations aimed at monitoring polluting or hazardous activities via the legislation on sites classified for environmental protection. However, the provision transcends the borders of France either by way of European directives that are heavily influenced by French regulations or by the imperial decree dated 15 October 1810 that was retained or reworked by certain countries (Belgium, Netherlands, etc.) where it was applied under Napoleon's rule.

As you can see, Paris is an ideal choice to organise this European seminar to exchange our views and bring together our ideas on industrial accidents.

We wish you a memorable two-day stay in Paris. I sincerely hope that the representatives of the 21 EU states, as well as Croatia and Turkey who graciously honoured our invitation will be tempted to visit us again.

Opening address

Laurent MICHEL

Director of Pollution and Risk Prevention

As the Director of Pollution and Risk Prevention, it is with great pleasure and enthusiasm that I inaugurate this seminar on industrial accidentology feedback organised for the 7th time within the framework of the IMPEL network of European inspectors.

I would first of all like to thank DRIRE Ile de France and its Chairman Philippe Ledenvic for their active involvement in organising this event along with BARPI.

I am also very pleased to see such a strong and unprecedented participation of inspectors from the different states. With 230 participants from the 21 Member States of the European Union, as well as Croatia and Turkey taking part, the participation of inspectors has increased by 50% and that of represented states has more than doubled. The atmosphere is now conducive to ensure a high-quality exchange based on the diversity of our cultures and inspection methods.

I would like to thank the inspectors from the 23 states for having accepted our invitation in such large numbers and extend them a warm welcome. I am especially thankful to those who accepted to prepare a presentation. With the analysis of 19 accidents in our programme schedule, of which 7 occurred abroad, we are close to achieving our target set during our last seminar in Caen in 2005 which required that half the presentations focus on accidents that occurred abroad.

At a time when France is gearing up to preside over the European Commission, this strong participation is reassuring in paving the way for an international dialogue and building a platform to exchange and enrich our views. The aim is to make headway together and faster while drawing from the diversity of our experiences. To this effect, the IMPEL network is a real opportunity for all of us.

*

After the terrible explosion that occurred in Toulouse in September 2001 that resulted in 30 deaths, thousands of victims and social upheaval for the residents, France had to make drastic amendments to its legislation. From now on, risk prevention focuses on the following four areas:

1. Reduce risks to a greater extent at source with technical and organisational measures implemented by the operators under the supervision of inspectors of classified facilities.
2. Improve consultation and involvement of staff and general public in the risk management process,
3. Limit the exposure of people to risks by a controlled and well-designed town planning policy around the most dangerous establishments by gradually implementing the Technological Risk Prevention Plans (TRPP)
4. Prepare to confront any crisis situations and manage accidents with suitable contingency plans.

Accidentology feedback is a crucial factor in developing and perfecting this tool. It must continue to regularly provide food for thought for both operators and local authorities who need to position themselves based on the reality. The analysis of situations of a recent or distant past remains in fact a practical and reliable way to make an assessment or provide solutions to issues waiting to be addressed.

For instance, the Buncefield accident that will be presented this afternoon by our colleague from the United Kingdom contributed to the efforts of the working group set up to assess the effects of dangerous phenomena and design tools to develop TRPPs for inflammable liquid depots.

To this effect, I would like to take the opportunity to thank the French inspectors who have considerably contributed along with the SEI agents in the sectorial working groups managed by the DRIRE that bring together representatives of trade unions, experts and operators. This joint effort enables us to progress, sector by sector, in our assessment and risk management methods. These tools that are already functional for some or in the process of being developed for others arm us well to tackle the vital issue of TRPP.

*

Even though much progress has been achieved over the past few years in feedback, there is still scope for improvement in several fields that require our attention:

1° Ensure a better usage of feedback in risk analysis, danger analysis and expert reports. To break new ground, theory must go hand in hand with practise to widen the scope, better grasp the strong points and drawbacks of preventive measures, take into account all organisational errors and compare results of analysis with actual facts.

2° We must also ensure that the right balance is struck between perspectives of analysis and the follow-up of field practices. On-site inspections are important to ensure compliance with the stipulated technical recommendations. They must also enable the operator to manage at all times the basic failures that occur during the service life of the facility. I would like constant vigilance to be exercised on the application of the continuous improvement process within the framework of Article 7 of the order dated 10 May 2000.

3° The third orientation relates to declaration and analysis of accidents and incidents that constitute statutory obligations for the operator. Compliance with these provisions is indispensable for the information and feedback capitalisation chain to function properly. Moreover, the inspection must not be lenient with operators who fail to:

- declare accidents or incidents
- submit corresponding reports in reasonable time frames
- and update documents in their basic failure management systems in accordance with the SEVESO directive.

4° The last area of improvement includes better reporting to BARPI. With a view to rationalise information exchange, a first step was taken in November 2005 with the mandatory use of an accident or incident reporting format. Since last April, a second step forward is on the verge of being taken with the introduction of data entry directly onto a secure internet site. This aims at simplifying data import from the ARIA base for more complex analysis to be performed in greater numbers for the professionals in the field of prevention. I request the French inspectors to systematically use this new information transmission tool for accidents and incidents declared by operators. I would also request you to report to BARPI basic failures in risk reduction measures identified during inspection that are rare or provide a learning experience.

The information sharing stage with all the players is a corollary to this orientation. To this effect, I would like to remind you that BARPI provides its players with certain analysis and review tools focusing on the accidentology of classified facilities. 33,000 accident reviews, accident description sheets, review and recommendations can be accessed from the website aria.ecologie.gouv.fr.

*

Beyond technical aspects, the 30 July 2003 legislation on technological risk prevention has clearly emphasised on the need for enhanced public information with the setting up of Local Information and Consultation Committees that must be kept informed (in application of the article L 125-2 for experts) of all accidents or incidents involving the safety of facilities.

In fact, history reminds us that implementing actions and procedures regardless of their efficiency in the design, operation or inspection of the facilities does not rule out the risk of a major accident. Consequently, right from the implementation of a dangerous procedure, the players involved are forced to take all possible measures to reduce the risk of occurrence and minimise the severity of the potential consequences. Logically speaking, must our society expect other accidents and prepare for any possible major accident? This undoubtedly calls for not only contingency plans equipped with the best possible adapted measures but also a true dialogue with the public on the limits of risk prevention.

It also involves outside emergency situations, providing the civil society with the information that helps it form an opinion on the realities and difficulties of prevention and make it a part of the risk management procedure.

Incidents of note or visible from outside the facilities provide the operators with the opportunity to communicate in a slightly less stringent and more efficient context than that of the accident. The experiment conducted for more than a year in 8 regions in France highlights the extent of the lack of local information in the civil society in this field.

In view of this observation and upon the recommendation of the Director of Pollution and Risk Prevention, three professional organisations namely the Union des Industries Chimiques (French Chemical Industry Association), Union Française des Industries Pétrolières (French Petroleum Industry Association) and Groupe d'Etudes et de Sécurité des Industries Pétrolières et chimiques (French Study and Safety Group on Petroleum and Chemical Industries), in partnership with the French Ministry of Ecology, decided in December to launch a new nation-wide information campaign. For "top-tier" and "bottom-tier" Seveso facilities, it involves developing an information hotline with the general public, associations, elected representatives and local opinion relays in the event of major incidents or the ones viewed from outside.

This tool, founded on a fully voluntary basis by companies, involves solid determination of all concerned players and must be sustainable. Furthermore, I am counting on the support of the inspectors of classified facilities to promote, support and sustain this action not only with each Seveso facility operator regardless of whether they are members of the above-mentioned bodies, but also with specialised consultation organisations (S3PI, CLIC, etc.) where the main concerned entities are represented.

*

I thank you for your attention and invite you start the session of presentations without any further delay. Our seminar focuses on the analysis of about twenty accident cases.

The agenda covers a variety of subjects, among which figure:

- Sudden failure of installations
- Surcharge, leaks, spillage or clogging of units
- Dust explosion cases
- Facility maintenance and outsourcing certain operations.

It goes without saying that these technical aspects will be examined under the "organisational and human factor" angle, thus underlying further progress.

Each presentation shall last for half an hour with 15 to 20 minutes devoted to the speech, followed by a 10 to 15 minute discussion.

May I add that your conference kit contains various documents including a review named "Analogies" prepared by BARPI. This document is available in both French and English and provides a transversal review of accidents in the ARIA database that are similar to the ones that will be presented to us.

I now request Mr. Philippe FRICOU, inspector of classified facilities in DRIRE Rhône-Alpes to give us an overview of the CHAMPAGNIER accident.

Detonation
Pipeline
Chlorine
Hydrogen
Ferric chloride
Tracing system
Corrosion
lock-out
Maintenance

Chlorine pipeline explosion
21 May 2005
Champagnier [Isère]
France

THE CONCERNED INSTALLATIONS

Sites:

The plant, which is a part of the Pont-de-Claix chemical platform, manufactures chlorine and sodium. It also operates a chlorine transport line used to transfer a part of the manufactured chlorine to a user site mainly producing chloroprene by chlorinating butadiene.

Both the manufacturer and user sites are classified “top-tier” Seveso sites and employ 280 and 250 persons respectively.

Involved unit:

The 3,600 m long 5.6 mm thick above-ground pipeline with an internal diameter of 8 inches (207 mm) is used to transport chlorine gas between the two above mentioned sites. The pipeline is mainly located on premises owned by the user except for a part running through a public traffic lane.

It was built in 1961 and initially used to transport anhydrous hydrogen chloride (HCl) until 1975. Then from 1986, it transported deoxygenated and dried chlorine (Cl_2). This pipeline was not in service between 1975 and 1986.

The pipeline is steel coated and thermally insulated throughout its length, and fitted on its upper outer part with a skin effect electric tracing system comprising two independent loops of 1800 m, one on the manufacturer side and the other on the user side. When operational, the absolute pressure of chlorine gas in the pipeline is 5.3 bar (4.3 relative bar) for a skin temperature maintained between 25 and 30°C.

This transport pipeline, which did not have a public interest clearance (Déclaration d’Intérêt Générale DIG), is governed by a prefectural order issued in 1986 under the classified facilities.

THE ACCIDENT, ITS COURSE, EFFECTS AND CONSEQUENCES

Accident:

On **21 May 2005 at about 10.50 am,** there was a major explosion at the chlorine transport line at 150 m from the delivery point at the user site that was heard several kilometres in the vicinity. This was followed by the emission of a reddish cloud.

Source: DRIRE Rhône-Alpes

Consequences:

The accident claimed no victims. There was however substantial vegetation and material damage. Since the transfer of chlorine was suspended the previous day, the quantity of chlorine released into the atmosphere was estimated to be 475 kg. The chlorine transport line was severed at its end at a length of 64 m into 3 segments and fragments were projected mainly into:

- The user site:
  - ✓ a 20 to 30 kg fragment at 180 m from the severed zone of the chlorine transport line ,
  - ✓ a 10 to 20 kg fragment at 150 m.
- In the field where the chlorine transport line is located :
  - ✓ a 30 to 40 kg fragment at 85 m,
  - ✓ a 10 to 20 kg fragment at 70 m.
- On the road heading North:
  - ✓ a 10 to 20 kg fragment at 60 m.

Source: DRIRE Rhône-Alpes

Near the rupture zone closest to the manufacturer site, the immediate environment was covered with a dark red powder mainly comprising ferric chloride ($FeCl_3$) contained in the passivation film of the pipeline.

The damage recorded (helical shaped fragment, pressure wave, etc.) confirms the explosion's detonating nature.

Source: DRIRE Rhône-Alpes

Source: DRIRE Rhône-Alpes

There was also substantial damage to the nearby facilities:

✓ The damage on the siding and the rainwater gutters of a building in the user site can be attributed to the blast. One of the parts projected damaged a roof.

✓ Four other pipelines (100 mm diameter) – two nitrogen (13 bar, 2 to 3,000 m^3/h), one oxygen (10 bar) and one not in service (under nitrogen at atmospheric pressure) – installed on the same above-ground rack as the chlorine transport line, were also damaged (deformed, pierced, folded, etc.). However, no leaks were observed.

✓ Electric, telephone and fire alarm cables that ran along the rack were also severed, thus cutting all communication links between the two control rooms of the manufacturer and user sites.

Among the several observations made during the enquiry, one of them included the presence of considerable amounts of solid deposits in the exploded pipeline.

Source: DRIRE Rhône-Alpes

European scale of industrial accidents

By applying the rating rules of the 18 parameters of the scale made official in February 1994 by the Committee of Competent Authorities of the Member States that oversees the application of the 'SEVESO' directive, and considering the available information, the accident can be characterised by the following 4 indices:

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

The 475 kg of chlorine released represent 1.8 % of the corresponding Seveso threshold (25 t), i.e. level 3 of the "dangerous substance released" index (Q1 parameter).

ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

The explosion is due to the presence of a **mixture of hydrogen** (fuel) **and chlorine** (combustive-fuel), **ignited by prolonged increase in temperature** (ignition source). Detonation was amplified by the reflection of the pressure wave on the closed end valve.

- The presence of chlorine is obvious due to the activity of the site.

- The presence of hydrogen is due to complex physico-chemical phenomena:

An incident in **April 2001** (branch connection left open during rainy season while the chlorine transport line had been place in a trough during the replacement of an insulation valve of a pressure sensor) allowed humidity to enter and hydrate a part of the ferric chloride contained in the passivation film. This hydrated ferric chloride was deposited in its solid form in the operational pipeline between April 2001 and May 2005.

Source : DRIRE Rhône-Alpes

On **18 May 2005**, the transmission cable of the heating system temperature regulation sensor of the chlorine transport line was severed at the user site (while lifting the protective slabs), and the incident was neither reported nor the fault indication signal properly processed. Tests show that the cutting of the cable caused the electric tracing system to heat (folded back in absence of danger).

On **20 May 2005**, the shutdown of the first chlorination reactor at the user site caused the automatic chlorine supply valve to close. The excess pressure in the chlorine transport line subsequent to the valve's closing resulted in the shutdown of the second reactor by the high temperature warning alarm. This reactor was re-started around 2:00 and it shut down around 8:45.

Between 8:45 and 9:27, the pressure of chlorine in the pipeline recorded by the three sensors dropped from 4.2 to 3.5 bar. Both the automatic and manual end valves were shut and the flow of chlorine was stopped at 9:45. Between 10:55 and 11:25, the chlorine transport line was degassed to the treatment column designed for this purpose. The site that remained in an atmosphere of chlorine at a residual pressure of 0.25 bar was supposed to be safe during the 10 day shutdown for maintenance.

From 18 to 21 May 2005, since the temperature of the electric tracing system was not regulated the ferric chloride temperature in the pipeline increased to about 90℃. Investigations revealed that from 40℃ onwards, the deposit sampled from the pipeline mainly comprising ferric chloride hydrated by 6 water molecules ($FeCl_3$, 6 H_2O) started to liquefy. This resulted in a very corrosive acidic solution (hydrochloric acid formation - HCl) that reacted with the steel in the pipeline to form hydrogen (H_2) as illustrated by the following chemical reactions:

$$FeCl_3 + 3\ H_2O \leftrightarrow Fe(OH)_3 + 3\ HCl$$

$$Fe + 2\ HCl \rightarrow FeCl_2 + H_2$$

- The absence of transfer of materials by the pipeline limited heat transfer and resulted in the accumulation of an explosive mixture Cl_2 / H_2 (20%) that required a very small amount of energy (about 12 micro joules) to ignite it. Maintaining a maximum temperature of (90°C) for 72 hours created a possible ignition source of the accident.

ACTION TAKEN

After assessing the safety of the partially destroyed structure whose temperature remained especially high after the accident and implementing the initial emergency measures such as clogging the severed parts of the pipeline, detailed investigations were carried out at both the sites to study a host of hypothesises regarding the origin of the explosion: chlorine and CO mixture, mixture of chlorine and organic compounds, etc.

At the start of July, the operator was required to clean the inside of the pipeline twice by shot-blasting with granite aggregates in a flow of dry nitrogen. The pipeline was inspected using endoscopy and radiography to assess the efficiency of the cleaning operations. The first cleaning operation resulted in the removal of about 3,000 kg of solid material mainly composed of ferric chloride, nitrate and iron sulphate. The second cleaning operation was made mandatory given the results of the endoscopy inspections and resulted in the removal of 4.4 kg of residual deposit.
Since the precise mechanism behind the formation of these deposits (over and above the past deposits) is unknown, endoscopy inspections are regularly carried out at the 6th month, at the 12th and then annually.

The operator replaced the last 400 meters of the pipeline damaged by the accident, with the new part of the pipeline subjected to several inspections especially a weld test and inspection. After assembly, the inside of the whole chlorine transport line was cleaned and dried.

Lastly, a risk analysis using the safety review method on the diagrams brought forth reliable solutions to avoid such an accident from reoccurring and led to several improvements:

✓ Replacement of heater cables with self regulating cables (temperature attained can be regulated) fitted with an independent high temperature safety device

✓ Addition of extra skin temperature sensors along the chlorine transport line

✓ Installation of an emergency stop function with decompression of the chlorine transport line (closing valves at the ends and opening the degassing valve to the chlorine gas treatment system)

✓ Modification of the degassing valve safety position: it will be opened upon loss of fluid or will have an emergency air network.

Besides these above mentioned measures, the danger study is updated and completed by analysing the best technological solutions to transport chlorine.

Further to these operations carried out between June and August 2004, the conditional re-start of activity was authorised by the prefectural order dated 09/08/2005 based on the DRIRE report dated 28 July 2005 and after the approval of the Isère regional hygiene committee that had an exceptional meeting for this purpose on 8 August 2005.

LESSONS LEARNT

Subsequent to this accident, the Eurochlor recommendations were reviewed to adapt the safety conditions of a pipe to the time period during which the transfer operations are stopped:

✓ short term stoppage (few hours): always avoid contact with humidity.

✓ prolonged stoppage or operation: it is recommended to purge the collector to limit the quantity of residual chlorine followed by flushing with an inert gas. It is also recommended to stop tracing to avoid any supply of energy.

For "long" pipes, these recommendations figure in the GEST 7325.

Before taking into account the technical knowledge gained on the operation of facilities using chlorine, the organisational and human factors involved in this accident must be underlined, especially in terms of:

✓ Repair-work whose impact could still be felt after several years

✓ Removal of facilities from service during shutdown for maintenance

✓ Treatment of failures and alarms.

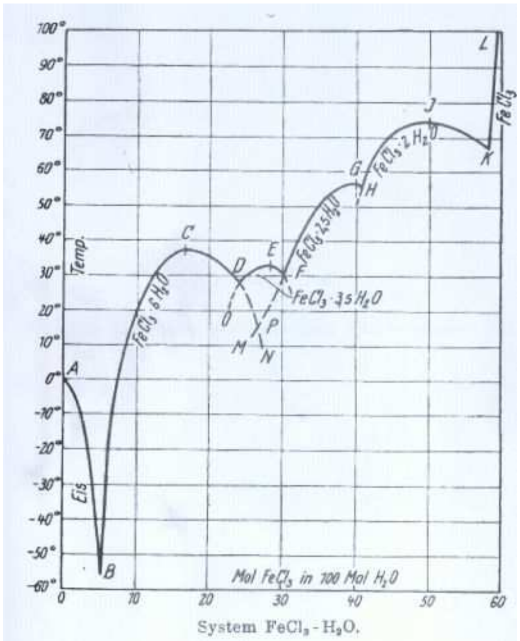
As part of the feedback for chlorine transport pipelines, this accident brings to light three critical points:

✓ Monitoring temperature even during shutdown periods

✓ Protection of structures against humidity

✓ Inspection of pipeline surfaces especially to check for formation of deposits.

Several technical recommendations have been proposed by experts following this accident:



Source : Kirk-Othmer encyclopedia of chemical technology ; vol 6 ; 2004 (fifth edition)

✓When the chlorine pipeline is removed from service, it must not be kept under chlorine but purged before being isolated or stored under a low flow of nitrogen. It is also advisable to stop all tracing systems to avoid input of energy;

✓ Avoid bringing the structure in contact with water

✓ Monitor the condition of the inner walls of the pipeline: presence of hydrate is a potential and permanent source of hydrogen and is thus risky given the very low ignition energy of the chlorine – hydrogen mixture (around 12 micro joules as per stoichiometrical studies). The absence of hydrate must be regularly checked for as the formation of ferric chloride protects the steel (passivation) only if $FeCl_3$ does not lead to the formation of hydrates whose fusion may occur in a wide range of temperatures starting from –55℃ (see $FeCl_3$ and H_2O solid and liquid phase diagram) resulting in a corrosive liquid that rapidly eats away the steel by releasing hydrogen.

✓ It is important to have dry chlorine and maintain activity in the structure to avoid any accumulation of dangerous substances.

Given the extensive use of chlorine, this accident feedback must be used not only for pipelines but also for all types of sites and facilities (reactors, bottles, etc.) that are likely to work with chlorine and be accidentally exposed to humidity. For these facilities, the appearance of a dangerous phenomenon like the ones given below depends mainly on the following factors:

- $FeCl_3$ formation on the container walls
- Ratio of the surface covered by $FeCl_3$ and the container volume
- Humidity level inside the container
- Treatment procedures applied to any likely cleaning operations of the hydrated $FeCl_3$ with an alkaline solution
- Fusion of ferric chloride hydrate that may occur in a wide range of temperatures (from –55℃) and result in acid attack with the formation of hydrogen
- Hydrogen and chlorine concentration ratio influencing combustion conditions and speed
- Renewal rate of gas phase of the container
- Mixture initiation energy coming from varied sources such as turbulent gas flow in the pipeline, impact on the walls, etc.
- Container drag factor likely to influence the combustion speed

Agrochemical/Phytosanitary products
Storage
Toxic fumes
Extinguishing water
Confinement
Organisation / Procedure
Lift pump
Partitioning
Automatic extinguishing
Anti-intrusion device

Fire in a pesticide warehouse

27 June 2005

Béziers – [Languedoc-Roussillon]

France

THE INSTALLATIONS IN QUESTION

Installation concerned

The company formulates, packages and stores solid and liquid agropharmaceutical products (insecticides and fungicides). The production site at Béziers includes 2 operational units:

- the liquids unit (water and solvent-based)
- the solids unit (powders and granulates).

Main products stored at the site

	Risks
Liquid and solid substances (classes T', T, others)	Emissions of toxic products in case of fire Pollution from firefighting water

The company operates 9 production and/or storage building located on 17 ha of land:

- a set of buildings designated " A,B,C,D " and a building " R " dedicated to the powder and granulate activity,
- a set of buildings designated " G,H,I " dedicated to the liquids activity,
- a active material and/or finished product storage building, designated "T"
- an above-ground flammable liquid storage facility, and several buildings used for offices, cafeteria and laboratory...
- a 10,000 ml firefighting water recovery basin and two 600 m3 water reservoirs.

THE ACCIDENT, ITS BEHAVIOUR, EFFECTS AND CONSEQUENCES

The accident

On June 27, 2005, at around 3 am, a fire started in a building consisting of 4 sub-assemblies (A,B,C,D) for the formulation, packaging and storage of agropharmaceutic products.

The site employs a guardian. No personnel were at the site at the time.

At 3.05 am, the guard was alerted by the fire alarm in the workshop D1 (upper part of zone D). After confirming on site that there was actually a fire, he contacted both the fire and rescue department and the executive on duty at around 3.10 am.

The firemen at the scene at 3.25 am noted that zones B,C and D of the building were engulfed in flames. At around 3.40 am, the fire had spread throughout the building.

The operator activated the site's retention system by blocking the rainwater network (inflatable balloons). The gas at the site was shut off at around 4.10 am, then at 4.25 by the gas utility.

As the site had no electrical backup, the site had no power.

The Special Intervention Plan was put into motion at 4.22 am. A safety perimeter of 400 m was established in cooperation with the prefectoral authorities and the various administrative services concerned, based on the quantities of products involved and evaluated by the operator and the duration of the fire (instead of 200 m provided for by the danger study).

Following a failure of the site's lifting pump, the operator contacted a specialised company which arrived at 5.33 am to pump the polluted firefighting water into the retaining basin and transfer it into the hermetic 10,000 m3 basin designed for this purpose. A fixed pumping installation was then set up at the end of the day.

The firemen conducted aerial reconnaissance by helicopter at around 8.15 am. A significant plume of smoke extended all the way to Coursan (roughly fifteen kilometres in the direction of Narbonne).

The fire was brought under control at around 8 am although continued burning until late morning. The building was destroyed.

The Special Intervention Plan was lifted at 16.15 am.

A judicial inquiry was opened prohibiting intervention on the building's "remains". Products continued to smoulder under the watchful eye of the firemen until July 4th and then by the operator thereafter.

The slow combustion lead to more or less important wisps of smoke with the fire restarting occasionally.

Buildings on fire

Consequences

On the day of the fire, Monday, June 27th, 2005, the operator presented the Classified Installations Inspectorate an evaluation of the situation and the compensatory measures to be implemented in order to limit the environmental impact and prevent increasing the damage.

Findings:

- widespread fire in building A, B, C, D,

- recovery of the firefighting water in the lower portion of the building by pump trucks from the specialised company into the 10,000 ml basin after a back-up pump was put into service,

- the site was secured by special balloons to block the firefighting water and by closing the natural gas supply line,

- significant release of smoke,

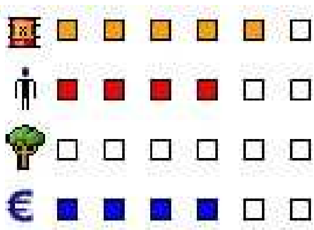
- precise list of physico-chemical data and quantities of products in building A,B,C,D not immediately provided by the operator to the intervention services due to the electrical and computer networks being unavailable.

Plume of smoke rising above the site

European scale of industrial accidents

By applying the rating rules of the 18 parameters of the scale made official in February 1994 by the Committee of Competent Authorities of the Member States that oversees the application of the 'SEVESO' directive, the accident can be characterised by the following 4 indices.

Dangerous materials released
Human and social consequences
Environmental consequences
Economic consequences



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

The 87.73 tons of toxic substances involved in the fire represent 44% of the corresponding Seveso threshold (200 tons – toxic substances), which equals level 4 of the "quantities of dangerous materials" index according to parameter Q1 (Q1 between 10% and 100%).

The 98.92 tons of very toxic substances involved in the fire represent 495% of the corresponding Seveso threshold (20 tons – very toxic substances), which equals level 5 of the "quantities of dangerous materials" index according to parameter Q1 (Q1 between 10% and 100%).

The overall "dangerous materials released" rating is thus 5.

Parameter H7 of the "Human and social consequences" index is rated as level 4: 3,000 people were confined indoors for 12 hours ($5{,}000 \leq N \leq 50{,}000$ with N = number of residents evacuated or confined indoors > 2 h * number of hours).

Parameter €16 of the "economic consequences" rating is 4: an initial estimation evaluated production losses at 40 M€ (€16 between 10 and 50 M€).

ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

The origins and causes of the accident have still not been determined.

A judicial inquiry was conducted. The forensic police visited the site of the fire two times and the insurance company appointed experts to determine the cause. Several leads were explored:

- auto-catalytic decomposition of phytosanitary products,
- electrical short-circuit,
- gas leak,
- malicious mischief.

The auto-catalytic decomposition of products could lead to their ignition. However, it is generally a long process which always involves the release of fumes and odours. The guardian had passed by point D1 (upper part of building D) during his rounds at least 1 hour before the fire and had not noticed anything.

As far as the other hypotheses are concerned, neither the forensic police nor the insurance company experts were able to determine the cause of the fire, nor explain the speed at which the fire spread to the other buildings; possibly due to the lack of fire-break partitioning at the circulation alley level between buildings D and B.

During his round prior to the fire, the guard was supposed to open all the firebreak doors to facilitate the arrival of the first morning shift which starts at 5 am. The closure of these doors is triggered via a temperature fuse and not directly slaved to the fire detection system.

Firefighting water

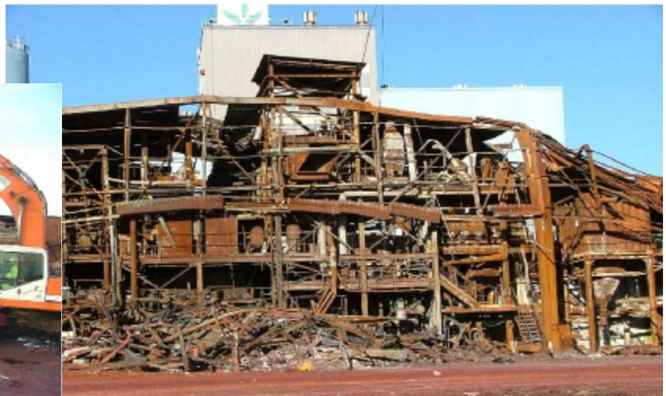
ACTION TAKEN

On June 28, 2005, the DRIRE proposed the Prefect of Hérault an emergency prefectoral order outlining the security of the site, monitoring of the environment and the conditions for restarting the units not effected by the fire.

In particular, the order required:

- the suspension of all the establishment's activities,
- the monitoring of the installations involved in the accident to prevent the fire from spreading to the adjacent installations,
- the control and protection of the site's installations, up to the re-establishing detection and extinguishing means, these means having to undergo prior verification before being placed back into service,
- the re-establishment of the site's electric and water networks so that they participate in the protection and alarm means,
- collect the firefighting water contained upstream of installations A,B,C,D and transfer them into the firefighting basin designed for that purpose,
- environmental monitoring including, as a minimum:
  - monitoring of the air quality near the site, at periods adapted to the evolution of the accident and meteorological conditions until the fire is completely put out,
  - monitoring of the quality of underground water at the site and soil and surface water pollution outside the site. This monitoring focuses on the chemical substances released during the fire.
- elimination of the firefighting water in a centre authorised to do so. All resumption of activity cannot be considered until 80% of the fire basin's capacity can be used,
- the demolition of buildings A,B,C,D and the removal of structures, rubble and remaining products to appropriate processing centres,
- submittal of an accident report in application of article 38 of the order of September 21, 1977.

Furthermore, on 7/07/2005, the operator was requested to have the sanitary impact of the fumes, released during the fire on the neighbouring populations, evaluated by a competent and recognised organisation.



Destruction of the burned out buildings

LESSONS LEARNT

Several lessons can be learnt from this accident:

✓ Concerning the fire:

- the fire's extremely rapid propagation to all the buildings placed side-by-side, while the products being stored were considered to be "flammables",
- the non-pollution of surface and underground waters; the measures in place functioned correctly despite the failure of the lift pump,
- the discomfort of numerous people induced by the smoke from the fire, although the toxicity threshold for irreversible effects was not reached,
- combustion residues such as dioxins, phtalates, PAH, phytosanitary products, measured in the environment (soil and plants) show values that are not significantly different from those normally found in an urban or industrial zone,
- the need to improve communication of the authorities with regard to the press and the public, notably during the first hours of an accident,
- the difficulty to quickly obtain a list from the operator regarding the type and quantity of chemical substances involved.

Spread of the fire to several buildings

✓ Concerning the measures implemented within the reconstruction framework:

- the concrete structure's 2-hour fire resistance for walls and frameworks,
- the partitioning of each building to separate the raw materials from the formulation and packaging area, as well as the finished product storage part by 2-hour fire break walls, rising above the roof at least 1 m,
- automatic fire extinguishing backed up by foam with a high expansion ratio for each of the cells created,
- firebreak doors slaved to the fire detection system,
- installation of anti-intrusion devices,
- installation of a back-up electrical substation.

Petrochemistry
Polyethylene
Ethylene
Rupture disc
Clogging / Fouling
Equipment failure
Organisation / maintenance fault

Release of ethylene to the atmosphere
July 21, 2005 and September 21, 2005
Saint-Avold – [Moselle]
France

THE INSTALLATIONS IN QUESTION

The site

The establishment, located in Saint-Avold in the *département* of Moselle, is part of a vast industrial platform spread over 340 hectares, and created in 1954. The platform includes a variety of activities associated with the chemistry and petrochemistry sectors. The petrochemical activity of the establishment was developed during the 1960s with an initial steam cracker and a polyethylene manufacturing unit commissioned in 1969.

With 900 employees in 2006, its activities today range from basis petrochemical products (ethylene, propylene, benzene, and styrene) to consumer plastics (polyethylene and polystyrene).

This establishment includes a number of installations subject to authorisation with public utility easement. It is classified high-level "SEVESO" owing to the quantities of dangerous substances manufactured and implemented (flammable and/or toxic substances).

The unit concerned

The unit involved is a continuous low-density polyethylene manufacturing unit (LDPE). It consists of 3 production lines with a total capacity of 765 tons of LDPE/day. The process implemented involves the high-pressure radical polymerisation of the ethylene:

$$n\ CH_2{=}CH_2 \xrightarrow[\text{Peroxydes (initiators)}]{\text{P>1000 b} \atop T \approx 150\text{ to }300\ °C} (\text{-}CH_2\text{-}CH_2\text{-})_n$$

Considering the exothermal character of this reaction and due to the extreme flammability of ethylene, this unit represents a particularly dangerous hazard.

A simplified description of the reaction is as follows (see figure 1): the ethylene undergoes polymerisation in a reactor pressurised between 1,000 and 2,200 bar and at temperatures ranging from 150 to 300 ℃. The pressure i s controlled by a valve located at the outlet of the reactor; this valve also is used to extract the reagent / polyethylene mixture. The mixture is then directed to the separator of the Medium Pressure Return line where it is separated into two phases (approximately 20% polymers and 80% ethylene as the conversion rate of the reaction is in the order of 20%). The polyethylene drawn from the lower part is then conveyed to the high then low pressure hopper. The ethylene is also conveyed with the polymer phase.

The largest fraction, the ethylene which exits the upper portion, is cooled then recycled by the MPR line to the intake of the secondary compressor.

The low polymers (greases) are extracted during the cooling of the recycled ethylene in the medium pressure return lines. These polymers are trapped in the tanks (grease cylinders) which are purged to the grease hoppers one after the other. The greases can then be drawn or reinjected to the low-pressure hopper.

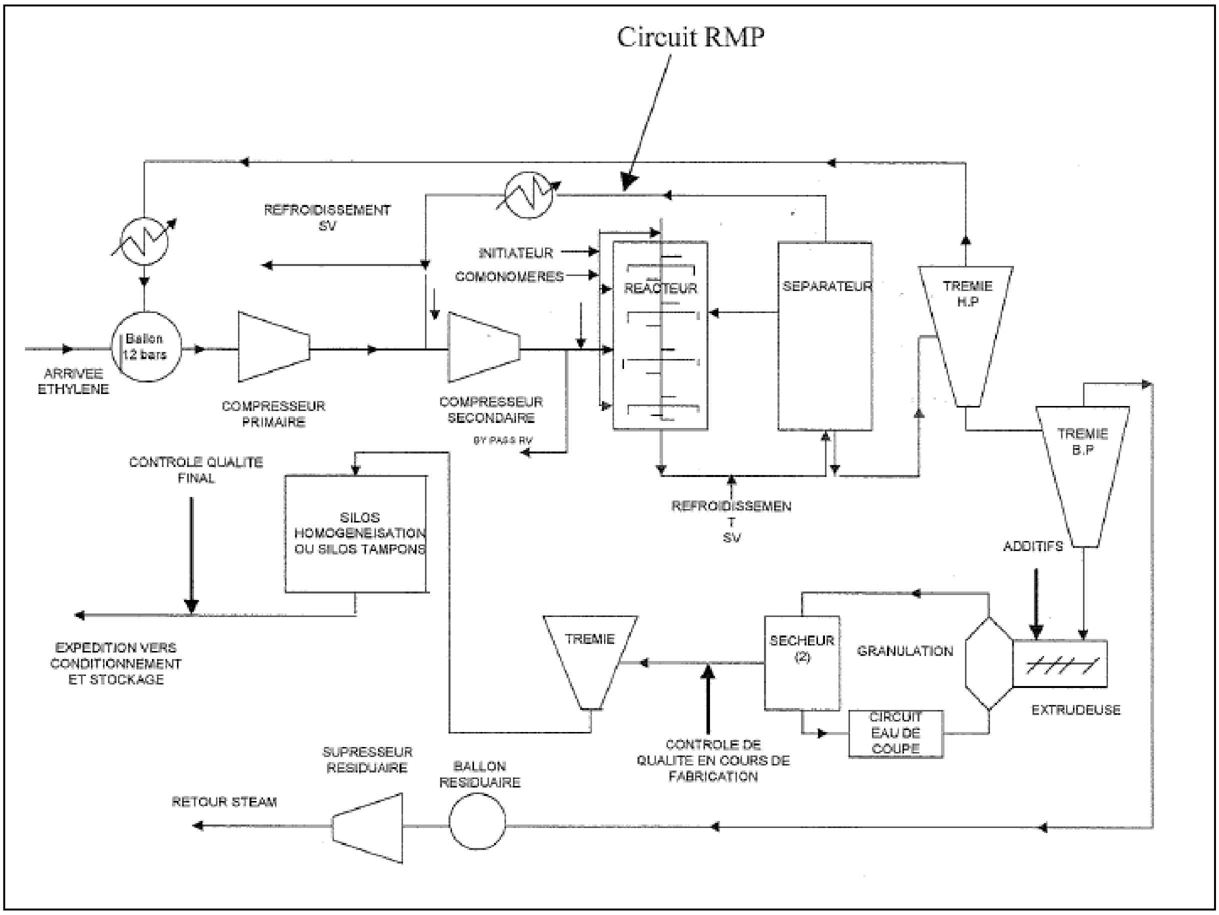


Figure 1: Simplified diagram of the process

THE ACCIDENTS, THEIR BEHAVIOUR, EFFECTS AND CONSEQUENCES

July 21, 2005: rupture of disc resulting in the release of 3.2 t of ethylene to the atmosphere

The accident:

On July 10, 2005, a leak was detected on the filling valve of a grease cylinder (MPR) on line 42 in the workshop; the cylinder was cooled down and was not in use pending servicing by the operating and maintenance crews. The repair took place July 20: the line was shut down for 4 hours for servicing, then restarted the same day at around 6 pm.

On July 21st, the primary compressor tripped two times due to a fault detected on the lubrication system of the compressor. Shortly after the line was restarted after the compressor tripped the second time, the pressure measurement on the inlet of the secondary compressor indicated a value in excess of 300 bar while the valve at the outlet of the primary compressor should have opened at 284 bar. In addition, the primary compressor should have tripped off automatically (standby) at 270 bar. This did not happen. Noting the abnormal increase in pressure, the operator switched to manual mode to reduce the pressure. Too late: the pressure increased rapidly to 310 bar causing the disc protecting this part of the installation (MRP) to rupture and the release of 3.2 tons of ethylene into the atmosphere.

The consequences:

The event did not have an impact on people or the environment. The conduit of the rupture disc is directed toward a 20-meter high stack. The cloud thus dispersed rapidly. Dispersion models conducted by the operator showed that the cloud did not fall to the ground and that its flammability limits were a few limits from the stack; concerning the risks of cloud exploding, simulations showed that the explosive mass in the ethylene cloud was too small (6 to 7 kg) to generate an explosion in an unconfined space.

European scale of industrial accidents

By applying the rating rules of the 18 parameters of the scale made official in February 1994 by the Committee of Competent Authorities of the Member States which oversees the application of the 'SEVESO' directive, the accident can be characterised by the following 4 indices, based on the information available.

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

The quantity of ethylene released into the atmosphere was evaluated at 3.2 tons. The upper classification threshold associated with extremely flammable gases is set at 50 tons. Parameter Q1 is thus rated as 3 (3.2 x 100/50=6.4%).

The incident had no human, social or environmental consequences. The economic consequences were well below the classification threshold.

September 21, 2005: rupture of disc resulting in the release of 1.4 t of ethylene to the atmosphere

The accident:

On September 21, 2005 at 6.15, line 41 of the polyethylene unit was shut down for programmed maintenance to be performed during the day. According to the established shut-down procedure, the reactor is rinsed automatically, and purged three times. Each purge (or flushing operation) is conducted in two phases:

- the ethylene reactor is pressurised to 600 bar with the secondary compressor,
- depressurisation to the MRP line.

During depressurisation of the first flushing operation, a rupture disc opened on the grease cylinder of the MRP line, resulting in the release of 1.4 tons of ethylene to the atmosphere.

The consequences:

As with the event which took place July 21st, this accident had no human or environmental impact (rapid dispersion at altitude and a quantity released less than that of 07/21).

European scale of industrial accidents

The accident can be characterised by the following 4 indexes:

The quantity of ethylene released into the atmosphere was evaluated at 1.4 tons. The upper classification threshold associated with extremely flammable gases is set at 50 tons. Parameter Q1 is thus rated as 3 (1.4 x 100/50=2.8%).

The incident had no human, social or environmental consequences. The economic consequences were well below the classification threshold.

ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENTS

July 21, 2005: rupture of disc resulting in the release of 3.2 t of ethylene to the atmosphere

The various investigations conducted following the accidents showed that two malfunctions were necessary in order for the pressure on the discharge side of the primary compressor to exceed 310 bar and lead to the rupture of the disc protecting this section:

- The primary compressor did not trip off at 270 bar as designed. The pressure control gauge was partially plugged, thus leading to a measurement taken into account by the controller that was actually lower than the actual pressure. The operator, having noted an abnormal pressure increase in the unit, switched the primary compressor control to manual to reduce the pressure. Switching to manual inactivated the automatic tripping mechanism of the compressor.

- The valve, theoretically calibrated at 284 bar, did not open at this pressure. This malfunction resulted from a maintenance operation during which the valve replacement procedure was not respected (calibration pressure > 310 bar).

The increase in pressure was thus an aggravating factor to these two malfunctions. The analyses following the incident tend to show that the increase in pressure was aggravated by an abnormally high level of clogging in the MPR section due to several days of operation without purging the grease.

It should be noted that the rupture disc was efficient in performing its role in protecting the equipment.

September 21, 2005: rupture of disc resulting in the release of 1.4 t of ethylene to the atmosphere

The release of the disc occurred following an increase in pressure in the MPR line during the reactor rinsing phase after the programmed maintenance shut-down. The dismantling of the equipment in order to replace the failed rupture disc revealed that the check valves on the MPR line were clogged with grease. In fact, during the production shut-down and subsequent rinsing operation, variations in pressure and output in the MPR line moved the accumulated grease onto the check valves to the point that they became plugged.

For line 41, a larger quantity of grease than normal is associated with the introduction of co-monomers, required to obtain certain quantities of polyethylene manufactured.

ACTION TAKEN

July 21, 2005: rupture of disc resulting in the release of 3.2 t of ethylene to the atmosphere

The operator was required to apply several provisions as stipulated by an additional prefectoral order:

- modification of the tripping conditions of the primary compressor so that this operation is active both in automatic and manual mode,

- fail-safe operation of the pressure measurement triggering the tripping sequence,

- Integration of the valve replacement procedure in the training and certification process,

- formalisation of grease cylinder operating rules to prevent clogging of the lines. Furthermore, the operator was requested to further complete its danger study with an analysis of the causes and consequences of the clogging in the MPR sections.

September 21, 2005: rupture of disc resulting in the release of 1.4 t of ethylene to the atmosphere

Reflective thinking regarding the technology of the check valves used was required to reduce the accumulation of grease in this equipment. This study lead to the removal of this equipment following risk analyses showing that their removal would not downgrade the unit's level of safety. These check valves were initially installed to ensure safety.

In addition, as proper cleaning of the installation has an impact on safety, formal procedures were drawn up outlining the type and frequency of the cleaning operations to be performed. These operations are now checked and recorded. Performance indicators were defined to determine the efficiency of these cleaning operations.

These provisions were registered by an additional prefectoral order.

LESSONS LEARNT

The first incident was an advance warning signal of the risk associated with the lines clogging with grease. The second incident only confirmed this risk by underlining that the equipment initially installed to provide a safety function, can also be responsible for causing incidents. These two events show the need to conduct risk analysis, including for the installation of "safety" equipment so that they do not add additional risks that are greater than those that they are intended to prevent.

The installation of safety devices must thus be prepared and be subject to safety analyses as any modification made to a dangerous installation, notably those classified as high-level SEVESO.

Furthermore, these two incidents illustrate:

- that switching an automated action to manual may inactivate an automatic safety feature.
- that replacing "ultimate" safety devices such as a safety valve or rupture disc must be governed by the strict application of clear and pragmatic instructions.

Release of sulphur dichloride and hydrogen chloride

April 26, 2006

Catenoy – [Oise]

France

Fine chemicals
Distillation
Pressure sensor
Control valve
Design / dimensioning
Lock-out/lock-out removal

THE CONCERNED INSTALLATIONS

The site

The chemical plant manufactures intermediate chemical products used in the synthesis of antioxidants that in turn are used to manufacture industrial and general consumption products in order to improve their performance characteristics (plastic materials, electric cables, and foodstuffs, etc.).

The site, which employs roughly 100 people, runs reactions in which phenol compounds are alkylated by isobutene, and then the resultant molecules are cross-linked by sulphidation using sulphur dichloride. The distillation columns used in these workshops, which include 20 to 40 theoretical platforms, can operate in vacuum up to 250 °C. The production equipment mainly includes around ten reactors ranging from 6 to 26 m^3.

The plant is subject to authorisation with public easement (AS) particularly for the storage of sulphur dichloride; the last prefectoral order governing the operation dates back to August 30, 1996.

The unit concerned

The sulphur dichloride (SCl_2) distillation unit involved in the accident comprises the following elements:

- a boiler with a 150 kg capacity
- a ∅ 300 mm distillation column comprising two layers each measuring 1.5 m high
- control equipment (steam supply valve, SCl_2 supply valve, etc.)
- safety equipment (process PLC, pressure and temperature sensors, pressure switch, …).

The sulphur monochloride and dichloride mixture delivered to the site is enriched with dichloride through continuous distillation; it is then stabilised with phosphorous trichloride (PCl3) before being transferred to the TBM6 [2,2’-thiobis (3-methyl 6-tertiobutyl phenol) or 2,2’-thiobis(6-tertiobutyl metacresol)] synthesis or sulphidation installations.

The operator monitoring the distillation of the crude dichloride is also in charge of:

- regularly inspecting the installation,
- recording production parameters
- adjusting the opening of the distilled dichloride filling valve to maintain the stability of the column's sensitive temperatures and to ensure a regular flow of distilled dichloride.

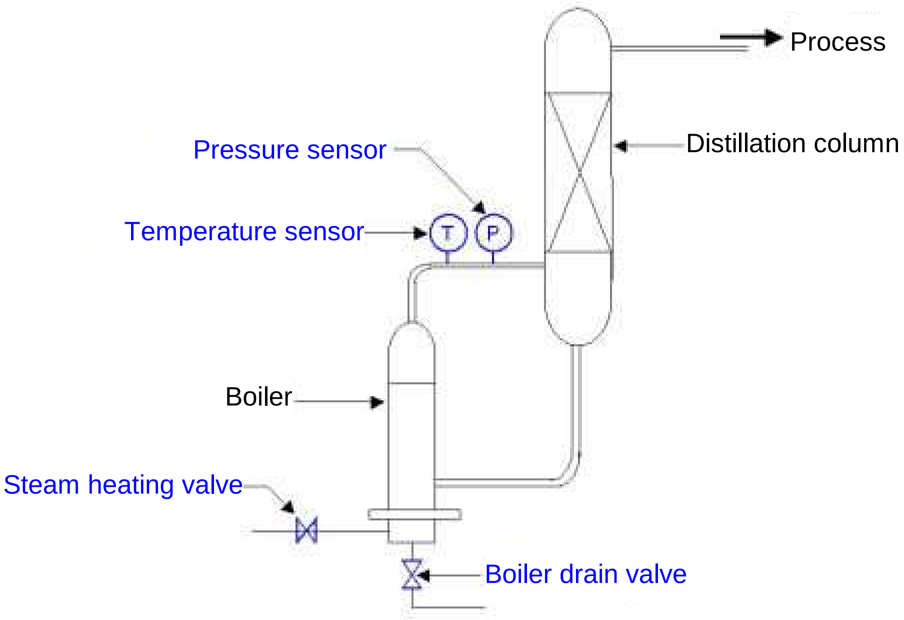
Distillation column

Sources: DRIRE Picardie

THE ACCIDENT, ITS COURSE, EFFECTS AND CONSEQUENCES

The accident

On April 26, 2006, the sulphur dichloride installation was operating normally.

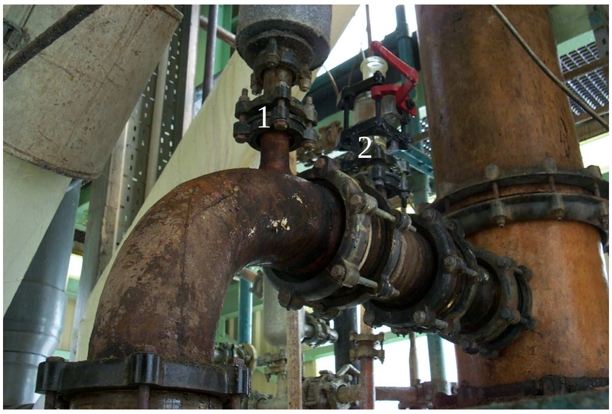


Boiler
Sources: DRIRE Picardie

At 7.50 am, an excess pressure of 108 mbar was recorded at the outlet of the boiler containing sulphur dichloride. The installation then automatically switched to standby mode owing the high-pressure safety system (threshold = 100 mbar). The sulphur dichloride supply and heating steam control valves closed and the sulphur monochloride circulating pump shut down.

In the absence of heating, the installation began to cool down (boiler outlet temperature 28℃ at 9 am) although the pressure sensor on the boiler's junction pipe and the distillation column still indicated a high pressure. The investigations showed that this sensor was faulty; a work order stipulating its replacement with an identical sensor was thus drawn up by the workshop supervisor.

At 11.30 am, with the installation still shut down (heating setpoint at 0%, valves closed), the maintenance technician observed that it was impossible to drain the boiler when attempting to remove the pressure sensor in place.



Branch connection exiting the boiler (*Sources: DRIRE Picardie*)

1 : temperature sensor
2 : pressure sensor

He also noted that the pressure sensor could not be dismantled from its shut-off valve as the connecting bolts had seized. As he was unable to forcibly remove this part of the installation without risking a rupture of the metal/glass interface, the technician removed the entire assembly, thus allowing air to enter the installation via the sensor's branch connection (ND 25).

At 11.50 am, a release of hydrogen chloride (HCl) was observed in the distillation workshop.

At 12.05 pm, the alarm was sounded after 3 alarm triggering points were actuated. Two water curtains were set up around the column.

At 12.20 pm, the establishment's internal contingency plan was put into action and the decision to evacuate the site and implement a third water curtain was taken.

At 12.25 pm, two individuals from a second team, assisted by a third, were able to shut off the steam supply.

The external emergency services arrived at the site at 12.40 pm.

The internal contingency plan was stepped down at 1.30 pm, after the situation had returned to normal and a series of atmospheric measurements had been taken.

Consequences:

- Environmental consequences

No direct environmental consequences were recorded. The atmospheric hydrogen chloride measurements taken outside the site did not indicate any accidental pollution; only 50 ppm was recorded in the distillation column.

The 150 m^3 of water used by the water curtains deployed to neutralise the acid cloud was recovered (pH = 7), distilled and recycled in the process.

- Human consequences

The three employees who had entered the building during the operation had suffered from irritations and were thus hospitalised less than 24 hours.

- Activity and economic consequences

The activity downstream from the sulphur dichloride distillation operation, namely the synthesis of TBM6, was shut down for 18 days. Operating losses were evaluated at 270 k€.

European scale of industrial accidents

By applying the rating rules of the 18 parameters of the scale made official in February 1994 by the Committee of Competent Authorities of the Member States that oversees the application of the ‘SEVESO’ directive, and considering the available information, the accident can be characterised by the following 4 indices.

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

As the materials sulphur dichloride and hydrogen chloride are designated in the Seveso directive with thresholds of 1 t and 250 t respectively, the "dangerous materials released" index is at least equal to 1 (parameter Q1).

As three employees were hospitalised less than 24 h, the "human and social consequences" index is equal to 1 (parameter H5).

As the internal operating losses associated with the accident are less than 0.5 M€, the "economic consequences" index is equal to 1 (parameter €16)

ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

Various investigations were conducted on the process, products and intervention procedures to determine the cause of the accident.

The tests conducted on the electrical portion of the faulty sensor showed that it had operated normally during the accident. The faulty pressure measurement most likely resulted from solid deposits of impurities on the sensor membrane (PCl_5, sulphur, etc.)

The fault tree compiled by the operator, and subject to critical examination by a third-party expert, shows a combination of several undesirable initiating events:

- **the presence of 150 kg of sulphur dichloride in the boiler during the maintenance operation (lock-out defects)**: the potential hazard subsists as it was not possible to drain the boiler due to the clogged bottom valve. The analysis highlighted the presence of glass debris (failure of the mounting of the packing support disk) mixed with product deposits (low-quality sulphur dichloride) was the reason for the clogging;

- **boiler reheating** : when the high-pressure level was detected (> 100 mbar), the steam control valve heating the contents of the boiler was shut by the process control PLC. Disconnection of the sensor during its replacement triggers a –25 mbar signal to be transmitted that controls the re-opening of the steam control valve and reheating of the boiler;

- **pressure sensor branch connection open** : as the corrosion of the threaded fasteners of the pressure sensor's shut-off valve had essentially welded it to the mounting piping, the operators disassembled the entire valve/sensor assembly so as not to risk rupturing the metal/glass interface. This operation was not compliant with the initial work order.

An accident fault tree is provided in the appendix hereto.

ACTION TAKEN

Technical action

The operator took several measures immediately to secure the sulphur dichloride distillation unit:

- **reinforcement of the lock-out/lock-out removal procedure** on critical installations, reminder of rules and responsibilities and definition of a checklist for "routine" operations***;***

- **replacement of a pressure sensor** by a sensor using the same technology;

- **complete cleaning of the installations*:*** neutralisation of acid traces on the outside of equipment and cleaning of clogging residues inside the installation;

- **operational control of the installation and interlocks;**

- **modification of the shutter / pressure sensor assembly.**

In the medium term, the operator shall implement the following safety measures:

- creation of a **pre-completed chemical lock-out form** in case of intervention on the distillation column, in order to outline the installation's lock-out problems;

- **retightening of the liner support platform fixtures** on the distillation column and **shut-down**, after exchange with the supplier, **stabilisation of the sulphur dichloride with PCl_5** in order to reduce or halt the generation of glass debris and product deposits;

- installation of a **fail safe loop** (pressure switch at top of column, safety relays and On/Off valve upstream from the steam control valve) **independent of the control** restricting automatic restart after the high pressure threshold has been attained (manual reset mandatory);

- **formalisation of the test procedure** of alarm triggering points.

- **definition of sulphur dichloride distillation procedures, in normal and downgraded situations**: description of actions to be taken in case the sulphur dichloride storage tank is overfilled, and restart of the installation after a shutdown and/or an intervention;

- **study of possible deviations and inherent risks in each stage of the dichloride transfer and distillation**.

In the longer term, complementary actions are planned, including:

- **overhaul of the work request procedure** to clarify the roles and responsibilities of the staff involved;

- including the retightening of platform fixtures of the column in the **maintenance programme**;

- implementation of a **fail-safe configuration in the safety system** capable of securing the installation when the high pressure threshold is reached;
- **modification in the assembly of pressure sensors installed** on pipes without shut-off valves.

Finally, the manufacturer intends to improve the distillation column's overall safety level through the implementation of the following measures:

- a SIL2 type **second fail safe safety system**; (SIL: Safety Integrity Level – characterises the quality of the safety chain).
- **pressure sensor and pressure switch assembled "directly"** on the ND50 glass tubes to prevent all risk of clogging. This system will trigger the installation's safety system from a new safety PLC and **4 new dedicated automatic valves**, including a steam valve;
- a **valve calibrated at 300 mbar** installed at the top of the column and dimensioned to address the supposedly radical phenomenon (maximum opening of the boiler's steam valve);
- **pressure testing** of the column conducted at 300 mbar;
- an **alarm reported** on the workstation of the operator dedicated to the sulphur dichloride.

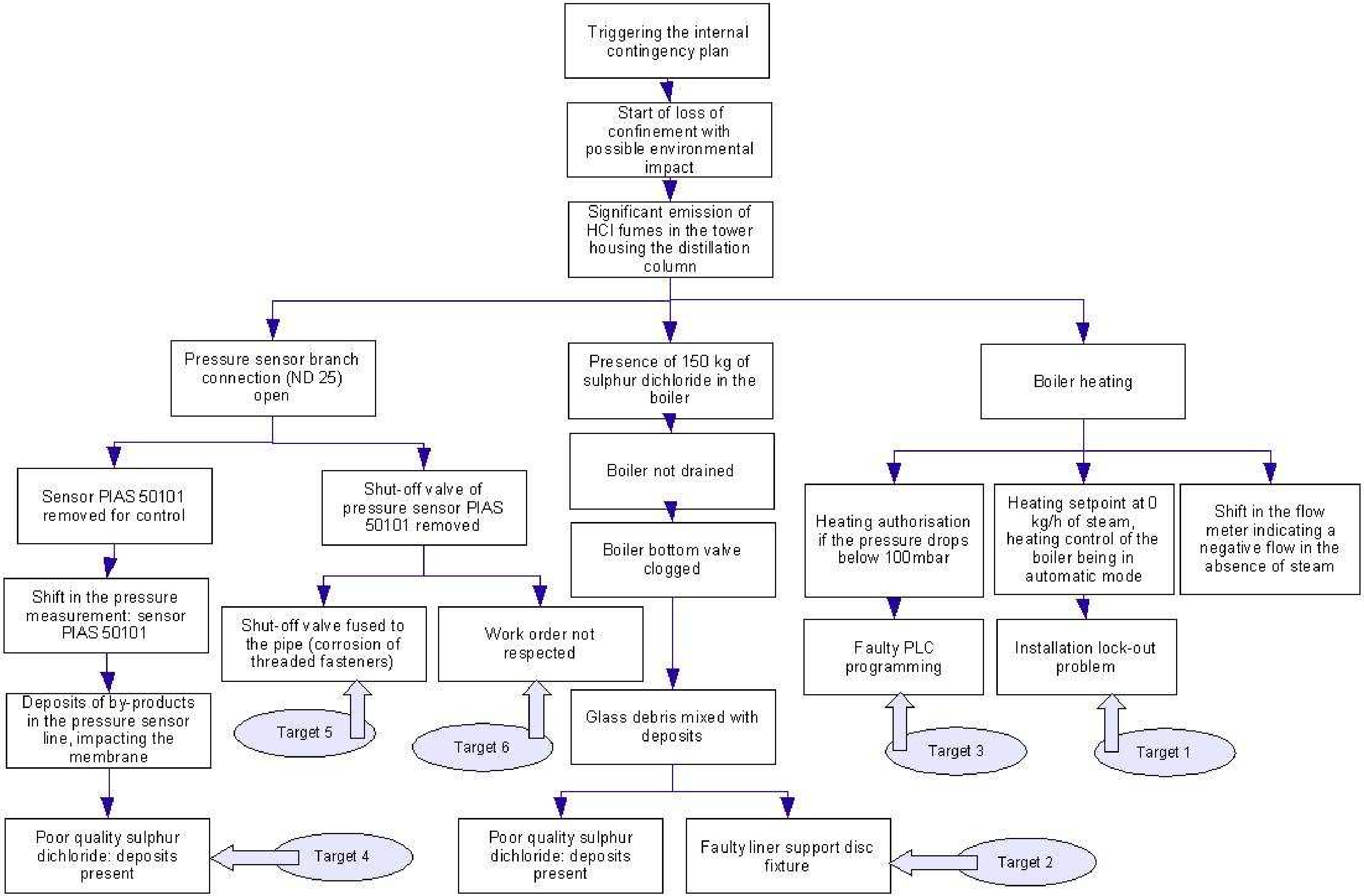
The cost of all these measures was evaluated at 93 k€.

LESSONS LEARNT

The accident, which occurred in an installation that had not been examined during the danger study, brought the following points to light:

- the importance of detecting, controlling and assessing the consequences of changes in the nature of stabilisers and other additives added to dangerous raw materials (sulphur dichloride) by suppliers. These modifications may be a source of triggering events (crystallisation and clogging in this case) and increased risk;
- Even if events that seem insignificant in the smooth running of the process such as the presence of glass debris from the lining of the distillation column coupled with the lack of a maintenance program on the production equipment (cleaning of the boiler) or safety equipment (clogging of the pressure sensor) do not directly lead to accidents, can have a considerable impact on the safety in downgraded modes;
- a routine, unusual or exceptional maintenance operation (replacement of a pressure sensor) must be subject to a complete prior risk analysis, in order to avoid creating conditions which could lead to an accident or aggravate the initial consequences. In case of dangerous substances, these operations must be monitored and re-evaluated according to the hazards of the intervention;
- the relative efficiency and the reliability of the procedures and more generally, organisational barriers (lock-out/lock-out removal);
- a control system (steam valve) for a process can in no way be considered a safety system and cannot be retained as such. In particular, the production PLCs follow logic and criteria which the intervention teams are not fully aware of and which do not necessarily take the downgraded modes and lock-out situations into account.
- the importance of installation design as early as the design phase (glass/metal interface);
- the importance of risk analysis and failure modes, as well as technical and organisational barriers, with maximum details, for the various "operating" modes.

APPENDIX: fault tree of the accident which occurred on April 26, 2006



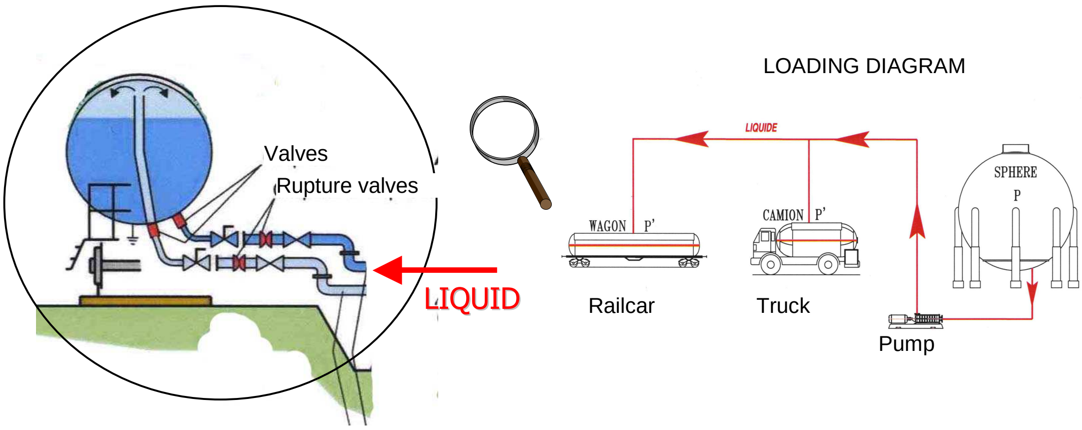
Release of LPG at a railcar tank
Loading station
March 21, 2005
Donges - [Loire Atlantique]
France

Release
LPG filling centre
Propane
Loading arm
Coupling
Corrosion
Underthickness
Chocks

THE INSTALLATIONS CONCERNED

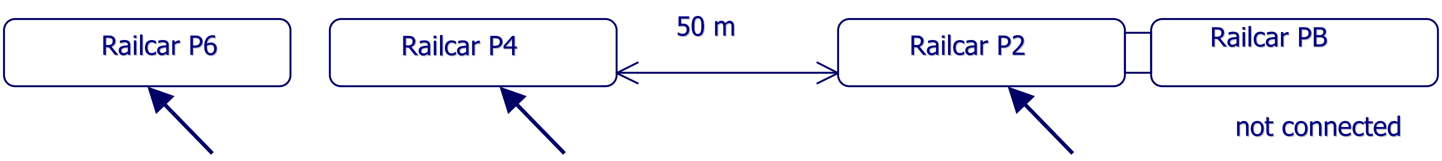
The release occurred at a railcar tank loading station in a liquid petroleum gas (LPG) filling centre supplied by a nearby refinery. The site's activity essentially involves the filling of trucks, railcars and gas cylinders from 2 spheres (butane and propane).

The railcar tank is filled with propane by the gaseous phase arm (spray filling), as shown in the diagram below:



THE ACCIDENT, ITS COURSE, EFFECTS AND CONSEQUENCES

The accident:



Four railcars were parked at the loading stations. The pump operator connected railcar P2 and began the loading operation.

The loading operation on railcar P4, located approximately 50 m, was nearing completion. The pump operator went to stop it.

When he returned to railcar P2, he noted that it had moved ripping away the loading arm.

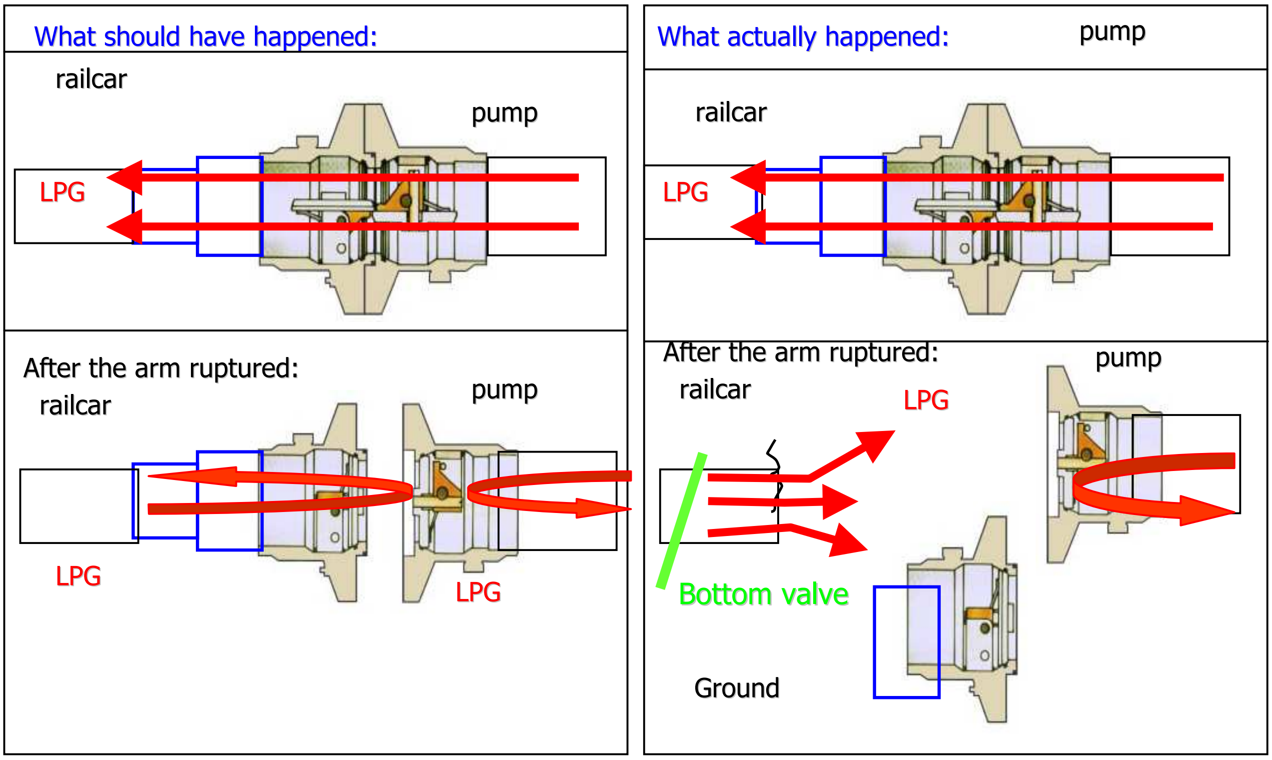
The slightly sloping track allowed the 2 hitched railcars (P2 and PB) to move, causing the threads on the terminal coupling of the transfer arm on the railcar side to rupture.

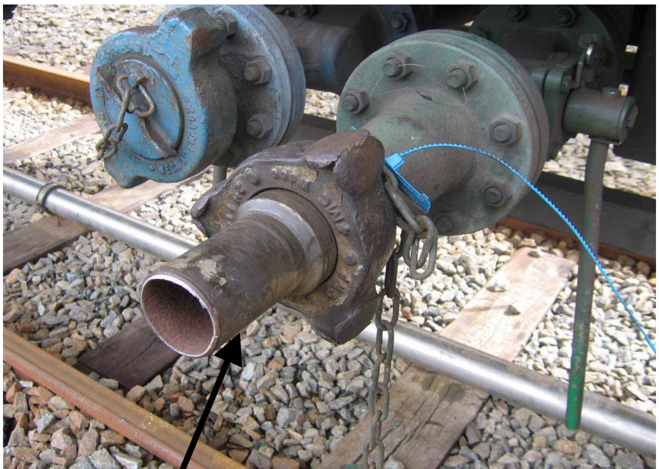
The safety valve on the loading station side was operational, and thus shut off the gas supply. The valve on the railcar tank side did not operate efficiently due to the severed coupling connected to the railcar.

The gas flowing from the railcar was able to be stopped by closing the tanker's bottom valve.

The consequences:

The incident had no consequence for the personnel present. Approximately 8 litres of liquefied propane was released, corresponding to the volume of the coupling that was severed.





Railcar tank side

Pump side

The severed coupling

Valve found on the ground

Valve closed

European scale of industrial accidents

By applying the rating rules of the 18 parameters of the scale made official in February 1994 by the Committee of Competent Authorities of the Member States which oversees the application of the 'SEVESO' directive, the accident can be characterised by the following 4 indices, based on the information available.

The parameters that comprise these indices and the corresponding rating method are available at the following address: http://www.aria.ecologie.gouv.fr
The level 1 rating for the quantities of dangerous materials released is attributed to the 8 litres of liquefied propane (parameter Q1).

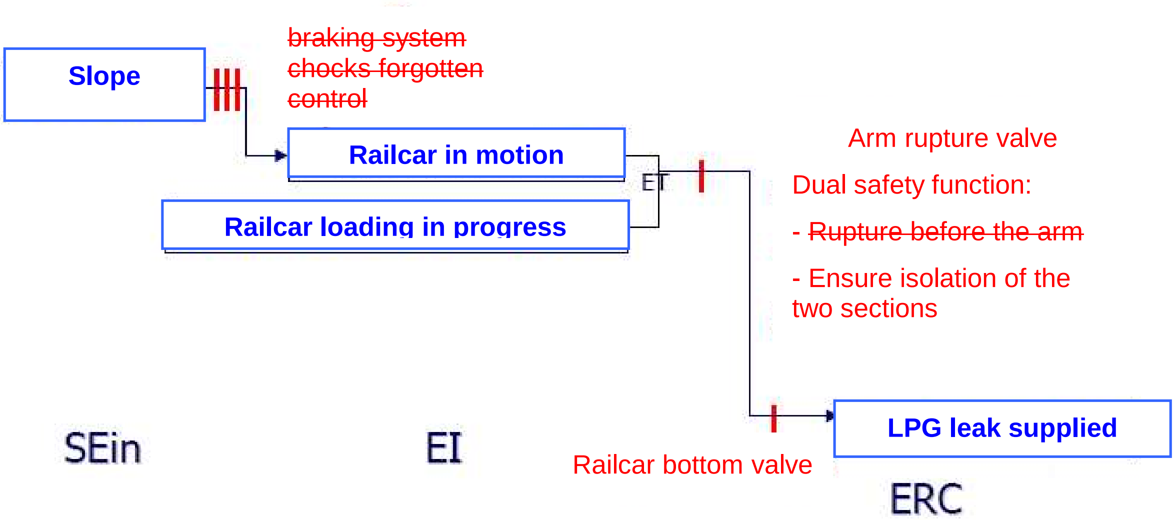
ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

The investigations conducted following the accident showed that the release of LPG resulted from a series of failures with regards to risk control measures (see diagram below).

The railcars' braking system was not in service, the chocks had been forgotten and no control was foreseen prior to the start of loading operations.

Furthermore, the coupling ruptured on the railcar side. The expert assessment conducted on this element showed an insufficient original thickness and extensive corrosion.

The railcar tank's bottom valve and the rupture valve (sphere side) operated, thus preventing the tank from draining completely and supplying the leak.



MEASURES TAKEN

Actions were promptly taken following the incident. Railcar loading operations were temporarily stopped pending the conclusions of the accident analysis and the modification of the loading procedure.

The main corrective measures adopted involved:

- ✓ Re-commissioning the railcars' pneumatic brakes
- ✓ The replacement of the couplings on all loading arms at the site following the expert evaluation of the arm involved in the accident
- ✓ An additional inspection by a second operator prior to the start of loading operations
- ✓ Additional training for operators

LESSONS LEARNT

The main feedback elements learnt from this event include the following:

- ✓ A second level inspection must be planned to ensure that the manual operations subject to human failure (placement of chocks, etc.) are performed correctly.
- ✓ The safety equipment may be faulty: a fail-safe configuration of the technical barriers, independent of one another, must be sought.

Spillage from a semi-buried jet fuel tank

December 30, 2005

Sainte-Marie – [Reunion Island] France

Spillage
Flammable liquid farms
Valves
Jet fuel
Human and organisational factor
Soil contamination
Level detection

THE INSTALLATIONS IN QUESTION

Sites involved:

Two hydrocarbon tank farms, located within the town of Sainte-Marie (Reunion Island) were involved:

1. Depot A

The establishment was created in 1975 for storing and distributing jet fuel (Jet A1) for an airport complex. The facility has 14 employees.

The site features 2 aboveground tanks and an underground tank, as well as a tanker truck unloading station. Jet A1 fuel is delivered to the aircraft via an underground hydrant system from the depot to the airport's tarmac, connected to the aircraft via servicers during fuelling operations, or by a fuel tender for small quantities.

This establishment is subject to authorisation regarding the legislation of the Installations Classed for the Protection of the Environment. It is classified low-level "SEVESO" owing to the products handled. The last prefectoral order authorising the establishment to operate dates back to October 10, 1990.

2. Depot B

The facilities at the depot B include two semi-buried tanks built between 1977 and 1978. These storage tanks are connected via an underground pipeline to the depot A's pumping system whose storage, unloading-loading and distribution installations are just next to the depot B.

An agreement was reached between the two storage facilities to transfer the operational responsibility of the storage tanks B to the depot A provided that a minimum storage quantity is maintained. The hydrocarbon transfer installation between the two depots (pipeline + pumps) was governed by a temporary authorisation order of September 23rd, 2004, which was not renewed.

The facilities involved:

Four facilities were involved in the accident:

- R2 tank (540 m³) of the depot A,
- the truck unloading station,
- the hydrocarbon transfer facility between the two depots (two 100 m³/h pumps each),
- the half-buried SEA2 tank (1,000 m³) of the depot B.

The accident occurred during a fuelling operation at the depot A.

THE ACCIDENT, ITS BEHAVIOUR, ITS EFFECTS AND CONSEQUENCES

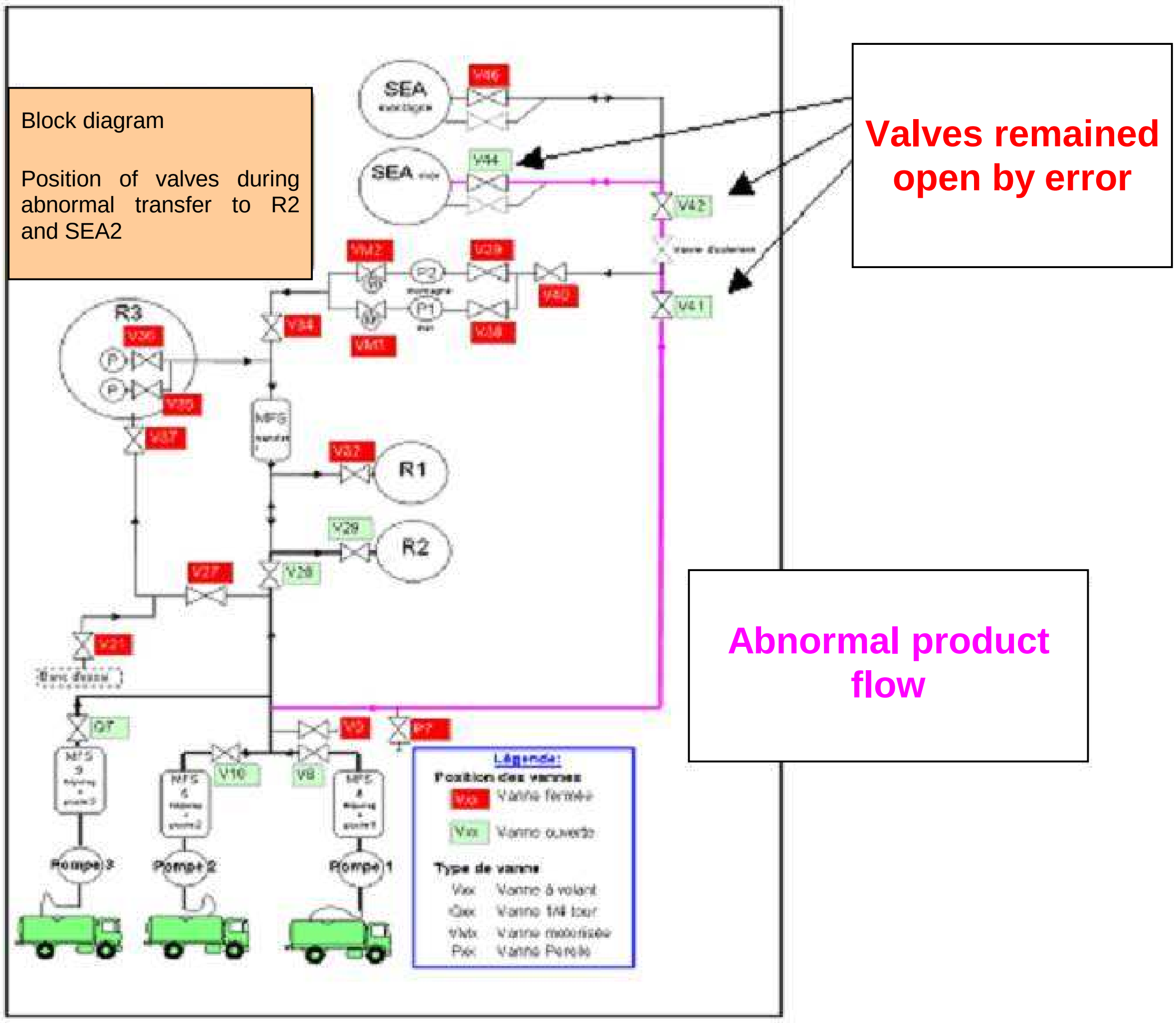
The accident:

On **Thursday, December 29th, 2005**, the SEA2 tank at the depot B was filled via the depot A. Upon completion of the filling operation, the worker of the facility A neglected to close the two valves on the interconnection piping and the supply valve on the SEA2 tank.

On **Friday, December 30th,** another worker at the facility A was instructed to fill one of the aboveground tanks of the depot A. The worker opened the valves to fill R2 aboveground tank although neglected to check if the valves, operated the day before had been properly closed. The unloading pumps propelled the jet fuel into the facility A's aboveground tank and into the SEA2 tank of the depot B.

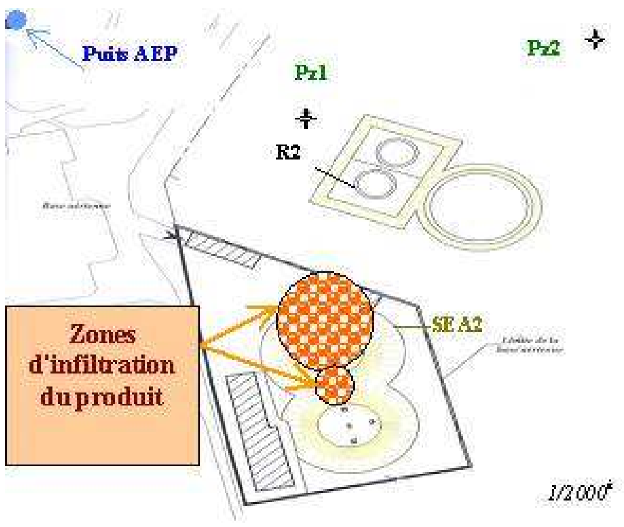
The high level detection safety alarm on the SEA2 tank did not function.

At around 8.30 am, a worker of the depot B noted jet fuel pouring from the two vents on the SEA2 tank: a phone call was made to the facility A to stop the transfer operation. The facility's emergency shutdown was activated which immediately stopped the transfer operation.



The consequences:

The quantity of jet fuel spilled was estimated at 33 m^3. The product spilled onto the surface covering the underground tank and seeped into the ground, outside the bund and into the common parking lot in the zone B. The parking lot is connected to a hydrocarbon separator, which quickly became saturated. Roughly one hundred litres of hydrocarbons thus entered the rainwater drainage system that spills into the sea.



Between 8.40 and 9.15 am, the personnel from both depots blocked off the rainwater drainage system with sand and other oleophilic materials. However, after noting that jet fuel was present in the rainwater network, a worker of the depot B rinsed the drainage system with a large quantity of water at around 9.30 am to prevent the risk of fire, causing sand and jet fuel to be conveyed toward the sea.

A drinking water well, located on zone B approximately 100-150 m downstream from the SEA2 tank, was shut down that same morning.

European scale of industrial accidents:

By applying the rating rules of the 18 parameters of the scale made official in February 1994 by the Committee of Competent Authorities of the Member States which oversees the application of the 'SEVESO' directive, the accident can be characterised by the following 4 indices, based on the information available.

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

With the 33 m^3 of jet fuel spilled, the "dangerous materials released" rating is thus 2 (parameter Q1).

Approximately 1,000 m² of soil required specific clean-up operations, thus resulting in a level 1 rating for the "environmental consequences" index (parameter Env13).

The cost of the environmental clean-up and rehabilitation operations is estimated at 800,000 €, i.e. level 3 for the "economic consequences" index (parameter € 18).

ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

The operating incident, which led to the pollution, was caused by a **series of human errors** committed during the verifications conducted prior to all tank-filling operations, **followed by the failure of a safety device**.

The series of human errors include:

- ✓ Failure to close the valves on the SEA2 tank upon completion of the transfer by the worker of the depot A who conducted operations on the day prior to the accident,
- ✓ Failure to inspect the position of the valves by the worker of the depot A in charge of the unloading tanker trucks before starting the operation.

The depot A had drawn up instructions for the transfer operations in May 2005, which did not include any verification to be conducted by the operator the site B. The personnel at the depot A were repeatedly advised of these instructions. However, it should be noted that the tanks of the depot A are filled very frequently (several times per day) while the tanks of the depot B are filled only twice per year. The above-mentioned instructions could not be put into practice by all of the workers at the depot A, as just one filling operation had taken place between May 2005 and the day of the accident. Since this operation is rarely performed, both the workers involved in the December 30th 2005 accident had overlooked the valve checking procedure associated with the transfer operations. The operator had not implemented special measures regarding the risks associated with this exceptional operation.

At the organisational level, the high level detector, installed on the depot B tank had not functioned due to faulty maintenance: new level detectors were supposed to have been installed but were not in place at the time of the accident.

ACTION TAKEN

With the advent of rainy season and given that the zone is located in a very rainy tropical region; tarps were installed at the site within 24 hours following the accident.

Following emergency operations that involved stopping the spillage, containing the fuel, shutting down the drinking water supply well, waste collection and the superficial clean-up of the zone, the initial digging operations were undertaken to remove the highly polluted soil as soon as possible. This required the tank's casing to be uncovered and the tank drained. The soiled earth was stored in bins on the site B prior to cleanup, and an initial review was conducted to determine the environmental impact of the accident. Research projects to install and equip a facility to treat the soil were undertaken.

▲ Product infiltration zones ©

▲ Digging operations round the SEA2 tank ©

Awaiting validation of these studies, operations at the drinking water station were suspended and the polluted soil, still in place, was covered with tarps to protect it from the cyclonic rains of the island.

An order was issued to define the restoration measures to be implemented.

In October 2006, the polluted soil storage bins were removed from the depot B parking lot to a site specially equipped to process the soil. The removal of the earth continued to the polluted zone. Treatment of the polluted soil using bio-venting was started in December 2006. Approximately 1,000 m^3 of soil has been removed since the day of the accident.

▲ Backfill around tank SEA2 ©

▲ Treatment of polluted soil ©

At the same time, the town of Sainte-Marie expressed its difficulty in procuring water following the closure of the well located at the depot B site. Analyses conducted by the operator of the depot A, and validated by the health authorities, show that the well water is not polluted. However, the drinking water supply well has not been placed back into service since the accident.

LESSONS LEARNT

The accident resulted from a series of malfunctions in the risk control measures (2 human errors + 1 organisational failure resulting in the malfunction of the level detector).

Several lessons can be learnt from this accident:

✓ The human factor:

- A decrease in worker vigilance when the same inspection is frequently repeated. A series of different workers, in charge of a similar inspection may increase the risk of negligence. Blindly "trusting" a colleague's verification is dangerous, even if it helps build relations and expedites operations. It is important to be vigilant during inspection.
- A procedure is not a protection against all human errors. Despite its circulation among staff, the reliability of an operating instruction remains fairly low.
- The frequency of an operation is to be considered in training and in the circulation of the instructions to workers. In small structures, where a verifier is not present, all operations at risk must be identified to determine those that require the implementation of passive measures.
- The consideration of the human factor is a necessary and crucial step.

✓ Concerning the organisational factor, this accident once again underscores the importance of inspection and keeping risk control measurements efficient over time.

In addition, the operators of both the depots A and B have started thinking along the following lines:

✓ The alarm report, in each of the structures, safety devices used in operations common to both depots,

✓ The exact description of actions to be performed by workers of both depots,

✓ The carrying out of common safety exercises.

No transfer operations have been conducted between the 2 depots since the accident.

Explosions followed by fire outbreak at an oil storage depot

December 11, 2005

Buncefield – United Kingdom

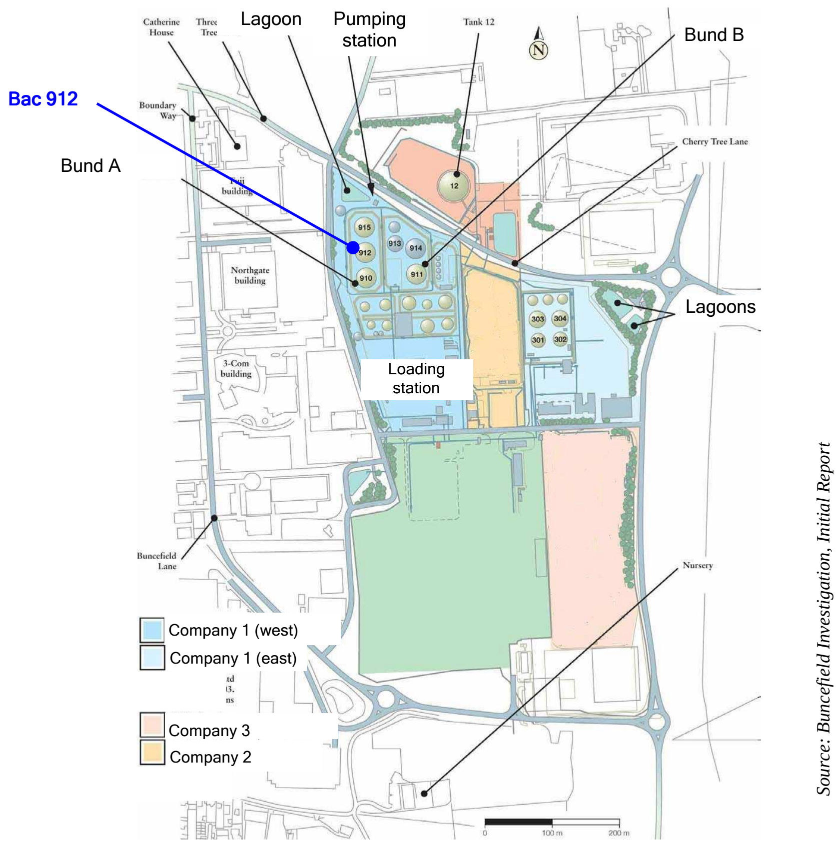
Explosion
Flammable liquids farm
Gasoline
Level detection
Automatic valve
Victims
Material damage
Transboundary effects

THE INSTALLATIONS IN QUESTION

The site:

The Buncefield oil storage depot, Great Britain's fifth largest storage site, is located 40 km north of London near the town of Hemel Hempstead, in Hertfordshire County. It typically stores 150,000 tons of fuel (gasoline, fuel oil, kerosene) for a total capacity of 273,000 m^3. This depot has the distinction of supplying kerosene via a pipeline to London's Luton and Heathrow Airports, the latter being Europe's biggest and busiest. These two sites have also implemented backup supply channels.

Diagram 1: Layout of the Buncefield Terminal



The oil storage depot houses three companies (see Diagram 1) and comprises three supply pipelines and two distribution lines. The company site where the accident occurred is divided into two sections as follows:

- The eastern part contains 7 fuel oil and kerosene tanks, totalling a capacity of approximately 26,000 m^3.
- The western part covers 16 fuel oil and gasoline tanks, for a total capacity of some 58,000 m^3, along with the truck filling stations, pipeline reception installations with 3 smaller admixture tanks and the control room.

This company operates around the clock, 24 hours a day.

Located between the eastern and western sites of the company incurring the loss, lies the oil storage depot's second firm, which is authorized to store up to 70,000 tons of fuel. Towards the south-eastern portion of the site, the 3rd company's depot has been set up with a total storage capacity for 75,000 tons of gasoline.

THE ACCIDENT, ITS BEHAVIOUR, ITS EFFECTS AND CONSEQUENCES

The accident:

- ***Sequencing of events:***

Beginning at 7:00 pm on December 10, Tank 912 with a floating screen, located in the sector of the first company's storage area A, received a delivery of unleaded gasoline via pipeline at an inflow rate of 550 m^3/hr.

December 11:

- At midnight, the storage site was closed and inventory verification was underway.
- At 3:00 am, the Tank 912 level gauge indicated a stable volume at 2/3 capacity, while supply delivery was ongoing at the same flow rate.
- At 5:20 am, Tank 912 began to overflow and a high-concentration air/fuel mix started to form.
- At 5:50 am, the parallel supply delivery of another tank was halted and the inflow rate of Tank 912 reached 890 m^3/hr, with the tank's supply valve remaining open.
- At 6:01 am, the first and most powerful explosion occurred, followed by a fire that spread to 21 of the facility's large storage tanks, as a direct result of the primary explosion, which detonated at the level of the Fuji and Northgate parking lots (see Diagram 1) located near the corresponding buildings. The explosion was heard at a distance of up to 160 km. British geological surveying teams would classify the seismic effects of the event at a 2.4 reading on the Richter scale.
- At 6:08 am, the emergency/rescue services were notified.
- At 6:27 and 6:28 am, two subsequent explosions occurred.
- At 9:00 am, the emergency response coordination team met.

Photo : www.buncefield-oil-fire-hemel-hempstead.wingedfeet.co.uk

Photograph 1: Devastated building at the terminal site

On December 12 at noon, the fire reached its maximum intensity; the fire extinction water supply mixed with fuels overflows the retention units. On December 14, additional and sizable leaks were detected at the retention areas and products from the site flow beyond facility boundaries.

Foam liquids were brought onsite and mixed with water pumped out of the Grand Union Canal located 3 km from the disaster zone. This operation, planned to commence at midnight, had to be postponed due to concerns over a possible environmental impact, especially out of concern for potential water quality impacts. More specifically, some of the extinction foam used contained perfluorooctane sulfonate (PFOS), a water and oil repellent, known to be a persistent, bioaccumulative and toxic substance and an endocrine disruptor. Nonetheless, given the state of emergency regarding the need for extinction resources, British authorities decided to implement these foams.

Fire-fighters began combating the blaze on December 12 at 8:20 am using 6 high-pressure water pumps capable of projecting 32,000 litres of water and foam liquid per minute. Within a few hours, while half of the tanks onsite were ablaze, crews succeeded in containing the fire. By the beginning of the evening, operations were suspended due to the explosion risk.

Over 600 fire-fighters then worked together to pour a tremendous quantity of foam onto the terminal in order to suffocate the flames. They finally extinguished the fire after some 60 hours of fighting, yet on the morning of December 14, vapours emanating from one of the larger tanks that until then had been spared from the conflagration caught fire. This outbreak however could be contained by the crew until extinction due to the lack of fuel source.

Emergency services declared the fire extinguished on December 15. In all, 786 m^3 of foam liquid and 68,000 m^3 of water (53,000 m^3 from supply sources and 15,000 m^3 recycled) were used and 30 km of pipes placed into service. At the height of fire intensity, 180 emergency personnel, 20 vehicles and 26 pumps were deployed.

Photo credit: www.buncefield-oil-fire-hemel-hempstead.wingedfeet.co.uk

Photograph 2: Pipes supplying water to emergency teams

Emergency units had to cope with several difficulties during their mission. First of all, fire fighting equipment had been destroyed by the explosions. The site's water supply reserves could not be used due to destruction of the pumping station located north of retention zone A (see Diagram 1), which had enabled managing onsite water flows. The northern lagoon (fire extinction water supply) had also incurred serious damage. No onsite means of extinction could be employed by fire-fighters on this sector of the terminal. Moreover, the site was covered by a mix of extinction water and fuels flowing out from tanks, thereby hindering access to the various installations.

- ***The main explosion:***

Despite the erroneous information provided by the tank's level indicators, temperature recordings measured within the supply pipeline and inside Tank 912 subsequently enabled confirming that this tank had in effect been filled.

At 5:30 am, tank capacity had been reached and by 5:38 the cloud that formed at the tank base was already visible on video recordings and extended 1 m in thickness, increasing to 2 m by 5:46 am. The tank had thus started to overflow and the explosive cloud that had gathered was spreading over the entire site covering a surface area of 80,000 m². At 5:50 am, the cloud had already moved beyond the company's perimeter; the ensuing explosion was much more violent than the UVCE (Unconfined Vapour Cloud Explosions) type phenomenological models would have predicted:

- **700 to 1,000 mbar at the level of the ignition zone (Fuji and Northgate car parks)**, according to the initial report issued by the British Experts' Committee assigned the Buncefield accident, **whereas calculations based on a mathematical model would have yielded 20-50 mbar;**

- 7-10 mbar at a 2-km distance from the site.

According to surveillance camera videos, the first and most powerful explosion, which occurred on the Northgate parking lot, would have been preceded by another smaller-intensity explosion 1 or 2 seconds prior.

Other lesser explosions occurred subsequently.

The consequences:

- ***Material consequences:***

The blast from the explosion caused **sizable damage within a 800-m radius:** shattered windows, doors broken, the warehouse wall completely destroyed, the roof on a neighbouring house blown off, etc. Cars parked nearby were burned.

On the site of Company No. 1, the damage inventoried consisted of:

- Western sector: All primary storage tanks were destroyed by the fire, except for 2 smaller tanks and 5 small vertical cylinders which incurred minor damage;
- Loading station (western sector), located approximately 200 m from the storage centre: the siding was damaged, but the trucks present remained by and large intact;
- Control room (western sector), also located 200 m from the storage centre: the steel-framed building with panels displayed no effects on its partition walls, yet the interior suspended ceilings revealed some damage;
- Eastern sector: tank roofs experienced structural impacts due to the blast from the explosion.

On the site of the second company, 4 tanks were destroyed by the fire and another smaller tank damaged. Company No. 3 sustained fewer losses.

The houses lying closest to the terminal were heavily affected and residents had to be temporarily housed elsewhere during repair work. A total of 300 other dwellings incurred more minor damage.

- ***Human consequences:***

Of the 43 accident victims, the majority sustained cuts due to broken glass; one was more seriously injured and suffered respiratory problems due to the effects of environmental pressurization. All 10 employees present onsite at the time of the accident were safe.

- ***Environmental consequences:***

Impact on air quality

A tremendous black cloud containing irritating substances rose more than 300 m off the ground and propagated over the southern part of England, migrated over France's Brittany and Normandy coastal regions on December 12, 2005, before moving southwest in the direction of Spain.

Local authorities advised residents living near the terminal to remain indoors; 2,000 individuals were evacuated and then authorized to return home the same evening. England's M1 motorway connecting London with the Midlands remained closed for several days out of fear of repeat explosions.

According to the Health Protection Agency (HPA), the smoke plume was primarily composed of carbon monoxide, carbon dioxide, nitrogen dioxide, volatile organic compounds and polycyclic aromatic hydrocarbons. A portion of the smoke plume generated by the fire rose in altitude and, carried by wind currents, reached France. The French monitoring networks reported that indicators in the country's metropolitan areas reached by the cloud did not reveal any significant degradation in air quality attributable to the accident. A French health and safety institute concluded that, given the smoke plume's composition and level of atmospheric dispersion, the Buncefield fire should not have any adverse health impact on the French population.

Impact on soil and water

A portion of the extinction water could not be contained onsite and flowed into the natural environment, polluting the soil and both surface and underground water resources.

Boreholes were drilled on the terminal site and around its periphery to obtain a reading of the pollution of surface soil layers as a result of the presence of hydrocarbons and fire extinction water.

Once the accident was over, a quality tracking system was implemented for surface water and groundwater within potentially-impacted zones in order to determine the effects of this accident over the short and long term as well as to discern the pollution extension mechanism. In this aim, a large number of piezometers were installed. Pollution due to hydrocarbons and residue from fire fighting foam was detected in groundwater beneath the Buncefield fuel depot and within a radius of more than 2 km to the north, east and southeast.

As an ancillary incident, 800 m^3 of previously-stored extinction water were inadvertently conveyed to a treatment plant and then discharged into the River Colne, a tributary of the Thames. An investigation was conducted following this incident.

Furthermore, some of the liquid foams used contained perfluorooctane sulfonate (PFOS), a water and oil repellent that incites the spreading of fire extinction foams. This product is persistent within the natural environment, a bioaccumulative agent and an endocrine disruptor. Its presence in surface water was investigated for the first time as a consequence of the Buncefield fire. PFOS was indeed detected in small quantities in water extracted from both the Ver and Colne Rivers a few days after the accident. No direct impact could be discerned and a monitoring program was introduced to measure all environmental impacts related to this substance. The potable water threshold of 3 µg/l was not reached in the analysis performed on water intended for human consumption.

- ***Financial consequences:***

The total cost of this accident is still not known in definitive terms yet should exceed 750 million euros; the rebuilding of terminal installations would have amounted to 37 million and the product loss value estimated at 52 million. Other companies located within the industrial zone also sustained substantial damage: some twenty businesses employing a total of 500 personnel were destroyed, while another sixty firms accounting for 3,500 jobs incurred major damage.

European scale of industrial accidents:

By applying the rating rules of the 18 parameters of the scale made official in February 1994 by the Committee of Competent Authorities of the Member States which oversees the application of the 'SEVESO' directive, the accident can be characterized by the following 4 indexes, based on the information available.

The parameters which compose these indexes and the corresponding rating method are indicated in the appendix hereto and are available at the following address: http://www.aria.ecologie.gouv.fr/

The index relative to quantities of hazardous substances equals 5 since approximately a third of the 35,000 m^3 of hydrocarbons stored onsite at the time of the accident escaped or were destroyed in the fire (parameter Q1). Parameter Q2 relative to the quantity of substances that actually contributed to the explosion in TNT equivalences has been rated at a level 3 given that major damage could be observed at distances of up to 800 m.

The index relative to human and social consequences is evaluated at 6 since 4,000 people were forced out of work as a result of damage caused by the explosion on buildings belonging to some 80 companies. The 2,000 nearby residents evacuated from their homes for a half-day yields a level 5 for the H7 parameter and the 43 injured victims reflect a level 4 for the H4 parameter.

The index relative to economic impacts also equals 6, given that the total cost incurred due to the accident should, in all likelihood, wind up topping the 750 million euros.

Since the environmental impacts were not precisely known (i.e. pollution of the water, air and soils), the corresponding index value cannot be determined.

THE ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

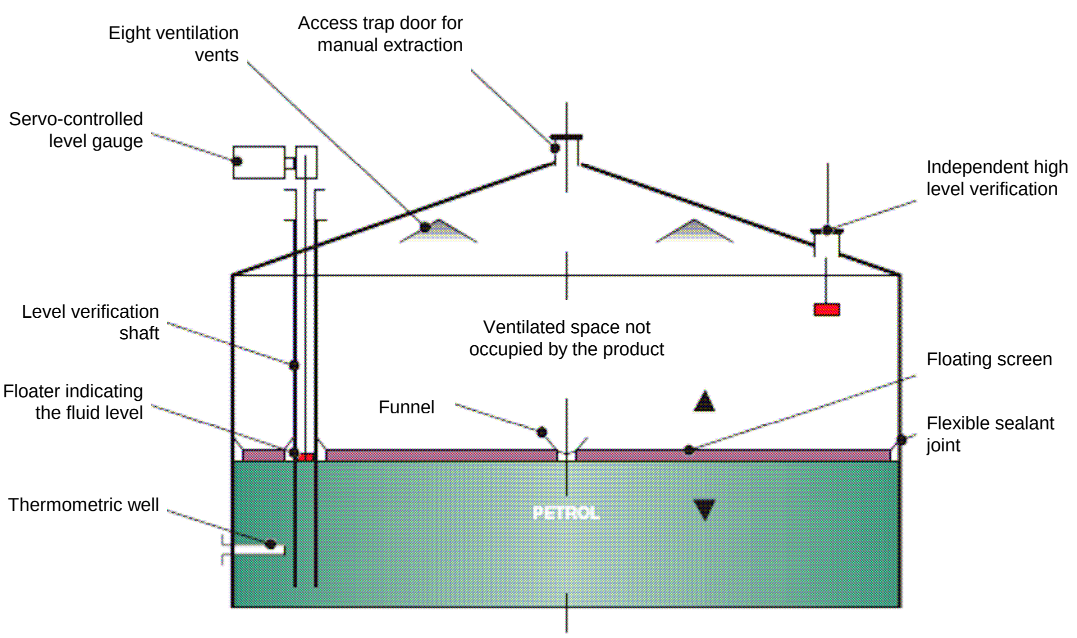
Control and measurement system installed on the tanks:

Tank 912 was equipped with a wide array of measurement instruments: fluid level, temperature, etc. This equipment was connected to an automatic tank gauging system common to all tanks located on the Company 1 site. Data recordings were transmitted and verified within a control room where a single operator is able to activate various remote-controlled valves. The **automatic tank gauging system** also makes it possible to interpret information and correlate it with critical event scenarios, which if detected by the system trigger an alarm. All measurement readings are recorded, thereby creating a system that relies upon a large amount of input data.

The tank had moreover been equipped with an **independent, "high level" control system** with both a visual and sound alarm that at the same time closes the pertinent set of valves on the piping network. An alert is sent to the instrumentation consoles and computer monitoring system of the carrier, who must then also proceed with closing the client's distribution valve.

Moreover, a control room switch allows cancelling the transmitted signal sent to the fuel supplier during the "high level" test periods. When placed in the active mode, a red indicator lights up on the control panel.

Diagram 2: Control instrumentation present on Tank 912



Source: Buncefield Investigation, Third progress report

Accident causes:

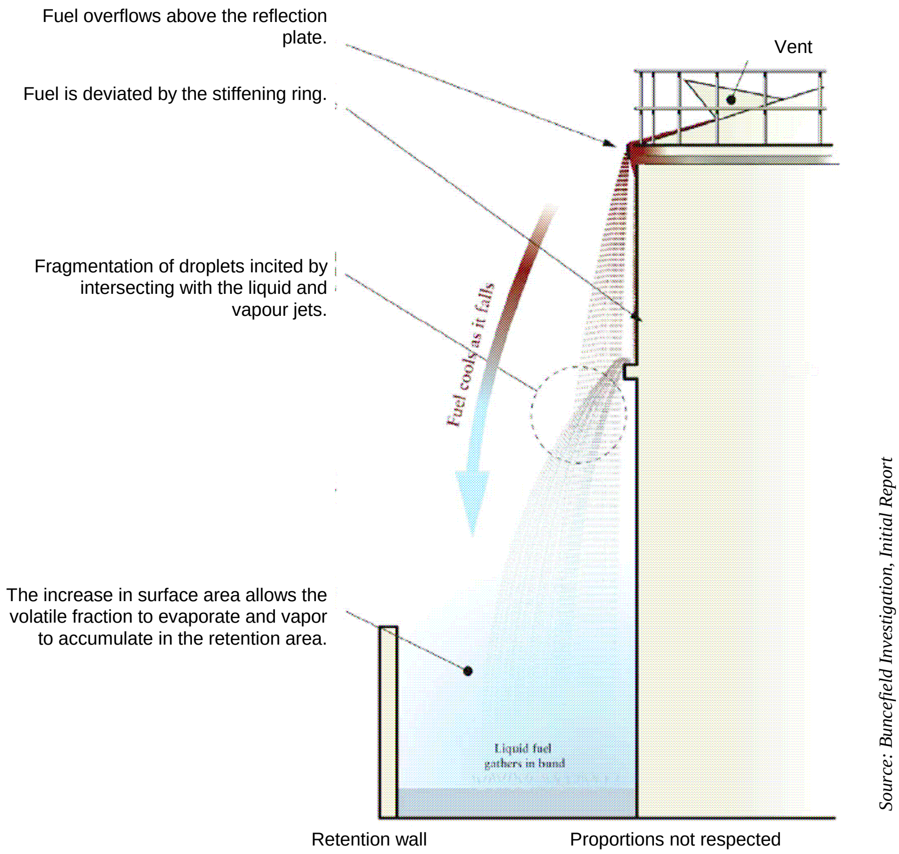
Neither of the two automatic level detection systems within the tank, as detailed above, was operable, and the gasoline supply into Tank 912 was not shut off. An expert evaluation was conducted to determine the reasons for malfunction of the automatic control and tank gauging systems. Following tank overflow, an explosive cloud formed and then spread over the site.

The information stemming from the gasoline distribution control system indicates that no high-level alarm from the first company's western site had been received. It was not possible however to test the high-level control gauge nor even verify the state of cables between Tank 912 and the substation, due to the extent of damage sustained. The high-level gauge could be located and assessed.

The first and most violent explosion occurred at the level of the Fuji and Northgate parking lots, completely devastating this part of the site. By spreading over this uncluttered zone, the necessary explosive conditions (i.e. a concentration lying between the lower explosive limit - LEL - and the upper explosive limit - UEL) were in fact attained. Gasoline vaporization was facilitated by 2 factors:

- Initially, yet to a more minor extent, product flow deviation by means of a tank stiffening ring (see Diagram 3).
- But more importantly, the high concentration of non-stabilized butane (10%) in this type of "winter" fuel incited both a high amount of gas evaporation even at relatively low temperatures (high vapour pressure: 70 - 100 kPa) and the formation of a butane cloud (estimated at several tons, given the quantity of gasoline that poured out).

Diagram 3: Tank 912 overflow phenomenon



An estimation of effects from excess pressure at the level of the Fuji and Northgate parking lots (700 to 1,000 mbar) is not consistent with current understanding of the UVCE phenomenon (modelled level: 20 to 50 mbar).

In its report entitled "*Buncefield Explosion Mechanism - Advisory Group Report*" released on August 16, 2007, the MIIB (Major Incident Investigation Board) group of experts forwarded the hypothesis of an acceleration in the flame front caused by turbulence created when moving past the alignment of landscaped alleyways.

Two hypotheses have been adopted for the actual cloud ignition locations: either the backup generator booth or, more likely, the emergency pump utility room upon start-up of the site emergency backup system.

ACTION TAKEN

Subsequent to this accident, an independent commission was set up in order to pursue investigations on the causes and consequences of the terminal explosion: "Buncefield Major Incident Investigation Board" (MIIB). One of the key emphases consisted of understanding the phenomenon that occurred and the set of circumstances that led to such unexpected over-pressurization effects.

From a more technical standpoint, various operations were performed onsite in order to limit secondary pollution and facilitate site access, particularly for the purpose of conducting the necessary research:

- Fire extinction water and other polluted water that could have been contained onsite was discharged during the three-week period following the accident and then stored on various sites. The 12,000 m³ of the most polluted extinction water were treated by the reverse osmosis process. The less polluted water (4,000 m³) was stored while awaiting an adapted form of treatment.
- The site was cleared to facilitate access. In February 2006, retention zone A, which includes Tank 912, was made accessible for the first time. The presence of inflammable vapour was subjected to monitoring.
- The southern part of the terminal, which sustained less damage, was renovated during the month of August to enable discharging stored fuel supplies. The third company based onsite undertook, in September 2006, transfer operations necessary for continuing with the tank investigations. It is anticipated that site installations will be fully dismantled by the end of 2007.

The British Ministry of the Environment launched, as a first time initiative, a national campaign of PFOS analysis in groundwater, with 150 measurement points already selected. The Ministry is also working on producing a modelling software to predict the evolution of pollutant flows in aquifers.

British authorities started disseminating, as of February 2006, to all operators of English installations similar to the Buncefield fuel terminal a list of safety actions to be performed immediately (operational safety, personnel training, management system robustness, effective introduction of best practices regarding precautions, emergency intervention and accident response actions, etc.). Inspections were thereafter scheduled in order to verify installation compliance and the adequate implementation of intended safety measures, along with publication of an analysis report. Other recommendations were subsequently disseminated, focusing on proper operating techniques for safety equipment and barriers (pipelines, tank overflow prevention, valves, retention basins, etc.).

Once this set of tasks had been accomplished, MIIB published several documents offering feedback on this accident:

- 3 progress reports on the investigation into the Buncefield accident: *Progress report Buncefield*, (February 21, 2006); *Second progress report* (April 11, 2006); *Third progress report* (May 9, 2006).
- *"Recommendations on the design and operations of fuel storage sites",* March 29, 2007.
- *"Recommendations on emergency preparedness for, response to and recovery from major incidents*", July 17, 2007.
- *"Safety and environmental standards for fuel storage sites - Buncefield Standards Task Group (BSTG) - Final report",* July 24, 2007.
- *"Buncefield explosion mechanism - Advisory Group Report"*, August 16, 2007.

Following this accident, inspections were also conducted inside fuel storage terminals in France and other European countries.

LESSONS LEARNED

Although the survey and investigation reports have not all been issued, a number of lessons can already be drawn from this accident.

First of all, the potential of a very extensive explosive cloud forming must not be overlooked when predicting hazardous phenomena, and precautions relative to possible offsite ignition sources must be anticipated. This approach can be justified even more vigorously given that the products involved are highly inflammable. Moreover, understanding the explosion phenomenon of an inflammable cloud needs to be sharpened in order to better predict the over-pressurization effects being generated.

This accident raises various organizational aspects as well, i.e.:

- ✓ Contractually speaking, fuel storage sites are given limited manoeuvring room regarding the quantities of product they receive; they are not in a position to refuse delivery and are thus faced with tight logistics constraints and very narrow safety margins.
- ✓ Buncefield terminal installations and associated infrastructure were not recent. Had they been sufficiently well maintained?
- ✓ Were operator qualifications and knowledge of hazards adequate?
- ✓ Would the involvement of several entities (terminal operator, pipe carrier) have exerted an influence over general safety management functions?
- ✓ The good working order and potential to perform periodic inspections (by both operators and competent authorities) with respect to monitoring data recordings, detection and alarm systems, both in terms of prevention and in the event of an accident.
- ✓ Heightened vigilance during transfer of the non-stabilized "winter" type products and products with high butane concentrations (specific to Great Britain).
- ✓ Gap between the evolution of the sinister visible on the CCTV and the personnel's response.

From a technical point of view, many aspects need to be pursued and improved on sites such as Buncefield, namely:

- ✓ Electronic monitoring/verification and associated alarms on the tanks and pipes to provide appropriate alerts in the event of malfunction;
- ✓ Detection of inflammable vapours immediately adjacent to tanks and pipes;
- ✓ Reactions upon detection of abnormal conditions, such as the automatic closing of supply valves and pipeline inflow valves;
- ✓ The extent to which auxiliary tank components serves to avoid or contribute to formation of an inflammable vapour cloud (e.g. stiffening ring);
- ✓ The place and/or means for protecting backup installations;
- ✓ The structural integrity of confinement facilities and the proper design of retention basins.

The human consequences could have taken dramatic proportions, yet the time and day of the accident kept the number of people located near or on the specific site, which is typically extremely busy, quite low. Furthermore, the issue of urbanized areas located around high-risk sites such as fuel terminals once again gets raised.

This version is not yet finalized and includes information available through October 8, 2007.

Release of liquid and gaseous hydrocarbons by the valves of the atmospheric distillation tower of a refinery

07 August 2005

La Mède – [Bouches du Rhône]
France

Accidental release
Refinery
Atmospheric distillation
Hydrocarbons
Start-up
Valves
Alarms
Human and organisational factor
Overfilling of unit

THE INSTALLATIONS IN QUESTION

Site

The facility concerned is located since 1935 in the La Mède site between the towns of Châteauneuf-les-Martigues and Martigues, on the southern banks of the Berre lake at about 40 km to the west of Marseille. The site covers 250 hectares in the lower part of a rocky dale open to the east. This refinery has an annual crude oil refining capacity of 8 million tonnes. It converts crude oil into fuels (LPG, petrol, gas oil, kerosene), domestic and industrial fuel oils and also manufactures non-energy products such as sulphur, road asphalts, high-gravity gasoline (naphtha) and propylene. This facility mainly includes all standard crude oil refining units (atmospheric distillation, vacuum distillation, catalytic cracker, catalytic reforming, isomerisation, and alkylation).

Unit involved

The unit involved in the accident is the C1 atmospheric distillation tower commissioned in 1968 and located in the eastern side of the refinery.

Crude oil enters the main tower of the unit at a temperature of 380 °C. It is then refined and divided into 6 main fractions ranging from the heaviest by-product exiting from the bottom of the tower to the lightest product exiting from the top of the tower.

The atmospheric distillation tower is fitted with five safety valves whose released waste is not recovered by the flare network.

THE ACCIDENT, ITS BEHAVIOUR, ITS EFFECTS AND CONSEQUENCES

Background

The units in the eastern sector have been de-commissioned since 27 July 2005 due to a social conflict. The resumption of operations was decided by the staff on Saturday 6 August in the morning. The various units were all re-started at the same time.

The operating procedures used on site are of the "Operguid" type. Since the unit was not drained during its shutdown, it was started as per the "on level" procedure.

Accident

On 07 August 2005 at 4.46 p.m., the valves of the atmospheric distillation tower opened causing the liquid and gaseous hydrocarbons to be released from the top of the tower for 5 minutes.

Since the facility was stopped "on level", crude oil was already present in the tower at 50% of its maximum level at the bottom of the tower.

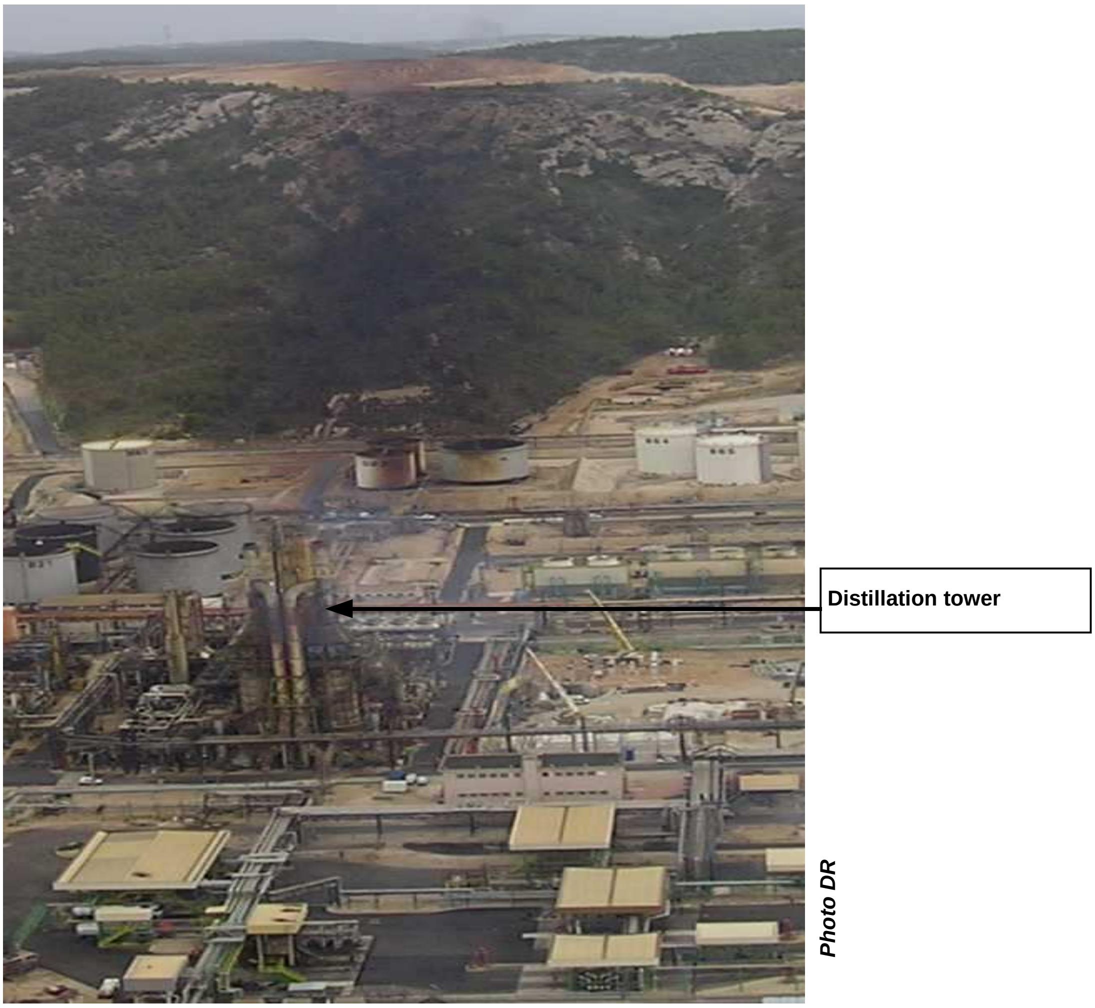
The unit start-up took place in several steps: the first step involved cold re-circulation of crude oil in the unit, i.e. the crude oil is pumped from a tank and circulated in the entire circuit including the distillation tower and different equipment (balloons, etc.) and sent back to the same tank.

After inspecting the various equipment of the same line, preparing several parts of the tower for operation and numerous inspections, the technicians switched on the furnaces to heat the crude oil. The C1 tower and its sidestream drums are filled subsequent to the slightly higher injected flow rate in the circuit as compared to the extracted flow rate towards the tank. Since the hot product occupies more volume than the cold product, the pressure in the C1 tower exceeds the valve loading values, causing the valves to open and release a mixture of liquid and gaseous hydrocarbons made up of crude oil and other distillation products such as gas oil, LPG, etc..

Consequences

The opening of the valves led to the release of about 10 to 20 tonnes of liquid and gaseous hydrocarbons into the atmosphere (pressure greater than 3 bars and temperature at about 300 °C) and a superficial pollution of the soil and vegetation that spread south due to windy conditions to the village of Sausset-les-Pins situated 7 km away. There were violent winds from the north blowing that day.

Note that the “cloud” floated past one of the two flares of the refinery.

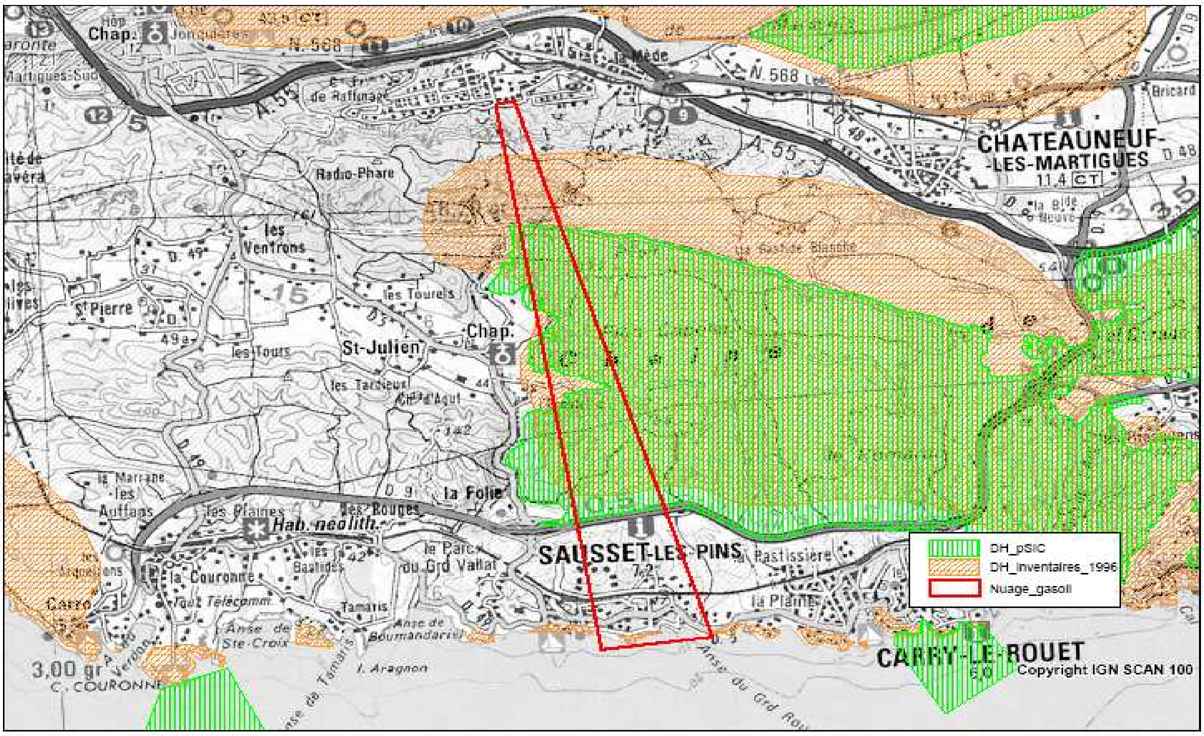


General aerial view of the unit and traces of spill in the neighbouring environment.

Photo DR

General aerial view of the unit and traces of spill in the environment south of the site

IMPACT NUAGE GASOIL TOTAL 07/08/2005
(INTERACTION AVEC ZONAGES NATURA 2000)



The Inspection of Classified Facilities was informed of the incident by the health authorities and the residents of Sausset-les-Pins, and not by the operator who was unaware of the consequences.

The 70 children in a youth camp were required to stay indoors and seven among them were examined by a doctor.

Some people were affected by the released product and one person was hospitalised.

Numerous houses (563), cars (726) and swimming pools (132) were polluted by the hydrocarbon fallout.

European scale of industrial accidents

By applying the rating rules of the 18 parameters of the scale made official in February 1994 by the Committee of Competent Authorities of the Member States which oversees the application of the 'SEVESO' directive, the accident can be characterised by the following 4 indices, based on the information available.

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

The index concerning the release of dangerous materials is set at level 4 as between 10 and 20 tonnes of hydrocarbons made up of extremely inflammable liquids as defined in part II of appendix 1 of the Seveso directive (top tier 50 tonnes) were released during the incident (Q1 parameter).

The social and human consequence index is set at 3 as 8 members of the public were affected including one of them was hospitalised (H5 parameter).

The environmental consequence rating is set at 3, the clean-up operations were carried out over a surface of 9 hectares (Env13 parameter)

The economic impact of the incident including clean-up of houses, swimming pools, cars, etc. by the operator is estimated between 2 to 10 million euros. The production losses that are higher than 2 million euros explain the level 3 attributed to the economic consequences index (parameter € 16).

ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

This accident mainly resulted from:

- a series of incidents involving the incorrect application of the start-up procedure resulting in a loss of indicator level control in the distillation tower and in the lateral strippers making it more difficult to monitor the unit during this delicate phase.

None of the control systems were able to indicate this anomaly which was repeated during four successive shifts.

The procedure clearly stated that the level at the bottom of the atmospheric distillation tower must be at 50% of its maximum level, which was the case at the start of operations.
The tower was gradually filled due to the slight positive difference between the deliveries of the loading and unloading pumps during recirculation from the crude oil tank to the distillation tower and return to the crude oil tank.
It is to be noted that once the level reached at the bottom of the tower is 100%, the operator no longer has direct access to information on the effective level of liquid in the tower. He only knows that the bottom of the tower is full up.
During a shift, an operator lowered the level in the tower to 50%, but the tower was gradually filled up again.

- poor traceability of the operations performed and relay of information from one shift to the other.

In fact, implementing an accident prevention policy and the resulting safety management system must lead to the application of operating procedures to avoid such accidents.

- incompliance with the prefectoral authorisation order providing for the recovery of waste released by valves by the flare network or an equivalent solution if technically not feasible.

- ignoring alarms and absence of an automatic safety device control. In fact, the atmospheric distillation tower level indicator only triggers a visual and sound alarm relayed to the control room when the threshold value is exceeded.

Moreover, the operator did not inform the public, the Prefect and the Inspection of Classified Facilities of the incident as soon as possible; the operator himself realised the consequences of the accident after an hour.

ACTIONS TAKEN

The Inspection of Classified Facilities visited the site on the day of the accident.

Three other inspections took place in the 15 days that followed.

Inspections were also performed on the four other refineries in the south east of France with a view to minimise the risk of reoccurrence of such an accident and to understand the organisation currently used to start-up units on other sites.

The following points were mainly reviewed:

- Number of valves present on the atmospheric distillation tower whose released waste is recovered
- In the procedure used: presence of spot points, check list, required initial state, effort made in completing the follow-up documents;
- organisation of the control room;
- organisation of the teams working in shifts
- training of staff working in shifts
- specific start-up requirements (example: provision of additional staff, etc.)
- presence of detectors and follow-up systems
- information in the shift supervisor's manual
- information in the technician's manual

The facility resumed operations on the day following the incident.

The operator set up two safety lines:

- high pressure sensor in the tower with immediate stop of the furnace and the load after a 10 minute timeout compatible with the valve loading pressure
- sensor monitoring the filling of the tower with immediate stop of the furnace and the load after a 10 minute timeout

The ergonomic design of the control room was changed (the units were brought together by the control panel) and the teams working in shifts were reorganised.

The question of connecting the valves to the flares was studied at all refineries in France. Since then, this has been carried out at the site.

The ecological impact study showed that the release of hydrocarbons had no lasting impact on the flora and fauna.

On 8 June 2007, the operator was ordered by the police court to pay three fines of a cumulative value of 10,250€.

LESSONS LEARNT

Besides the human factor that played a major role in this accident, a failure of the Security Management System was also brought to notice resulting in the following changes:

- Proper completion of follow-up documents for operating procedures
- Improvement of communication during change of shifts
- Setting up of safety control systems to avoid belching of the tower
- Reorganisation of the control room and the teams in shifts
- Connection of valves to the flare network
- Assessment of the risk of belching in danger studies

This feedback providing a wealth of information was shared with the other refineries in France.

Leak on a pipe conveying MTBE

October 2004

Stein Port

The Netherlands

Petrochemistry
Soil pollution
Water table pollution
Construction defect
Welding
Human factor
Late detection

THE CONCERNED INSTALLATIONS

The site:

The 800-ha petrochemical complex near the port includes roughly ten different plants that produce approximately fifty or so chemical products, including methyl-tertio-butyl-ether (MTBE), benzene, toluene, ethylbenzene and xylene (BTEX).

The concerned installation

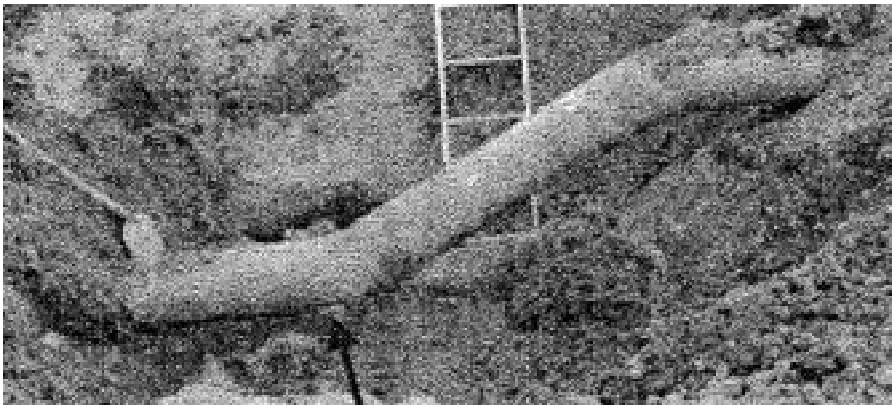
A 10'' (254 mm) diameter pipe used to transfer various products from the production facilities to the port's loading/unloading zone runs along the Juliana canal, also near the Meuse. Built in 1976 and designed to withstand a pressure up to 25 bar, the pipeline is operated at a service pressure of 2 bar.

THE ACCIDENT, ITS BEHAVIOUR, EFFECTS AND CONSEQUENCES

The accident

In October 2004, inconsistencies in the material balance between the MTBE sent by the production unit and that received at the port lead to an in-depth inspection on the transfer pipe. The inquiry revealed that 2,500 t (3,000 m³) of MTBE had been released through a crack in the pipe.

Despite annual inspections, the leak appeared to have existed for a number of years; the leak's initially low flow rate most likely increased progressively due to soil movements.



Portion of damaged pipeline
Source: VROM-Inspectie (The Netherlands)

In April 2005, even though soil and water table decontamination measures had been undertaken in the contaminated zone (see below), hydrocarbon pollution was detected in a pumping well at a drinking water facility 30 km downstream and which supplies 300,000 people. The pollution of Meuse was characterised by the presence of 5 µg/l of MTBE.

The investigations undertaken indicated that the pollution originated near the Stein port where nearly 200 m x 800 m of MTBE (300 mg/l) was detected above the water table, between the site's accident zone and the river. The transfer of MTBE from the pollution pocket to the river was evaluated between 50 and 100 kg/day. The Meuse is primarily supplied by rainfall, and thus its flow rate is highly variable (10 m³/s to 2,500 m³/s), as well as the observed level of MTBE pollution.

The consequences:

The release of 2,500 t of MTBE, responsible for the pollution of the water table and the Meuse, created a risk for:

- drinking water,
- aquatic life,
- swimming,
- agriculture and animal husbandry.

The cost of the decontamination and cleanup measures undertaken immediately following detection of the leak and implemented for several years was evaluated at more than 6 M€.

European scale of industrial accidents

By applying the rating rules of the 18 parameters of the scale made official in February 1994 by the Committee of Competent Authorities of the Member States that oversees the application of the 'SEVESO' directive, considering the available information, the accident can be characterised by the following 4 indices.

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

The Seveso Directive classifies MTBE as an "easily flammable liquid" with a threshold of 50,000 t; the 2,500 t released by the leak thus represent 5% of this threshold. The "dangerous materials released" index is thus level 3 (parameter Q1).

As the accident polluted at least 30 km of river (parameter Env14) and 16 ha of soil and water table pollution (parameter Env13) requiring decontamination, the "environmental consequences" index is at least equal to 4.

As the cost of the decontamination measures was estimated at more than 6 M€ (parameter €18), the "economic consequences" index is greater than or equal to 5.

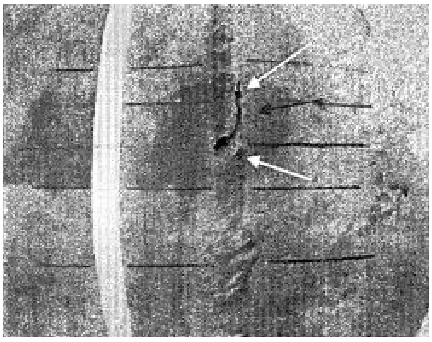
ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

A crack on a pipe weld resulted in the MTBE leak. This defect resulted from multiple failures during the construction of the pipeline.

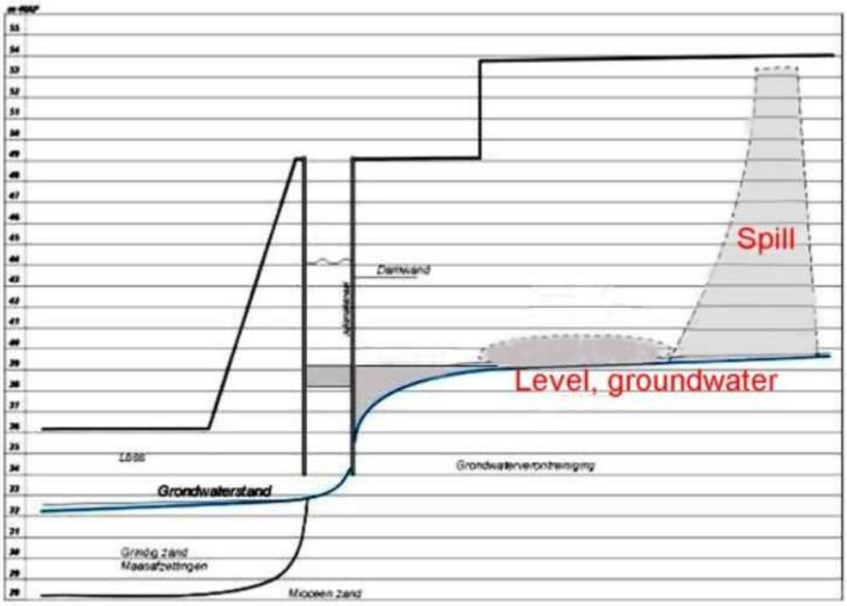
In 1976, construction began on each side of the project to save time. A difference of 70 cm in height between the two sections thus required the addition of an improvised S-shaped junction. Poor adjustment of this part required a 1.5 cm gap to be plugged by welding.

The welding of this junction part, poorly performed and left unchecked, caused the pipe to crack. The crack, the appearance of which remains difficult to establish, most certainly widened over time, notably due to ground motion.

The transfer of pollution from the leak zone to the Meuse, despite the presence of a 15-m deep reinforced steel dike (forming the Juliana canal) can be attributed to the presence of a strong water table current flowing through the Meuse gravel bed (see photo below).



Crack on the weld
Source: VROM-Inspectie (The Netherlands)



POLLUTION TRANSFER DIAGRAM
Sources: VROM-Inspectie (The Netherlands)

ACTION TAKEN

Following the detection of the pollution in October 2004, the pipeline was repaired and several methods were used to treat the site's polluted zone:

- removal of polluted soil,
- pumping of the supernatant MTBE above the water table,
- injection of air into the water table and treatment of the return vent air.

Furthermore, to prevent the pollution from spreading, the steel structure of the Juliana canal dike was reinforced up to 15 m in depth, i.e. below the level of the water level.

Following detection of the pollution in the Meuse in April 2005, the treatment program was extended to the zone located between the site and the river in late 2005 and brought up to full steam in early 2006.

Due to the absence of the pre-existing MTBE concentration limit values in the underground and surface water, strong pressure by the public authorities and opinion were required for the operator to implement these cleanup measures.

LESSONS LEARNT

A variety of lessons were learnt from this accident:

- in terms of regulations, the limit concentration values in underground and surface water for well-defined chemical products enable rehabilitation measures to be more easily imposed on operators responsible for causing pollution,

- technically speaking, due to their level of precision (1%), output control systems do not allow a leak of this type to be detected (low output, long duration, etc),

- the accident can be attributed to a series of certain number of organisational and human failures which could have been avoided:

- poor organisation of the canal construction project lead to improvise a solution to connect the 2 sections of pipe,
- poor welding and non-inspection of this junction,
- yearly inspection inefficient to detect the leak,
- underestimation of the risks and insufficient action taken when the pollution was detected, assuming that the pollution would not spread given the low solubility of MTBE.