Index

_ ANNEXES _

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, Sustainable Development and Spatial Planning 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 19^{th} 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 Risks 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.

Chlorine pipeline explosion
21 May, 2005
Champagnier [Isère]
France

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

THE INSTALLATIONS IN QUESTION

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℃.

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 BEHAVIOUR, 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℃) for 72 hours created a possible ignition source of the accident.

ACTIONS 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.

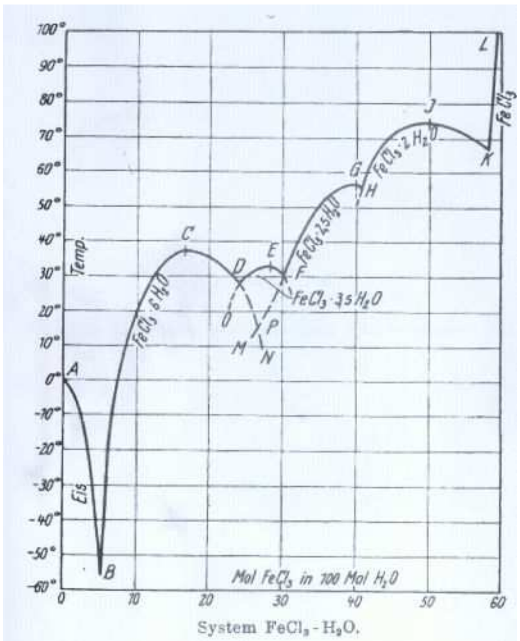
As part of the feedback for chlorine transport pipelines, this accident brings to light three critical points:

✓ 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

Fire in a pesticide warehouse

27 June, 2005

Béziers – [Languedoc-Roussillon] France

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

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.

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

ACTIONS TAKEN

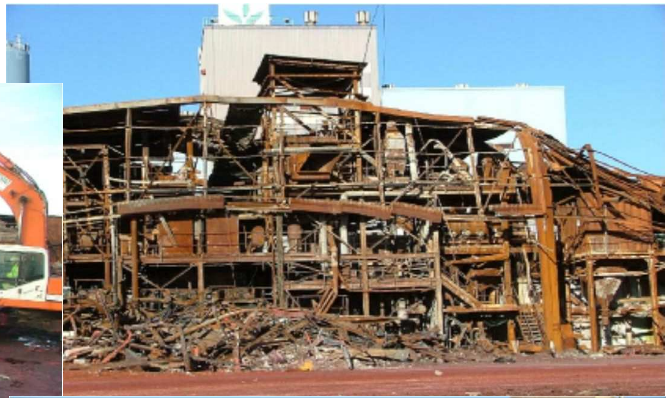
On June 28, 2005, the DRIRE proposed the Prefect of Hérault an emergency prefectoral order outlining the security of the site, monitoring of the environment and the conditions for restarting the units not effected by the fire.

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.

Release of ethylene to the atmosphere

21 July, 2005 and 21 September, 2005

Saint-Avold – [Moselle]

France

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

THE INSTALLATIONS IN QUESTION

The site:

The establishment, located in Saint-Avold in the county 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:

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

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 °C. The pressure is 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.

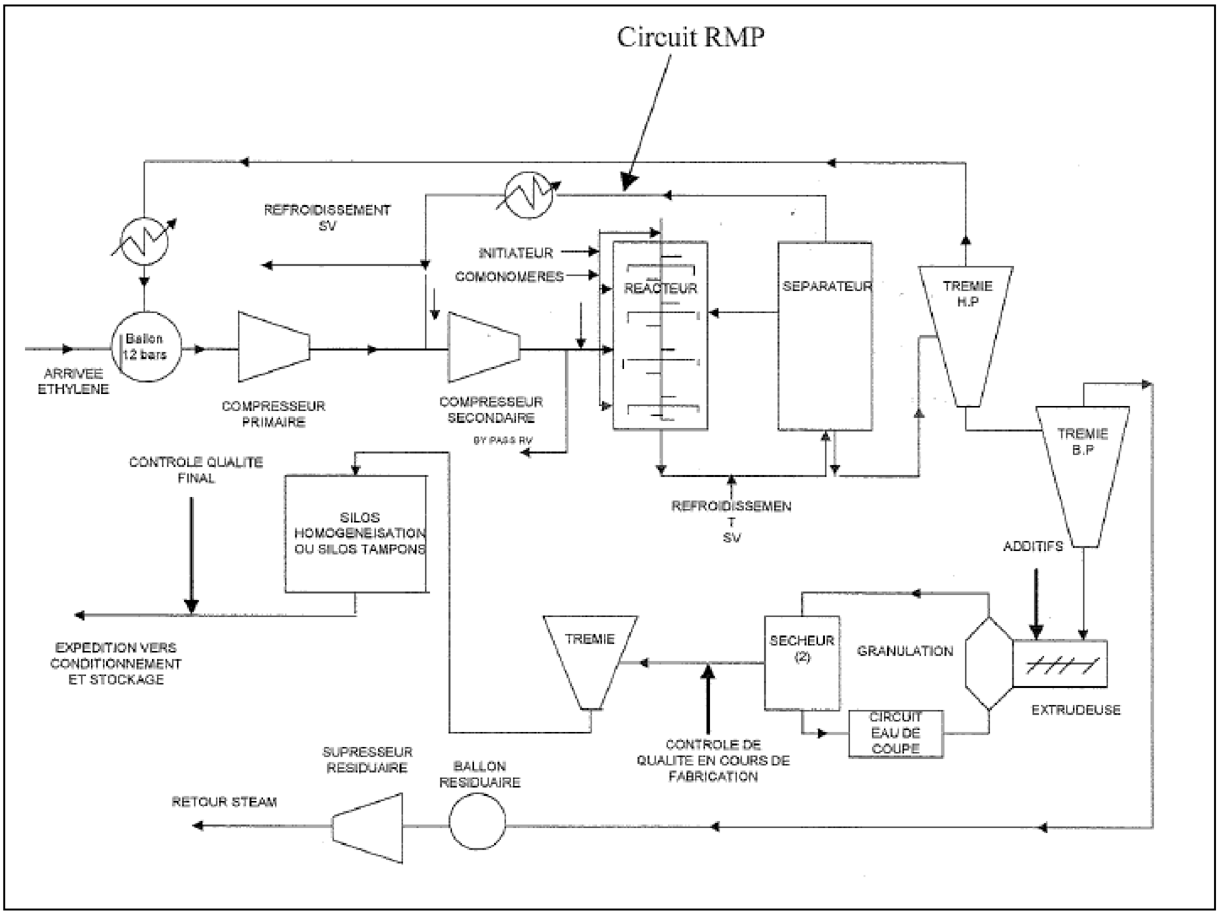


Figure 1: Simplified diagram of the process

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.

ACTIONS 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

26 April, 2006

Catenoy – [Oise]

France

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

THE INSTALLATIONS IN QUESTION

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 ℃. 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:

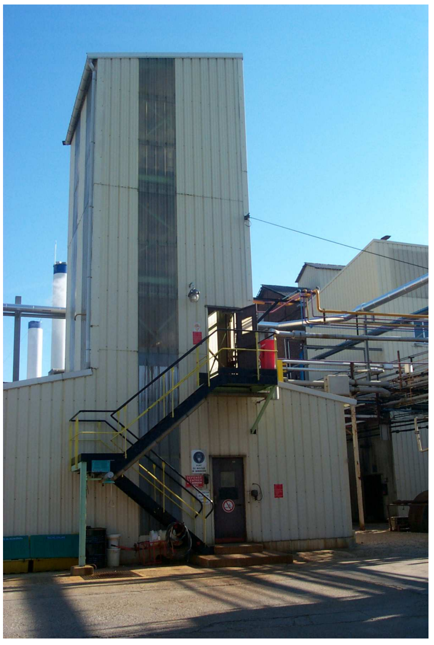
The sulphur dichloride (SCl_2) distillation unit involved in the accident comprises the following elements:

- 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.



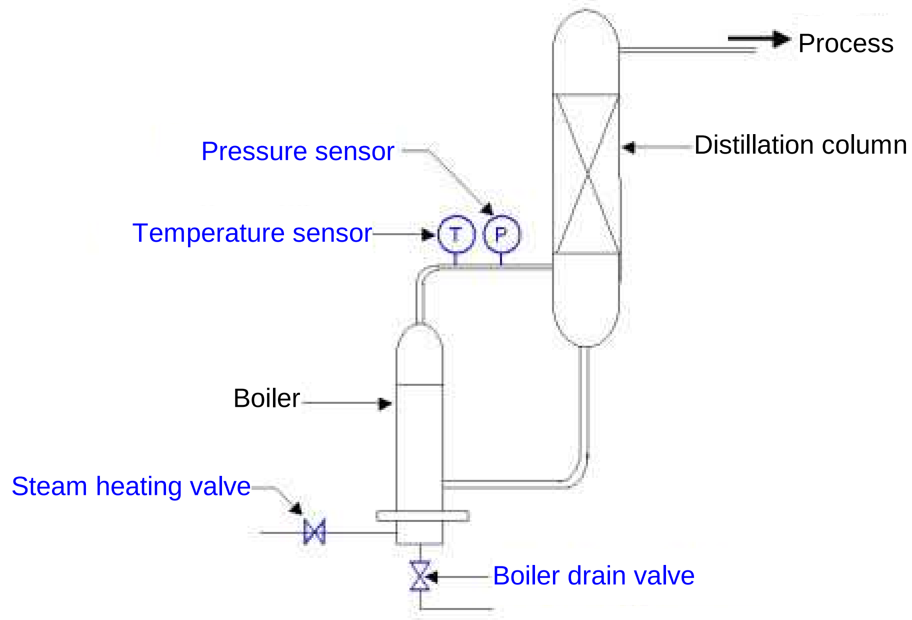
Distillation column

Sources: DRIRE Picardie

THE ACCIDENT, ITS BEHAVIOUR, 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.

ACTIONS 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.

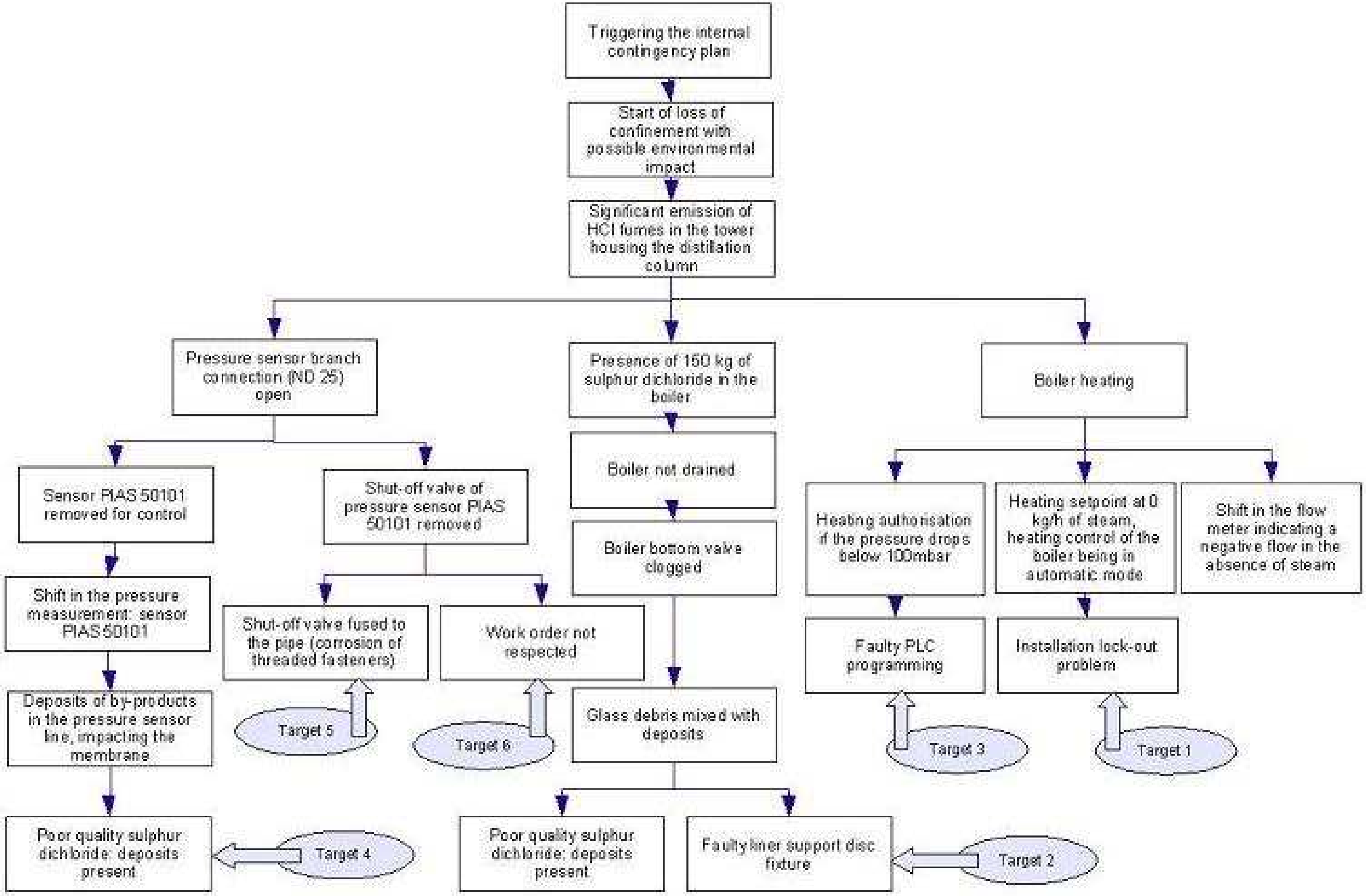
The cost of all these measures was evaluated at 93 k€.

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

21 March, 2005

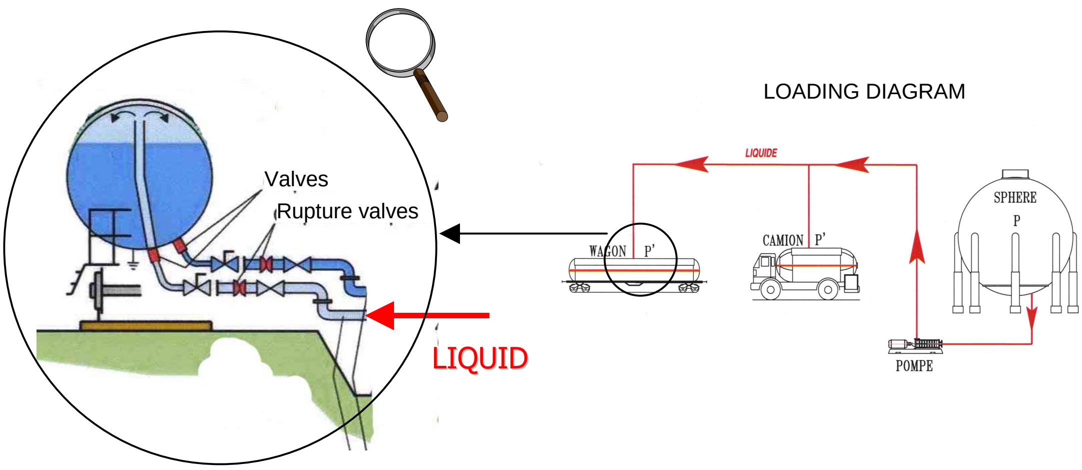
Donges - [Loire Atlantique] France

Release
LPG filling centre
Propane
Loading arm
Coupling
Corrosion
Underthickness
Chocks

THE INSTALLATIONS IN QUESTION

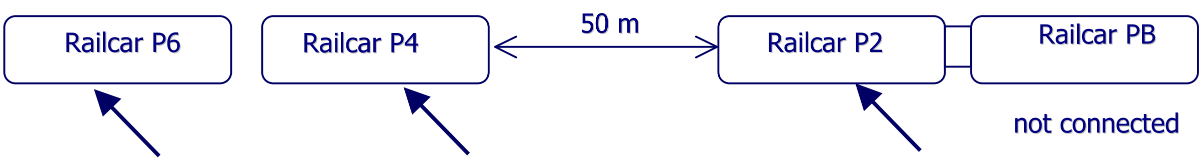
The release occurred at a railcar tank loading station in a liquid petroleum gas (LPG) filling centre supplied by a nearby refinery. The site's activity essentially involves the filling of trucks, railcars and gas cylinders from 2 spheres (butane and propane).

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



THE ACCIDENT, ITS BEHAVIOUR, 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.

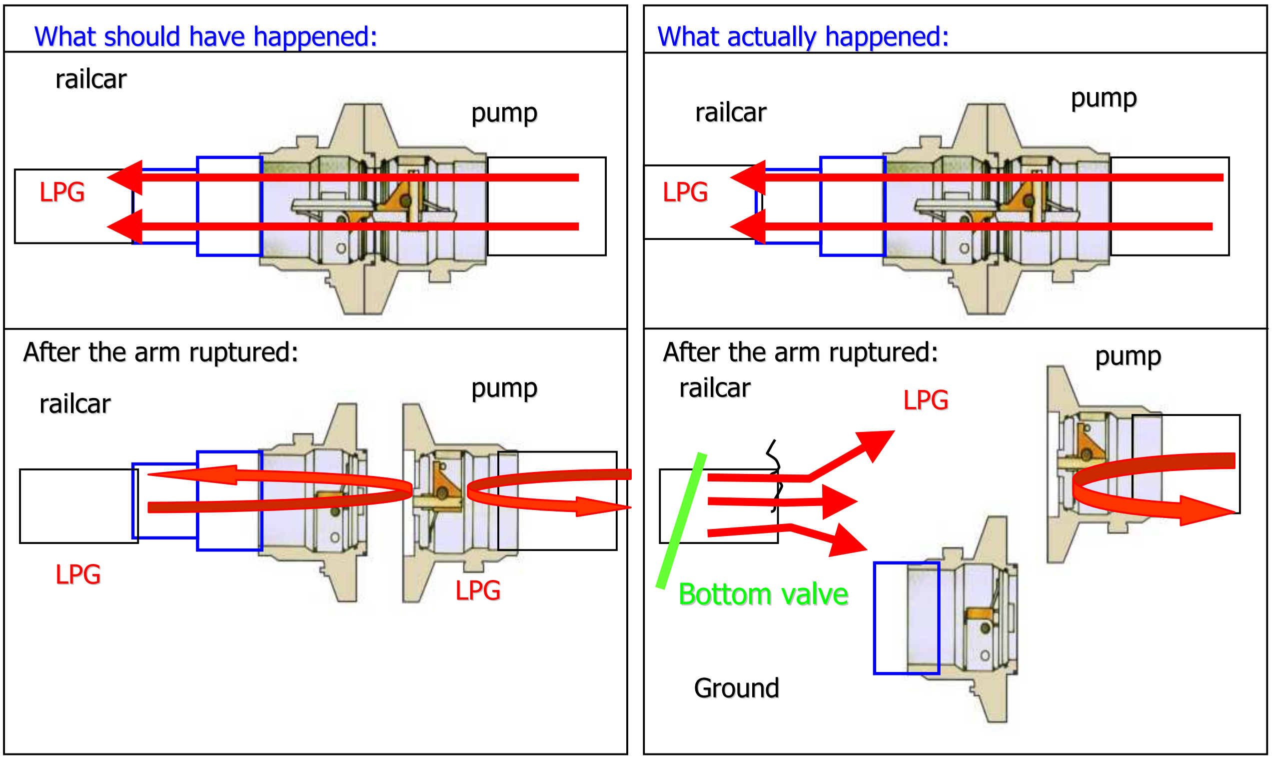
The slightly sloping track allowed the 2 hitched railcars (P2 and PB) to move, causing the threads on the terminal coupling of the transfer arm on the railcar side to rupture.

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).

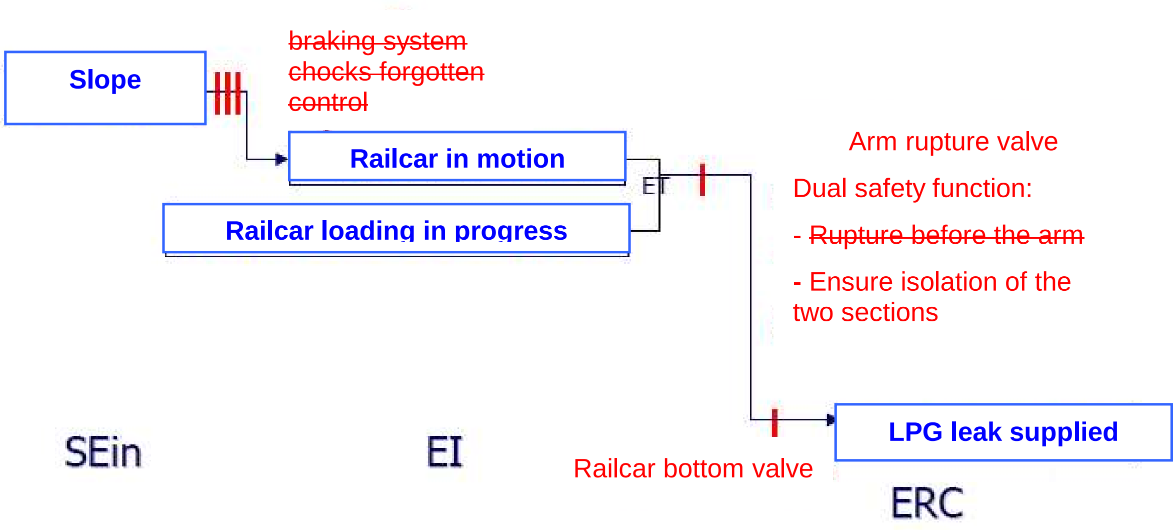
ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

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.



ACTIONS 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

30 December, 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, EFFECTS AND CONSEQUENCES

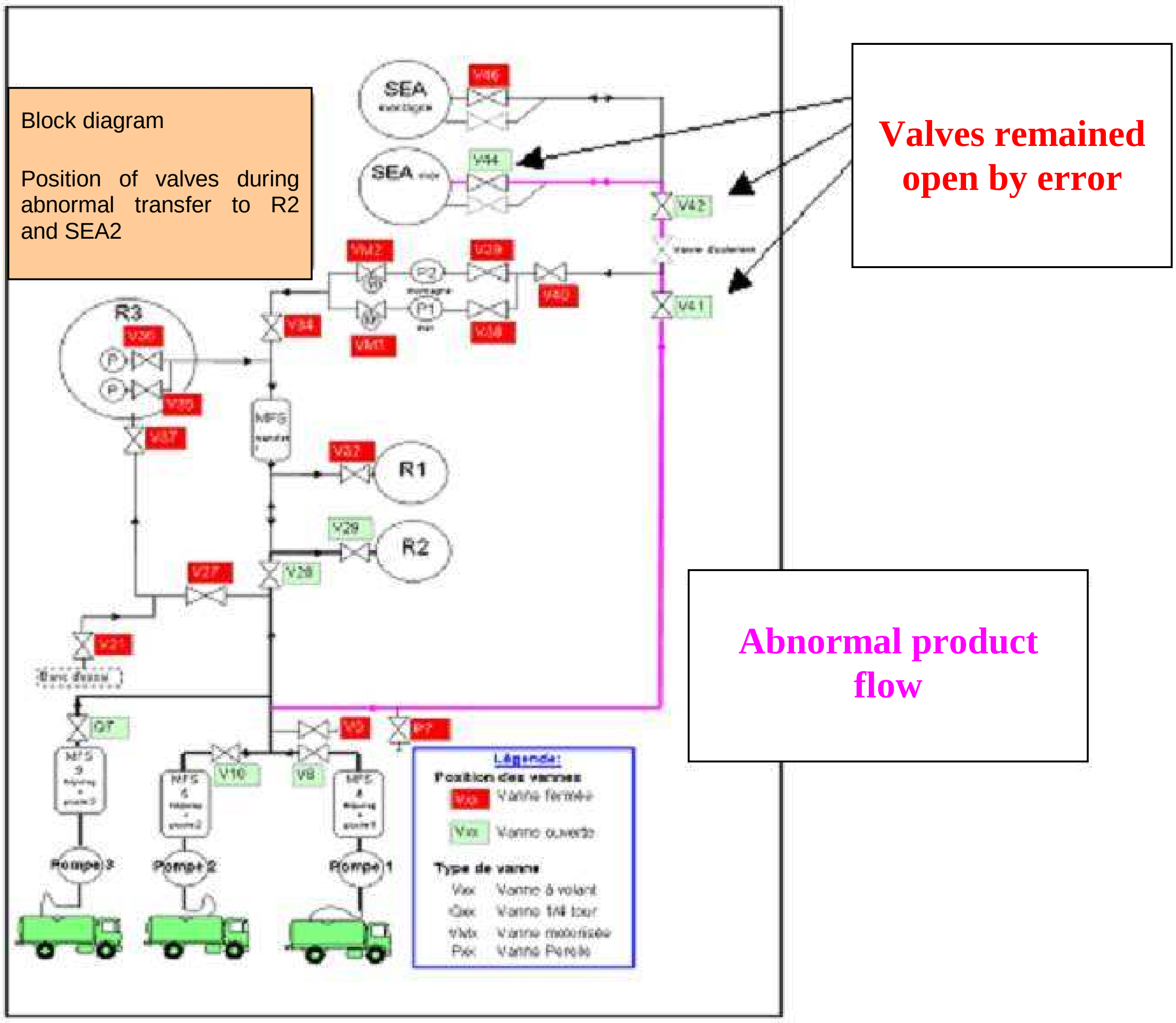
The accident:

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.

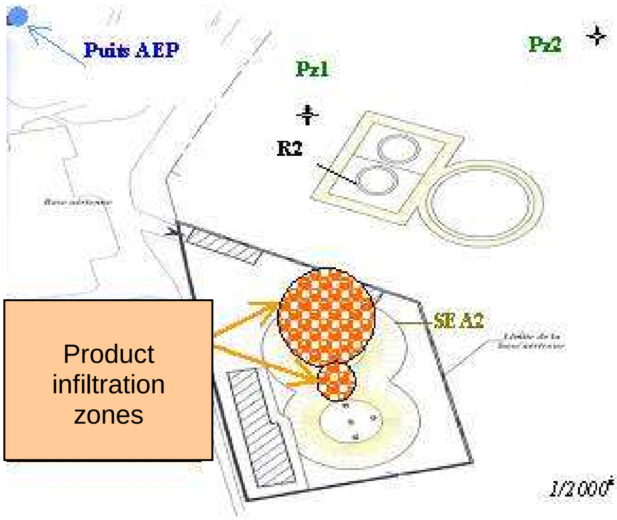
The high level detection safety alarm on the SEA2 tank did not function.

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.

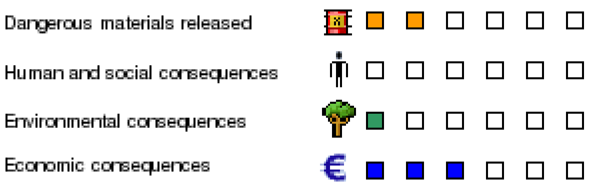


Between 8.40 and 9.15 am, the personnel from both depots blocked off the rainwater drainage system with sand and other oleophilic materials. However, after noting that jet fuel was present in the rainwater network, a worker of the depot B rinsed the drainage system with a large quantity of water at around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

ACTIONS 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 (photo DR)

▲ Digging operations round the SEA2 tank (Photo DR)

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 (photo DR)

▲ Treatment of polluted soil (photo DR)

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
11 December, 2005
Buncefield – United Kingdom

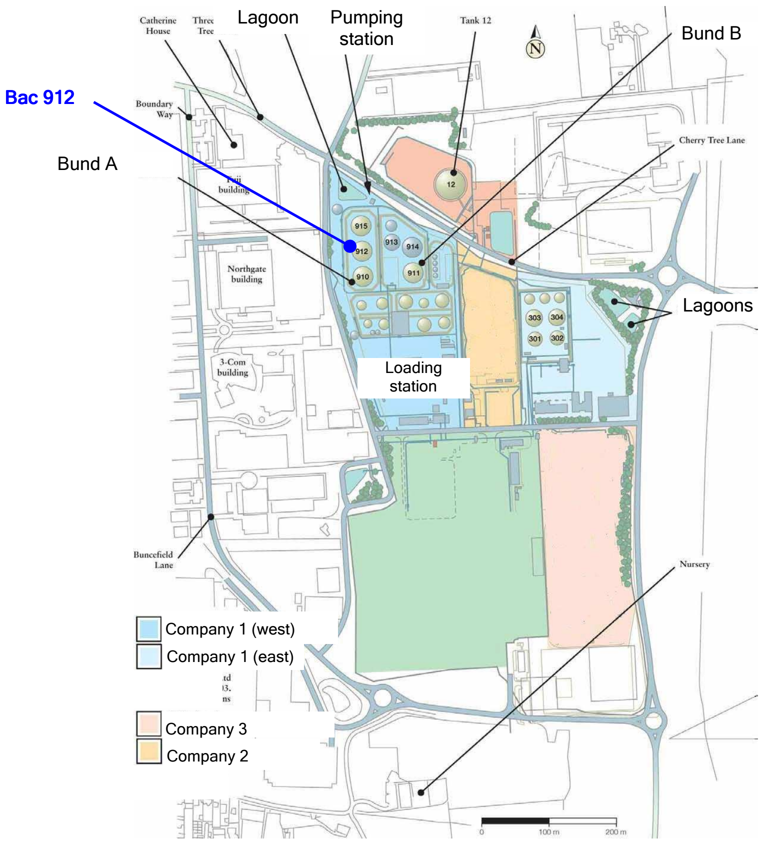
Explosion
Flammable liquids farm
Gasoline
Level detection
Automatic valve
Victims
Material damage
Transboundary effects

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



Source: Buncefield Investigation, Initial Report

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, 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.

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

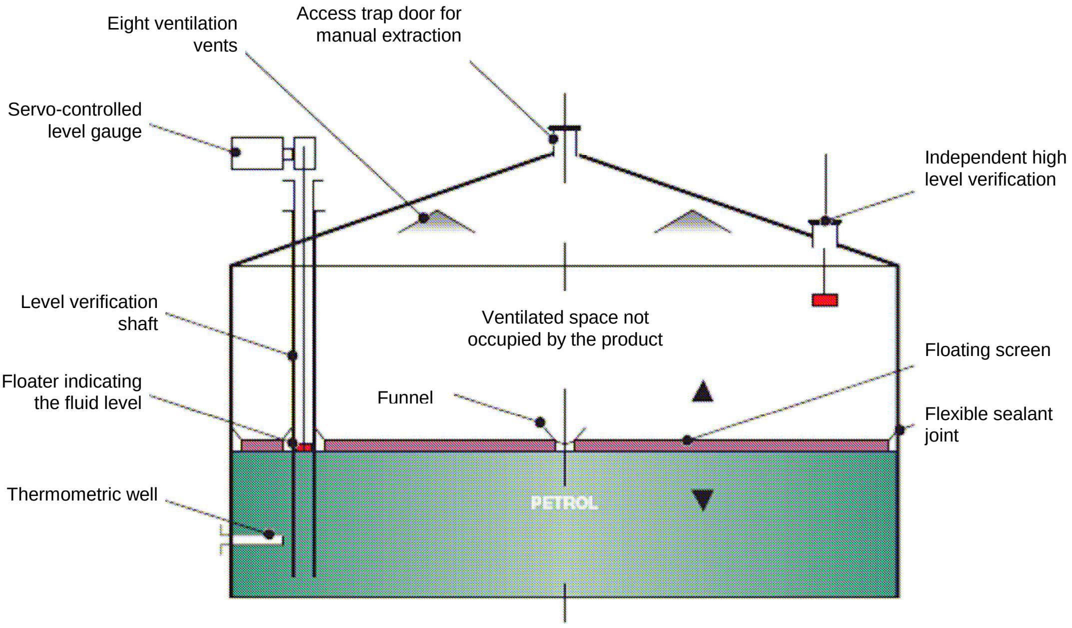
Control and measurement system installed on the tanks:

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:

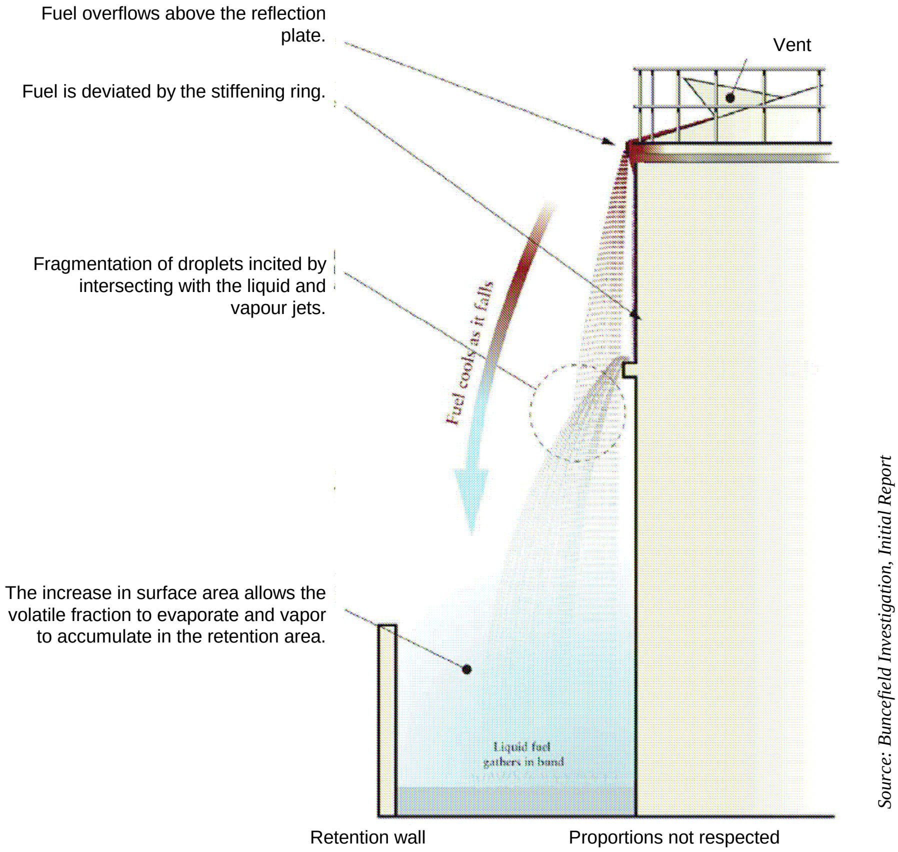
Neither of the two automatic level detection systems within the tank, as detailed above, was operable, and the gasoline supply into Tank 912 was not shut off. An expert evaluation was conducted to determine the reasons for malfunction of the automatic control and tank gauging systems. Following tank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

ACTIONS 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 LEARNT

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 8 October, 2007.

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

7 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, 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.

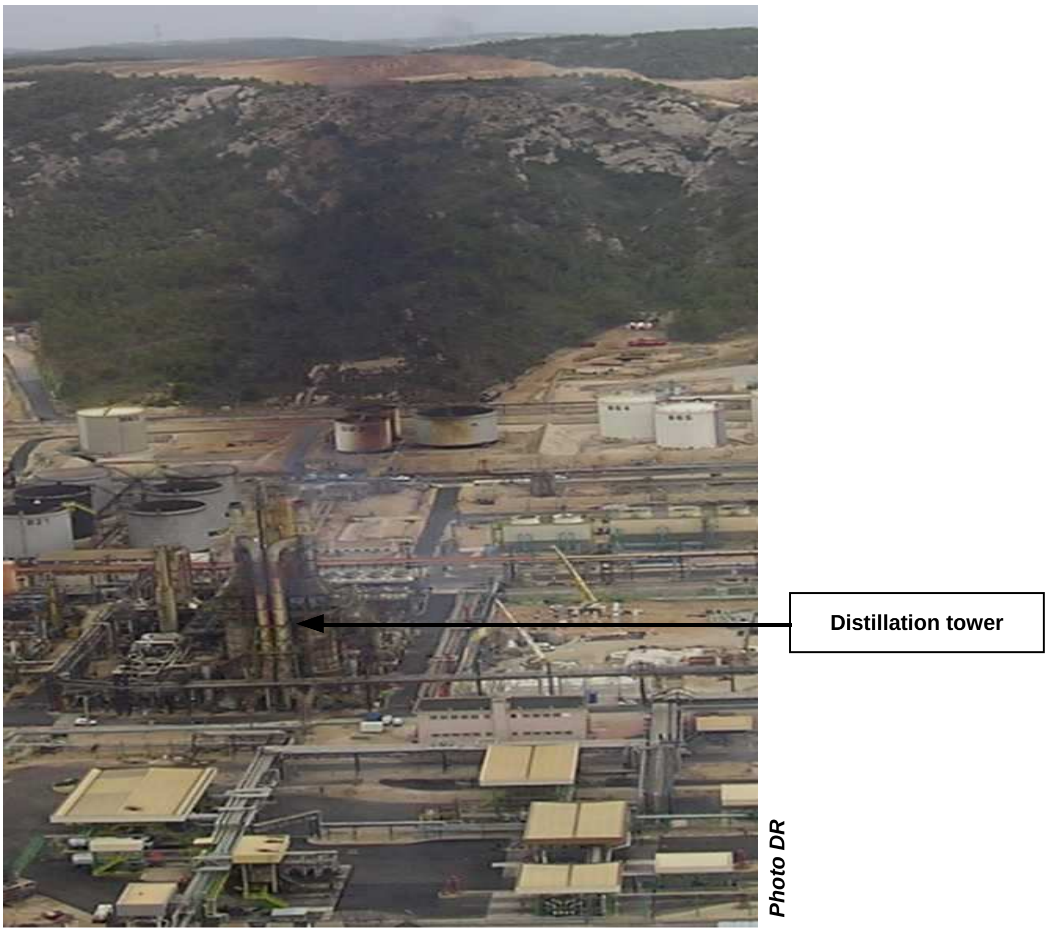
The unit start-up took place in several steps: the first step involved cold re-circulation of crude oil in the unit, i.e. the crude oil is pumped from a tank and circulated in the entire circuit including the distillation tower and different equipment (balloons, etc.) and sent back to the same tank.

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 ℃) 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.

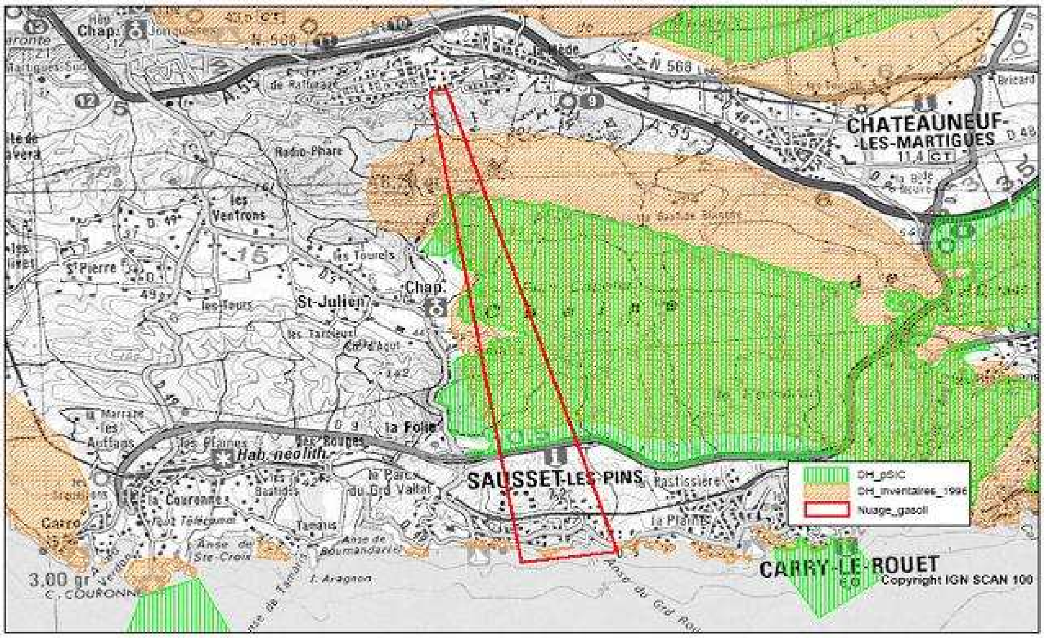


General aerial view of the unit and traces of spill in the neighbouring environment.

Photo DR

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

IMPACT NUAGE GASOIL 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 INSTALLATIONS IN QUESTION

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:

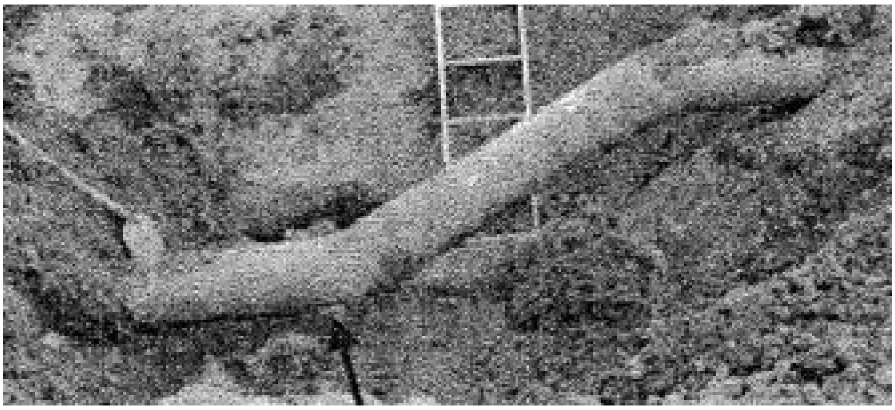
A 10'' (254 mm) diameter pipe used to transfer various products from the production facilities to the port's loading/unloading zone runs along the Juliana canal, also near the Meuse. Built in 1976 and designed to withstand a pressure up to 25 bar, the pipeline is operated at a service pressure of 2 bar.

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.

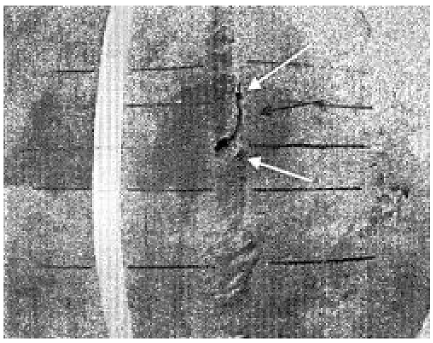
ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

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

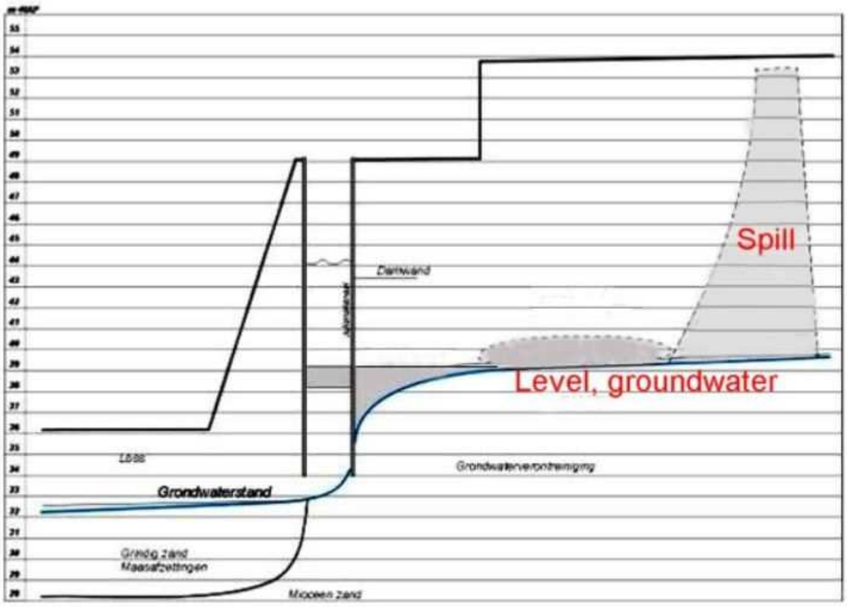
In 1976, construction began on each side of the project to save time. A difference of 70 cm in height between the two sections thus required the addition of an improvised S-shaped junction. Poor adjustment of this part required a 1.5 cm gap to be plugged by welding.

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)

ACTIONS 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.

Explosion of a wood chip refiner and fire

20 and 25 January, 2005

Corbenay – [Haute-Saône]

France

Explosion / Fire
Chipboard
Silos
Dust
Risk analysis
Organisation
Uncoupling
Thermal imaging camera
Vents

THE INSTALLATIONS IN QUESTION

The site:

The chipboard manufacturing plant, located in Corbenay, in the region of Haute-Saône, was set up in 1969 to produce chipboards for the furniture industry. The company then diversified to manufacture specific products for hardware stores. The main activities include :

✓ Furniture manufacturing,

✓ Specific products intended for the general public via hardware stores.

Since 1981, the company has been a 99.9%-owned subsidiary of a group, which is the leading furniture manufacturer in France and its primary customer.

In 2006, the plant manufactured 430,000 m^3 of chipboard produced from 542,000 tons of wood.

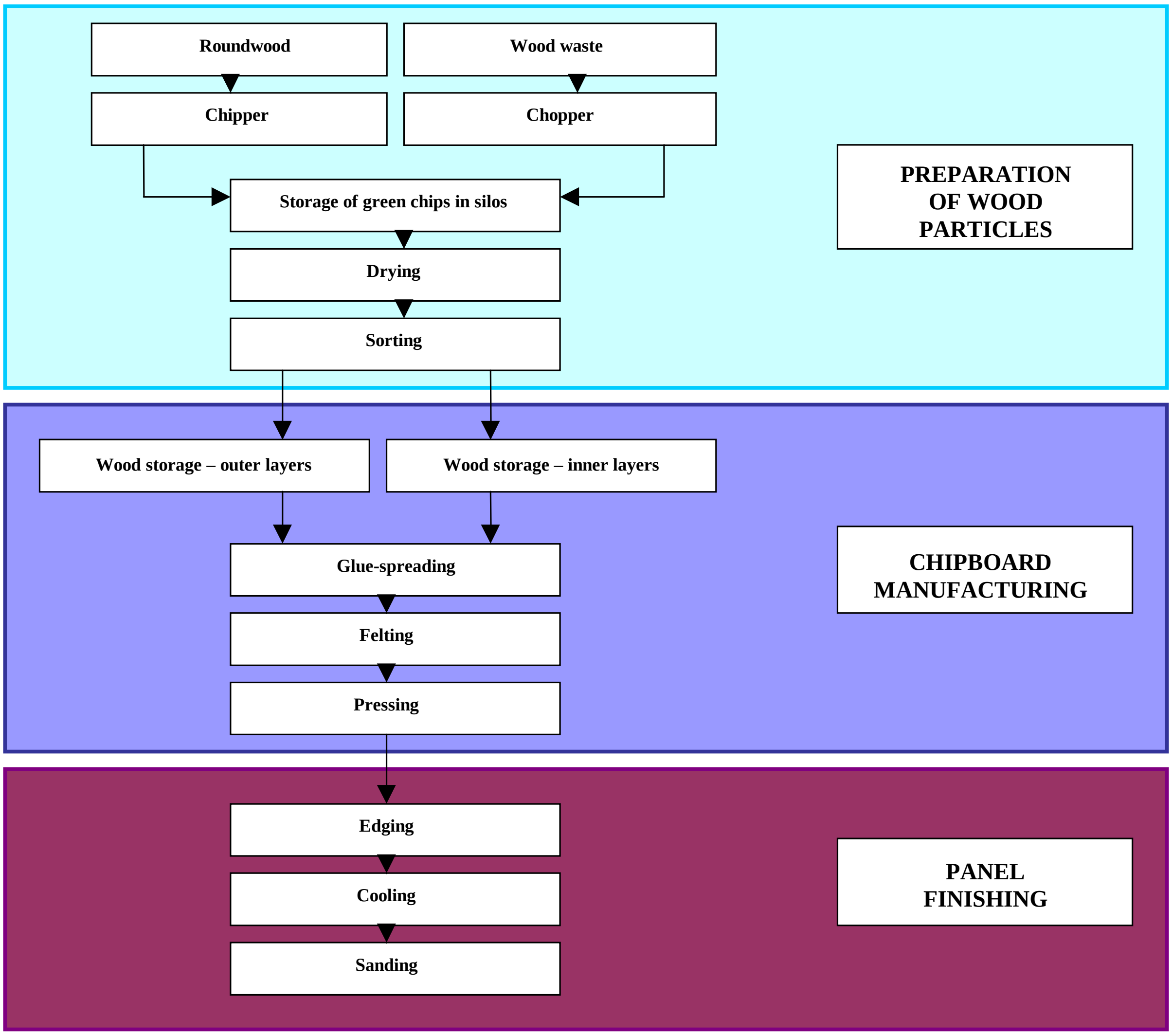
The plant employs 200 persons and posts sales of 75M euros.

This plant is a "classified" installation whose operation is subject to authorisation governed by the Prefectoral order of March 8, 2005.

The sector involved:

Chipboard is produced by hot-pressing a mixture of wood chips and glue. The wood chips are obtained by chipping up green wood, which is then dried and sorted. The chipboards are then produced through a series of glue-spreading and pressing operations.

The manufacturing process can be illustrated as follows:



The accident occurred in the wood chip preparation sector, after the chips had been dried.

Photo Drire France-Comté

THE ACCIDENT, THEIR BEHAVIOUR, EFFECTS AND CONSEQUENCES

The accident of January 20, 2005:

January 20, 2005 at 2.58 am, at part of the refiner breaks (the mill grinder that transforms large dry chips into small dry chips). The resulting spray of sparks is carried along by the suction and ventilation equipment.

At 2.58’02’’, the refiner's cyclone explodes. The force of the explosion causes it to rupture, despite the presence and operation of the vents. The fire spreads to all the adjoining installations: redler conveyors, suction equipment, air graders, sorters, dry silos, etc.

At 2.58’07’’, an explosion occurs in the suction equipment causing the vents to open.

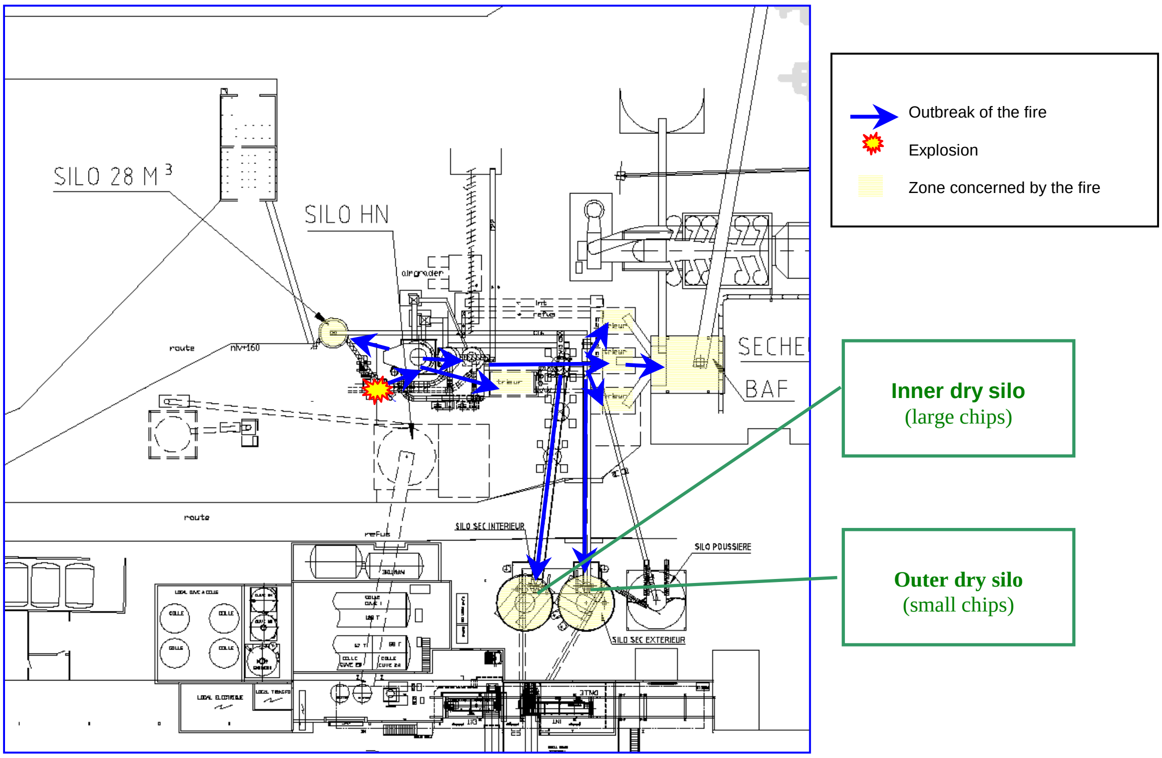
At 2.58’10’’, the "inner" and "outer" dry silos explode. The fire reaches the refiner silo, cyclones, cyclofilters and suction equipment, sorters, fire boxes and the "inner" and "outer" dry silos.

At 5.00 am, the fire was brought under control by the plant's firemen, and the public fire protection departments.

The following day at 8.30 am, the silos containing the dry chips were emptied to ensure that no embers remained.

Production operations resumed at 10.30 pm.

Schematic diagram of the chronology of explosions on January 20, 2005



The consequences:

The accident had no human casualties.

Material losses were evaluated at 250,000 euros, attributed to the replacement of the refiner (at the origin of the accident), and the damage caused to the sorter and cyclofilter. The silo and cyclofilter vents also have to be replaced. The plant also reported 750,000 euros in production losses due to the production line being shut down for two days.

The wood chips in the damaged silos were used in one of the plant's boilers. The fire fighting water was collected in a retaining pond and analysed before being released into the natural environment.

Photo Drire Franche-Comté

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, this first 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 of the "Dangerous materials released" index characterises the explosion that occurred (parameter Q2 : the quantity of explosive substances was estimated to be < 100 kg of TNT).

The index relative to the economic consequences is rated level 2 due to the production losses that were evaluated at 750,000 € (parameter €16).

The accident of January 25, 2005:

On January 25, 2005 at 6.10 am, an explosion followed by fire occurred inside the "inner" dry chip silo. The silo's vents opened, thus limiting the effects of the shock wave.

The production crew and the plant's firemen triggered the manual water injection system inside and outside the dry silos as well as inside the redler conveyors supplying the "inner" silo.

The firemen set up a water nozzle upon their arrival to cool down the silo. A second explosion occurred during the cooling operations.

This explosion caused the fire to spread to the building behind the silos.

The fire was quickly brought under control. Production operations resumed in the evening after the two "inner" and "outer" dry chip silos had been emptied.

The consequences:

The consequences were minimal in comparison to the first accident. The production shut-down was limited to 14 hours; the storage silo's explosion vents and electrical cable that melted during the fire must be replaced.

Operating losses were evaluated at approximately 45,000 euros.

Photo Drire Franche-Comté

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 second accident can be characterised by the following 4 indices, based on the information available.

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 level 1 rating of the "dangerous materials released" index characterises the explosion that occurred (parameter Q2 : the quantity of explosive substances was estimated to be < 100 kg of TNT).

ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENTS

The cause of the first accident was easily determined during the examination of the refiner. The breakage of the metal part created sparks that caused three explosions and the subsequent fire. The various safety devices installed by the operator were triggered :

- ✓ The vents on the silos and the cyclofilter opened, thus limiting the consequences of the explosions. The cyclofilter, however, had been torn open.
- ✓ The spark detection system coupled to the water injection points had reached alert level number 2, injecting water on a permanent basis.
- ✓ The sounding of the alarm in the control room enabled the company's firemen to intervene in less than 10 minutes. The internal response teams are organised in synergy with the firemen of the neighbouring company, a subsidiary of the same group. Furthermore, the operator had developed an emergency response manual outlining the emergency procedures to be followed in the event of an accident.
- ✓ The silos' sprinkler system was put into operation by a manual valve.

Immediately following the explosion, the burners were shut down thus securing the chip zone, the driers were reversed to stop the flow of dry chips and thus stop the supply of fuel.

The cause of the second accident was attributed to embers that had remained in the bottom of the "inner" dry chip silo, following the fire of January 20, 2005. Smouldering embers had been trapped under a very heavy bell-shaped piece of equipment, the silo's extraction unit. The fire had been smouldering for 4 days. In the morning of January 25, 2005, the silo's level had dropped until it was empty and the embers ignited the cell's dusty atmosphere, resulting in an explosion. The cause of the second explosion, which occurred while the installations were being cooled down (accident of January 25), was not determined. Several hypotheses were submitted : BLEVE, water gases, dust particles in suspension, etc.?

ACTIONS TAKEN

The operator implemented several protective measures following the first accident :

- ✓ the refining installation was uncoupled from the rest of the installations. As a result, a cyclofilter dedicated to the refiner was installed and a fire box was added.
- ✓ the emergency response procedure, comparable to an internal contingency plan, was submitted to evaluation by a third party.
- ✓ the rupture of the cyclofilter, even though vents had been installed, led the operator to check their dimensions.
- ✓ as for the second accident, failing to check for embers under the dry chip silo's extraction unit is the reason behind the accident. The following improvements were recommended :
- ✓ modification of procedures dealing with accident intervention and post-accident silo restart operations, with the addition of the verification of the extraction unit.
- ✓ the purchase of a thermal-imaging camera to check installations after a fire.
- ✓ call upon a third-party expert to inspect the installations, the safety systems and the intervention procedures. The main conclusions of the third-party inspection are presented below.

LESSONS LEARNT

The chipboard industry is subject to fire and explosion hazards, considering the manufacturing processes used, the presence of large quantities of combustible materials and the production of dust.

The safety measures implemented at the site, including spark detection equipment coupled with water injection systems, proved their efficiency. Feedback from the detections recorded by these systems will certainly reduce the frequency of fires and explosion.

The installation of uncoupling systems, separating the installations in to distinct units, prevents an explosion or fire from spreading to other equipment. The most recent one implemented corresponds to the installations downstream from the refiner vis à vis other cyclofilters and dry chip silos (following the accident of January 20, 2005).

The third-party inspection opened up avenues of improvement in terms of site safety, with namely:

- ✓ creation of an Internal Contingency Plan,
- ✓ the installation of vents on the buffer storage systems,
- ✓ the modification of safety instructions,
- ✓ the installation of a new flooding device in sorter T4,
- ✓ protection of the manual valves enabling the sorters to be sprayed down.

Polluted effluents released into the Cher River

14 September, 2005

Saint Victor – [Allier]

France

Toxic releases
Surface treatment
Cyanides
Equipment (failures)
Organisation
Human factor
Intervention / Rescue
Fish mortality

THE INSTALLATIONS IN QUESTION

The site:

The plant, located in the town of Saint Victor in the French region of Allier, was built in 1994 and designed to perform surface treatment operations on metal parts, particularly various grades of zinc plating on automobile parts. In 2005, the plant employed 34 persons and posted sales of 1.6 M euros.

The plant consists of a 3,530-m² covered building housing 2 surface treatment lines, a rack system and a bulk system. Both systems represent a total bath volume of 196 m^3.

Effluents from the surface treatment operation are treated in an internal detoxication station before being released into the Cher. This physico-chemical station includes a dechromatation, decyanidation, neutralisation and flocculation reactor and 2 filter presses designed to recover the metal hydroxides in the form of sludge and to reintroduce the filtrate (the "juice" extracted from pressing the flocculated effluent) into the top of the neutralisation stage.

This plant is a classified installation whose operation is authorised by the prefectoral order dated April 7th, 2005.

Photo DRIRE Auvergne

The unit concerned:

The metal treatment line concerned is used for the bulk treatment (in barrels) of automobile parts. It includes : zinc plating (galvanising), nickel plating and alkaline cyanide copper plating.

The accident was caused by a leak which occurred during a pumping operation on the treatment line's catchpit. It also involved the internal detoxication station used to treat industrial effluents.

THE ACCIDENT, ITS BEHAVIOUR, EFFECTS AND CONSEQUENCES

The accident:

Photo DRIRE Auvergne

On Wednesday, September 14th, 2005 around 8.15 pm, a technician discovered a leak on the multiple treatment line slightly before the end of his shift; a filter outlet pipe on a tank containing alkaline copper cyanide had become disconnected causing the bath (approx. 1,000 l) to flow into the concrete catchpit.

The technician **immediately** informed the laboratory/environment supervisor at his home. The supervisor ordered that the surface treatment line be stopped (including the shut down of the heating system) and that the liquid be left in the catchpit. The incident was recorded in the logbook used for this purpose.

On Thursday, September 15th, another technician, with 25 years experience in surface treatment, began his shift at **5 am**. The technician observed that the multiple surface treatment line's catchpit was full of liquid, and took note of the previous day's incident entered in the logbook. He decided to use a mobile pump to transfer the product into the tank containing concentrated alkaline cyanide effluents. During normal operation, an internal system recycles this bath which neutralises the cyanides before they are released into the natural environment.

At 8 am, the laboratory/environment supervisor discussed the incident of the previous day with this technician who explained that he had pumped the liquid from the surface treatment line's catchpit into the tank reserved for concentrated alkaline cyanide effluents. Then, as he does every morning around **9 am**, he read the pollutant concentration levels at the plant's final waste release point (by colorimetric analysis).

He noted that the cyanide content was abnormally high : above 2mg/l, with a limit value set at 0.1 mg/l. He **immediately** decided to close the final waste valve and shut off the water supplies to the surface treatment lines. The final waste was directed to the safety tank designed for this purpose.

After consulting the technician once again, the laboratory/environment supervisor realised that the liquid in the catchpit had been pumped into the chromic rinse tank instead of into the tank reserved for concentrated alkaline cyanide effluents.

Throughout the day of **Thursday, September 15th, 2005,** the laboratory/environment supervisor decontaminated the polluted reactors with sodium hypochlorite and transferred the water into the safety tank.

Cleaning operations on the chromate removal system continued throughout the entire day **of September 15th, 2005**.

On Friday, September 16th, 2005 at 8 am, the laboratory/environment supervisor performed a cyanide analysis on the outlet of the dechromatation and neutralisation system: no abnormal readings were noted. The internal treatment station was thus put back into operation.

Tests were taken hourly up to **11 am**, confirming the absence of cyanide.

At 12 pm, the filter presses used for sludge recovery were placed back into operation.

At around 3.30 pm, residents living along the Cher informed the Vallon-en-Sully *gendarmerie* of dead fish in the river. The National Commission for Fishing was informed and arrived at the site around **4.30 pm**. The inquiry to determine the origin of the fish mortality was rapidly directed toward the pipe releasing the surface treatment company's effluent into the Cher River.

At around 5 pm, the laboratory/environment supervisor was contacted by telephone at his home and informed of the findings. He returned to the site and analysed the industrial wastewater final release point : he again recorded the presence of cyanide. He immediately shut down the water supply to the detoxication station and the final waste release point. After analysing this new incident of pollution, the laboratory/environment supervisor determined that the sludge treatment operation caused the cyanides contained in the filter presses to be released.

All production operations were suspended **at 6 pm**.

On Monday, September 19th, 2005, the laboratory/environment supervisor cleaned the "sludge recovery" system, the neutralisation system, the flocculation chamber and the settling tank, as these reactors had become polluted by the cyanide after the sludge was recovered on the filter presses on **Friday, September 16, 2005**.

On Tuesday, September 20, 2005, the detoxication station was re-commissioned and checks were performed throughout the day : no trace of pollution was detected. All parameters of the effluents released were below the authorised limit, in compliance with the prefectoral order dated April 7, 2005.

The consequences:

Despite risks involving the release of hydrocyanic acid during the transfer of cyanide effluents in a treatment unit which may contain acid effluents, none of the technicians were injured in the accident.

With regards to the installation :

✓ the surface treatment line was not damaged,

✓ some elements of the internal detoxication station were polluted but they were able to be returned to operational condition rather quickly.

Outside the site:

✓ according to the plant operator's estimate, approximately 20 m^3 of effluents containing cyanides at a concentration of 3 to 5 g/l was released into the Cher River,

✓ fish mortality (approximately 2.5 tons) was reported by agents of the National Commission for Fishing,

✓ no health problems were reported by residents living near the site or near the point where the effluents were released into the Cher.

Photo DRIRE Auvergne

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 "Dangerous materials released" index received a rating of 2 as, according to the estimate, 70 kg of cyanide was released, which represents 0.35% of the SEVESO Directive's upper threshold for T^+ products (20t).

The level 3 of the "Environmental consequences" index is attributed to the 2.5 t of fish that were killed (parameter Env 10).

In addition, the lack of quantified data does not allow the "economic consequences" index to be determined.

ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

The investigations conducted during the accident, on the products and the process helped determine the causes of the accident rather quickly.

The release of pollutants into the river can be attributed to organisational and human errors:

✓ a technician transferred liquid containing dangerous products (alkaline copper cyanide) into a rinsing tank whose contents were not clearly and legibly indicated,

✓ as this rinsing tank was connected to a chromium detoxication treatment system, the cyanides were not eliminated and were thus released into the Cher at a concentration well above the authorised level,

✓ the lack of written instructions regarding the actions to be taken in the case of a malfunction of the surface treatment line lead the technician to rely on his own initiative, which proved to be unfortunate,

✓ after having detected non-compliant releases of effluent, the operator stopped its operations and cleaned the treatment installations. The cleaning operations were in fact incomplete and the cyanides which remained in a portion of the industrial wastewater treatment facility (filter press) were responsible for a second release of polluted effluent two days later.

ACTIONS TAKEN

The operator was formally notified that it must comply with the requirements applicable to the operation of its installations, and as stipulated in the authorisation order of April 7, 2005, **within 2 months**:

✓ the operations involving dangerous handling operations and the operation of installations in which a malfunction could result in prejudicial consequences for the surrounding area and the environment... shall be the subject of written procedures.

✓ without prejudice to the regulatory provisions concerning worker hygiene and safety, safety instructions were drawn up and permanently displayed in the workshop. In particularly, these instructions specify :

✓ the intervention procedures in the event of abnormal or accidental situations".

In the days following the accident, the operator initiated the following actions within its facility :

✓ the identification of the tanks was improved on the surface treatment lines and the associated piping,

✓ all pumping operations performed by technicians must be monitored by a supervisor,

✓ increasing technician awareness through the creation of new procedures and posters.

These measures were established and implemented in **January 2006**.

LESSONS LEARNT

A process, even through performed on a regular basis, may still be a potential source of accidents.

Following the investigations conducted after the accident, it was noted that the operation of a surface treatment line requires that the following conditions be controlled, as a minimum:

✓ the formalisation of documents stipulating the action to be taken in case of an atypical situation,

✓ information and training of technicians in the use of these documents through regular situational exercises.

Spill of heavy fuel oil in an oil terminal

21 June, 2003

Oil harbour of Göteborg - Sweden

Surface water contamination
Flammable liquids farm
Storage tank
Manhole
Heavy fuel oil
Maintenance
Procedures

THE INSTALLATIONS IN QUESTION

The accident happened at an oil terminal in the oil harbour of Göteborg, Sweden. The oil terminal is one of several oil terminals and oil storage companies in the oil harbour. It handles mainly petroleum products, of category 1, 2 and 3 inflammable liquids. It has a storage capacity of approximately 700 000 cbm, in 160 storage tanks and a few rock caverns, and is classified as a “Seveso II” company at the higher level according to the “Seveso II” European directive.

The oil harbour is located in the port of Göteborg at the estuary of the river Göta Älv at the west coast of Sweden. The oil harbour is responsible for the common service systems outside each oil terminal. The rain water drainage systems from the oil terminals end up in the harbour rain water drainage system. The rain water passes a contol basin, K1, a gravity separator and goes through a tunnel and a caisson to the estuary of the river Göta Älv in the open harbour.

THE ACCIDENT, ITS BEHAVIOUR, EFFECTS AND CONSEQUENCES

The accident:

At Saturday night 21 June, on Midsummer Eve holiday in Sweden, there was a spill of 328 metric tons of heavy fuel oil in the oil terminal during discharge of the product from a ship vessel to a storage tank. Approximately 50 tons of the heavy fuel oil reached the recipient. The oil passed the rain water drainage system, reached the open sea and contaminated beaches and seashores in the coast archipelago outside Göteborg.

On Friday 20 June 22.30 p.m., after a maintenance work, the discharge of heavy fuel oil from a ship vessel to storage tank No 375 was started by two operators. At the same time discharging to tank No 304 was ongoing.

At Saturday 21 June 00.30 a.m. when reading the level indicator the operators noticed that the level in tank No 375 did not continue to increase. The operators tried to increase the flow to tank No 375 by reducing the valve to tank No 304.

At 01.52 a.m. the operators discovered that the manhole of tank No 375 was open and oil was flowing out to the ground outside the tank and to a neighbour company in the harbour. The operators closed the valve to tank No 375 and also the manhole.

Oil spill outside tank No 375 was spread on the surrounding ground. Under the pipe rack (in the left) there was a rain water drainage sewer.

Photo: the insurance company (21 June 2003).

At 02.00 a.m. the terminal manager and a local cleaning company were informed about the accident.

The terminal manager arrived at 02.30 a.m., took over and informed the harbour service.

At 03.00 a.m. the cleaning operation started.

The ground at a neighbour company was filled with oil. Photo: the insurance company.

At 03.15 a.m. the harbour service staff inspected the harbour rain water drainage system and closed the outlet from the rain water drainage system basin K1. The basin K1 was full of oil.

At 04.15 a.m. oil booms were placed in the open port harbour at the outlet from the rain water drainage system. Oil lumps could be seen in the rain water drainage system outlet caisson and there was oil in the skimmer.

Cleaning procedures continued during Saturday and the authorities were informed about the accident. The Fire Brigade was informed on Saturday morning and they did not notice any oil in the open sea. The first indication of large environmental effects of the oil spill came on Sunday morning 22 June when the Swedish Coast Guard noticed oil on the opposite side of the river estuary.

The consequences:

Human effects.

- ✓ There were no personal injuries.

Material effects.

- ✓ The spill resulted in a contaminated area in the harbour of approximately 2000 – 2500 sq metres including the oil terminal and two neighbour company sites.
- ✓ The heavy fuel oil contaminated the harbour open rain water drainage system and the harbour oil contaminated drainage water system.
- ✓ Fishermen tools were contaminated and hundreds of yachts in several Göteborg harbours were contaminated too.

Environmental effects.

- ✓ Approximately 50 metric tons of the spilled heavy fuel oil reached the recipient.
- ✓ The spill resulted in environmental damage of a wide area at the coast archipelago outside Göteborg. The sea water was contaminated with high polyaromatic hydrocarbon (PAH) containing oil, beaches were contaminated, a small number of sea birds died and many birds were contaminated.
- ✓ The emitted heavy fuel oil contained high amounts of toxic PAH´s. In July 2003 significantly high levels of PAH metabolites were found in eelpouts caught in the area close to Fiskebäck, south of Göteborg. In November 2003 the levels of PAH metabolites in eelpouts caught in the same area were not higher than in eelpouts from other areas. The PAH containing oil had severe local effects shortly after the spillage but most of the area seemed to be recovered in November 2003.

The area outlined on the map shows how the oil was spread in the coast archipelago outside Göteborg. The oil spread in two main directions, south and west from the harbour of Göteborg.

Economic consequences.

- ✓ The total economic loss for the oil terminal was approximately 2,7 millions of EUR.

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.

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 irrelevance of the index concerning the quantity of dangerous materials released (in the meaning of the SEVESO Directive parameter Q1) is based on Concawe classification recommendations for heavy fuel oils, risk phrases R52/R53, which is not classified as a Seveso substance. The heavy fuel oil which was released was not classified with risk phrases and therefore it is not clear if it was a Seveso substance or not.

The level 4 of environmental consequences is due to the length of the water front which was approximately 20 km (parameter Env14). There were also consequences of contaminated surface of soil at a level 1, approximateley 0,2-0,25 ha. (parameter Env13).

The level 4 given to the economic consequences is due to the high cost of the loss of 328 tons of product and to cleaning and decontaminations costs of total 25 million Swedish kronor, i.e. almost 2.7 million euros (parameter €16 and €18).

There were no noticeable consequences regarding human aspects.

ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

The direct cause of the accident was the discharging of oil to a storage tank with an open manhole. The major latent factors which contibuted to the accident with the open manhole were :

- ✓ Communication. The accident happened after a shift take over after a maintenance work on the tank, and there was not enough information and communication between the two shifts.
- ✓ Operational procedures. Only a common practice procedure was available. Detailed check lists were missing for tank preparation and start-up process. Activities were carried out based on experience.
- ✓ Existing operational procedures were not followed and no double checks were made. The experienced operators did not double check the equipment before start-up. According to normal operation routine the operators should have done a control round out at the tank after the discharge had started. This check was not done.

Due to the Midsummer Eve holiday there were less personnel in the oil terminal than usual. The shift foreman was on vacation and the terminal manager had taken over the foreman's work.

The wide consequences of the accident were caused by a number of parameters :

- ✓ Wrong reaction. When the level in tank No 375 did not continue to increase the operators assumed there was some problem with the incoming flow. The operators did not go out and inspect the tank. Instead they increased the flow to tank No 375 by closing the valve to tank No 304. The oil was flowing out of the open manhole during one and a half hour before the operators went out to inspect the tank and discovered the open manhole.
- ✓ The normal emergency routines were not followed. According to harbour emergency plan, the harbour should be informed directly. It took more than one hour before the harbour staff was informed. When the harbour was informed the harbour staff inspected the rain water drainage basin K1 and noticed that it was filled with oil. Then the outlet of basin K1 was closed, too late.
- ✓ Cleaning activities started up early after the accident by the staff of the oil terminal. The behaviour of the operators and the terminal manager indicate that they were very stressed because of the accident. The Midsummer Eve holiday would also have some impact since the operating staff did not want to disturb people on vacation.
- ✓ The oil terminal is an old installation and therefore there were no bunds around the tank area where the accident occurred. The spilled oil was spread over a wide area on the surrounding ground. In a low point under a pipe rack close to the storage tank there was a rain water drainage sewer. A huge amount of heavy fuel oil reached the harbour rain water drainage system.
- ✓ There were no valves in the oil terminal rain water drainage system and therefore no possibility to shut off the contaminated part of the rain water drainage system.
- ✓ The density of this heavy fuel oil was higher than the density of water. The rain water drainage system is designed for oils lighter than water, based on gravity separators. There were no oil alarms installed in the rain water drainage system. The oil could not be seen on the surface in the open port and there were no specific routines for handling this kind of heavy fuel oil product.
- ✓ The booms that were placed in the open port harbour were not designed for heavy products. The heavy fuel oil formed clusters which were later detected between different layers of water where the river and the salt sea water meets, at 1-3 meters below the water surface in the river outside the harbour. Oil clusters were detected 2-10 meters below the surface in the sea south of Göteborg.

- ✓ The heavy fuel oil was probably mixed with lighter high aromatic oil and therefore the oil did not behave as expected. This heavy fuel oil formed clusters in the water and were spread over a wide area in the coast archipelago. The clusters dispersed and oil were detected on the sea water surface and on several beaches and harbours outside of Göteborg.

The oil formed clusters that did not float on the water.
The diameter of the clusters was 3 to 10 centimetres.
Photo: Swedish Coast Guard.

ACTIONS TAKEN

The accident occurred under normal operations, discharging of product from a ship vessel to a storage tank, and under normal conditions. The investigation team found five critical areas which were considered as relevant for actions:

- ✓ Operational procedures
- ✓ Emergency response
- ✓ Organisational related areas
- ✓ Communication
- ✓ Design

1. Operational procedures. Detailed procedures have been implemented for following operations:

- ✓ Detailed check list for shut down and preparation of equipment before start-up. Double checks between maintenace department and operating department.
- ✓ Detailed procedures for preparation of pump ways including all used pipes and tanks.
- ✓ One operator shall always be out at the tank at start of discharge until the tank level is above the manhole and above pipe connections and valves at the bottom of the tank.
- ✓ More routines and focus of the tank level increase rate have been implemented.
- ✓ A new routine for handling of heavy oil products has been implemented in the harbour system. The oil terminals have to inform the oil harbour staff before the arrival of ships with heavy oil products.
- ✓ Routines and procedures for work permit have been reviewed and improved.

2. Emergency response. The accident made it clear that the terminal staff did not fully understand what actions they were supposed to take in case of an emergency situation.

- ✓ The emergency plans of the oil harbour and the Oil terminal have been improved.
- ✓ A program for “Emergency response“ training is being implemented in the oil harbour together with the different oil terminals.
- ✓ The function of the tank level indication system has been clarified.

3. Organisational related areas. The accident showed that the operators had a tendency to use short cuts if possible. This behaviour indicated that there was a lack of risk and safety awareness in the oil terminal organisation.

- ✓ A yearly schedule for operator training has been implemented at the oil terminal.
- ✓ “Safety observation rounds” have been implemented at the oil terminal to verify safety awareness and that the operators work according to the procedures.
- ✓ The project “Safe Harbour” has been started in the oil harbour together with the different oil terminals. The project consists of 12 action areas of which some are described in this report.
- ✓ Different competence levels for all workers in the harbour have been defined and a safety course and “green card” for work in the harbour have been implemented.
- ✓ The involved terminal manager was replaced and lost his managing position. The involved operators were placed on daytime work after the accident. The CEO of the oil terminal lost his job due to the accident.

4. Communication.

- ✓ Routines for shift take over have been improved with a “shift take over checklist”.
- ✓ Emergency routines have been clarified at the oil terminal and at the oil harbour.

5. Design. The harbour systems are designed based on the principle that oil is lighter than water. The tank installations in the harbour are old and tank bunds are missing or are not sufficient in many cases. The following improvments have been made:

- ✓ The sewer under the pipe rack in the oil terminal has been connected to the harbour oil contaminated drainage water system and is no longer connected to the rain water drainage system.
- ✓ Oil alarms have been installed in the rain water drainage basins. In each basin there is now one oil alarm located at the surface and one oil alarm located in the bottom of the basin.
- ✓ Installation of oil alarm in the rain water drainage system at each oil terminal has been started.
- ✓ Installation of shut off valve of the rain water system at each oil terminal has been started.

The status of the storage tank bunds in the harbour is discussed and there will be improvements in the future.

LESSONS LEARNT

Lessons learnt from this accident include:

- ✓ The human factor has to be considered during design of process systems, operational procedures and check systems. There is always a possibility that routines will not be followed.
- ✓ The handling of heavy oil products in oil harbours has to be considered in safety reviews. Adjustments of system designs and operational procedures may be necessary for a safe handling of heavy oils.
- ✓ The characteristics of the heavy oil products have to be communicated to all persons involved.
- ✓ Safety awareness, frequent training of emergency plans and operational trainings are very important to avoid this kind of accidents.

Environmental consequences of the spill of heavy fuel oil in the oil harbour.

Photos: Stefan Larsson, West Water enterprise.

Fire in an aromatic extraction unit in a refinery

21 April, 2006

Notre-Dame de Gravenchon – [Haute-Normandie] – France

Refinery
Aromatic extraction unit
Distillates (vacuum)
Thermcouple well
Works
Sub-contracting
Safety management system
Communication

THE INSTALLATIONS IN QUESTION

The site;

For more than 60 years, the refinery has been located on the banks of the Seine in the Port-Jérôme industrial estate, within the commune of Notre-Dame de Gravenchon. The plant transforms crude oil into fuel (LPG, petrol, diesel fuel and kerosene), heating oils, bitumen and oils. The establishment includes all the conventional petroleum processing units (atmospheric distillation, vacuum distillation, catalytic cracker, catalytic reforming, isomerisation, and alkylation).

The unit concerned:

The unit involved in the accident is an aromatic extraction unit which uses NMP solvent (N-methyl-2-pyrrolidone, formula: C_5H_9NO). It is an oil processing unit based on vacuum distillation (distillates). The oils are processed oils with solvent in order to selectively extract certain compounds and thereby improve viscosity, colour, oxidation resistance and the lubricants' emulsion tendency.

The contact between the distillate and the solvent takes place in a counter current circulation system in a liquid/liquid extraction column in proportions and at a temperature which varies according to the nature of the distillate and the desired viscosity index. Two non-miscible phases form by gravity in the extraction tower: the "mixed raffinate", paraffin-based by nature and containing a small amount of solvent (10 to 20%), collected at the top of the column; "mixed extract", rich in solvent (85 to 95%) containing components that are eliminated and collected at the base of the tower.

After extraction and prior to storage, the raffinate and the extract are stripped of nitrogen to eliminate any traces of solvent.

The section of the unit involved in the incident is that involved in stripping the raffinate.

THE ACCIDENT, ITS BEHAVIOUR, EFFECTS AND CONSEQUENCES

Context:

After a major shutdown for regulatory inspection and work, the extraction unit was placed back into service on Tuesday, April 19th, 2006. Before being placed back into production, the unit was in recirculation phase and up to temperature (320°C / 3.5 bar) when the fire broke out.

The accident:

April 21, 2006 at 10.15 am: a fire was reported by an employee of an external company working in a structure of the extraction unit.

At 10.20 am: The unit's fixed firefighting means were manned by the operators pending the arrival of the mobile units: cooling and protection of the structures.

From 10.22 to 10.52 am: The mobile and fixed firefighting resources on the extraction unit were put into action (foam truck, foam nozzles, …).

At 10.40 am: The Internal Contingency Plan is put into motion.

At 10.56 am: The extraction tower and ancillary units decompressed and liquid inventories reduced to a minimum.

At 11.00 am: The fire was put out but structural cooling operations continued.

At 12.20 pm: The product leak is located (bottom line of the raffinate stripping tower) and continued spraying of the product leak.

At 1.25 pm: The internal contingency plan is lifted (prevention ensured by operators with the portable water canon).

At 3.00 pm: End of operations.

The fire was not sustained and remained localised in the raffinate stripping tower. The flames were quite high (in the order of 15 m), followed by decreasing and recovery periods.

Consequences:

The accident had no human consequences. The environmental impact was limited to smoke released by the fire. The liquid effluents generated by the firefighting operations (firefighting water, foam blanket…) were directed to a catch tank and no increase in pollution was noted in the Seine on the day of the incident. The release standards were respected.

On the equipment level, the following was established after the fire:

- Several main circuits were exposed to the flames, notably:

    - the bottom line of the raffinate stripping tower,

    - the transfer line between one of the two extract reheating ovens and the first nitrogen stripping column,

    - the line supporting the raffinate supply control valve from the extraction tower to the raffinate stripping column.

- The fire-resistant concrete protecting the skirts around the stripping and extraction towers received only superficial damage.

- The framework elements trapped in the fire were not deformed, except for two supporting beams.

- The aluminium sheeting covering the heat insulation of certain circuits were partially melted.

- Approximately 70 electrical and instrumentation cables were damaged by the fire.

- The junction boxes were not harmed in the fire (paint still intact).

- The heat lagging protected the metal enclosures of the equipment and piping from the fire.

- The scaffolding installed in the zone and engulfed in the flames remained intact, except for a single element whose tubing was seriously deformed and whose wood planks fuelled the fire.

It should be noted that the property damage remained essentially within the unit.

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 "dangerous materials released" is ranked 1 as 1.4 tons of raffinate (easily flammable liquid as per the Seveso Directive, Appendix I, part II) was released during the accident (parameter Q1).

The "economic consequences" index is rated 2 as the economic impact of the incident was calculated to be approximately 1 million euros in production losses, with property damage being evaluated at less than 40 k€ (parameter € 16).

The accident had no human or significant environmental consequences. The liquid effluents generated during the fire were recovered and processed in one of the refinery's treatment stations (in particular, no dangerous product was released into the Seine).

ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

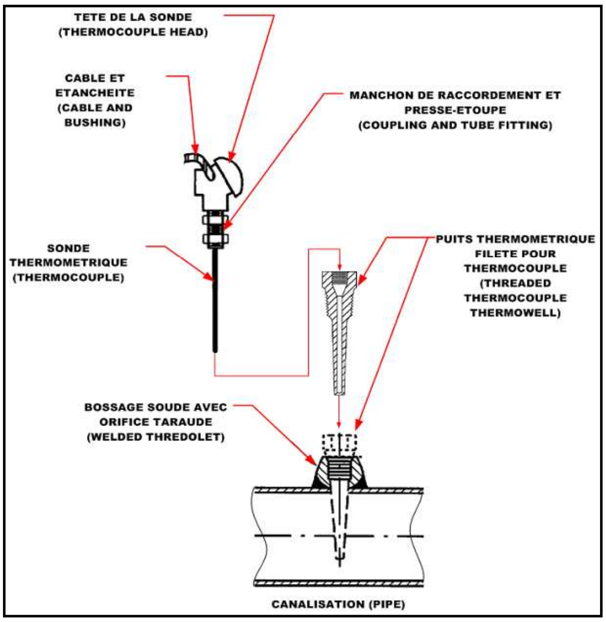
Origin and causes of the accident:

The analysis of the incident discovered that the thermocouple was improperly installed on the bottom circuit of the raffinate stripping tower. The installation was not in compliance with the construction drawing of a thermocouple well on a pipe.

A proper installation of a temperature sensor (see diagram below) adapted to the installations' service conditions would consist of the following:

1. A threaded boss on the pipe wall intended to receive the thermocouple;
2. Screwing of a "sensor pocket" on the aforementioned boss and reinforcement by means of a weld bead;
3. The thermocouple is then screwed into the pocket;
4. The wires are connected to a signal transmitter, once the cable is connected to the sensor by means of a coupling.

In this configuration, while ensuring a reliable temperature measurement, the thermowell guarantees that there will be no direct contact between the process fluid (for which we are attempting to measure the temperature) and the thermocouple. In the case of accidental rupture (contact between the process fluid and the thermocouple), the tube fitting limits/prevents the loss of confinement provided that the leak is not excessive.



Temperature sensor assembly diagram

The investigations conducted following the incident showed that the thermocouple had been installed without a "sensor pocket", thus without protection. The hot raffinate was thus in direct contact with the sensor. As the quantity of product was excessive and the fluid very hot (320 °C), the tube fitting was unable to properly maintain the seal, leading to self-ignition of the product released and in contact with the air. The equivalent diameter of the break at the pipe level is roughly 10 mm.

A pool of flame quickly spread across the ground, forming flames of 5 to 6 m. The fire reached the scaffolding planks within the structure, increasing the height of the flames up to approximately 15 m for 8 minutes. The firemen were able to put out the burning wood, allowing only the initial pool to burn.

Analysis of the fundamental causes of the incident:

1) Traceability of job site phases

The operator conducted more extensive research to determine the reasons behind the faulty thermocouple installation. During the major shutdown for regulatory inspection and work on the NMP extraction unit, the following elements were brought to light:

- The replacement of the line on which the thermocouple was installed, was planned and undertaken during the unit's major shut down.

- An initial request for work was not requested for the disassembly of the thermocouple on the button line of the raffinate's stripping tower. According to the individual managing instrumentation work, this procedure is normally performed by "Piping" crew supervisor. The "Instrumentation" organisation did not issue a permit authorising the disassembly of the thermocouple of the line to be replaced.

- No permit was issued to install a thermowell on the new bottom line of the raffinate stripping tower. No request was submitted to the "Instrumentation" organisation to provide the company working on the unit with a thermowell notably consisting of a "sensor pocket".

- The isometric drawing of the circuit and the list of required materials were given to the external company to perform the work on the new bottom line of the raffinate stripping tower. When the company's pipe fitter arrived at the site, the thermocouple had already been removed from the old line. He thought that it was an element reduced by ½" in diameter on the 1" dia. boss. (it was in fact a "sensor pocket" and not a ½" adapter fitting). He thus welded a 1" x ½" adapter fitting on the new section of line to have the same configuration as the old line.

- Once the welding operations were completed, the adapter fitting was equipped with a threaded plug to allow the new circuit to be tested. Once the leak test was performed, the plug was removed, thus leaving the pipe open.

- A work request was not made concerning the reinstallation of the thermocouple (normally submitted to the "Instrumentation" crew by the "Piping" crew); no permit was issued to reinstall the thermocouple on the new line.

- The piping company did not refit the thermocouple. The pipe work acceptance sheet relative to the extraction unit shows that the instrumentation was in place and reconnected just prior to restart. In the end, only three permits were granted for the following work: blinding, cold cutting, welding, grinding, testing and blind removal.

- It was not possible to establish who actually removed the thermocouple from the old line and who put it back in place on the new line.

2) Analysis of the failure of the safety bars

The piping company did not inform the operator that it had removed the adapter fitting which was not requested, nor that the thermowell indicated in the list of equipment had not been supplied.

The refinery's instrument specialists had never been involved in this operation.

The line's testing procedure had been accepted with an adapter fitting that had not been requested. The boss designed to receive the thermowell had also been plugged: it was thus impossible to identify that is was not in place.

When the line was accepted, neither the presence of the non-requested adapter fitting, nor the presence of the thermowell were identified.

The nitrogen flushing, leak testing and the introduction of cold then hot product, did not allow the well's absence to be detected prior to the incident.

ACTIONS TAKEN

The Classified Installations Inspectorate visited the facilities on the day of the incident. The Inspectorate requested that the operator provided an incident report before authorising the unit to restart. Owing to the operator's reactiveness in managing the incident and the "post-incident" measures taken, no administrative penalty was proposed.

The property damage was essentially limited to the instrumentation and pipe elements without involving all of the pressure tanks. The main work performed on the unit prior to its restart after the incident consisted of the following:

- partial or total replacement of approximately 70 instrument cables;

- the overhaul of certain control valves and various level measurement accessories;

- reworking of seals and the replacement of the threaded fasteners of parts exposed to the fire, in accordance with the inspection service's recommendations;

- the installation of a thermowell for a thermocouple on the bottom line of the raffinate stripping tower;

- the refurbishing of the analyser circuit and its support elements;

- reworking of the stuffing boxes on the valves exposed to the fire;

- replacement of destroyed or impregnated heat lagging;

- inspection of the electrical insulation of pumps and their drying;

- replacement of damaged spring boxes.

The damage to the guniting was also considered to be minor. The necessary repairs were undertaken to allow the installations to be placed back into service safely just a few days after the incident (the Classified Installations Inspectorate granted restart authorisation of the unit on April 25, 2006).

LESSONS LEARNT

In addition to the human error that resulted in significant property damage to the unit, the faulty installation on the thermocouple resulted in a **failure of the Safety Management System**:

- lack of communication between the refinery's "Piping" and "Instrumentation" departments,
- poor definition of each department's role,
- incorrect application of the procedures,
- non-compliant work acceptance,
- poor definition of the work requested of the external company.

The operator proposed to implement the following avenues of improvement with regard to the acceptance of piping work and the thermocouple installation process as defined in the Safety Management System:

1. Establish a "maintenance procedure" clearly stipulating the work to be performed by each trade (notably, "Piping" and "Instrumentation"). These procedures are developed by the refinery personnel and must be applied by the external companies. They describe the individual steps to follow regarding the inspection, repair and maintenance of technical systems. They must also display the list of spare parts required for the work to be performed and to establish the time required to perform the work.
2. Stipulate in the specific "Piping/Valves" Specifications intended for external companies, that the piping company is responsible for the installation of wells. This company must also procure the parts from the refinery's supervisory department, and so that all modification in relation to the isometric drawings must be reported to this same department.
3. Stipulate in the specific "Instrumentation" Specifications what verifications must be performed in order to ensure that a thermowell is present before installing a thermocouple.
4. Work with the platform's Inspection Department so that the lines equipped with thermowells are tested with the "sensor pockets" in place (plugging the pipe bosses intended to receive the thermowells is prohibited).
5. In the pipework acceptance phase, refuse all additional part added by the external company that does not appear on the isometric drawing.
6. Add a "thermowell" line to the "piping/valves" acceptance sheet.
7. Reinforce the message that only the refinery's instrumentation specialists are authorised to remove/install instruments.

This feedback, rich in information, was shared among other refinery units in which similar incidents could occur.

Emission of H_2S in a Waste Treatment Facility

5 November, 2005

Rhadereistedt - Germany

Slaughterhouse wastes
Fermentation facility
Defective installation
Unloading
Bacterial activity
Chemical reaction
First aid versus self - rescue

THE INSTALLATIONS IN QUESTION

The site involved is a fermentation facility where vegetable and animal waste are fermented under production of heat and energy. The waste was transported from the Netherlands. The site is located in Rhadereistedt (Germany) but may be representive for fermentation facilities in general.

THE ACCIDENT, ITS BEHAVIOUR, EFFECTS AND CONSEQUENCES

Waste that remains after slaughtering animals must rapidly be removed and processed. This prevents unpleasant odours and unsanitary situations. An important method which is used is processing the animal waste in fermentation facilities as a result of which biogas is generated. It is obvious that this biogas can be used for heating or electricity production. Also vegetable wastes can be processed in this manner and often these wastes are processed simultaneously with animal wastes.

Besides their energy-content waste also can have other useful applications, for example in the case of intestinal membranes of pigs. These membranes contain the substance Heparin which is used by the pharmaceutical industry as an anti-coagulant for human blood. For the transportation and the extraction process the waste is, due to pharmaceutical demands, stabilized with sodium bi-sulphite ($NaHSO_3$). The Heparin is separated by means of hydrolysis. Afterwards the remaining material is processed in a fermentation installation as described before.

The accident:

On the 5th of November 2005, after collecting the Heparin by a pharmaceutical company in the Netherlands, the remaining material was transported by truck to a fermentation facility in Rhadereistedt, Germany.

On site the normal unloading procedure was not followed due to a failure of the unloading equipment. The pit was open because the hoist used to close the heavy metal doors was defective. In this pit there were some remains present from earlier loads. While unloading the material a large quantity of hydrogen sulphide (H_2S) was emitted.

The consequences:

Due to the H_2S emission an operator was poisoned. Another operator, the truck driver and some other people who were present and/or came to rescue also suffered the toxic effects of H_2S. The outcome was 4 fatalities and one seriously ill in hospital.

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 quantity of dangerous materials released is set on level 1 because of the small quantity of hydrogen sulfide released (in weight). Although the concentration of hydrogen sulfide was very high from the point of view of toxicity for humas present.

The level 3 given to the human and social consequences is due to the number of casualties (4 fatalities and 1 person hospitalized).

No level was given to the environmental consequence because the emission in cubic metres/weigth was small and was vented away resulting in non-harmfull concentrations.

The level of economic consequences of the accident was low (no loss of expensive products, no damage).

ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

Facts:

1.Dutch pharmaceutical company extracts Heparin from intestinal membranes of pigs, stabilized with $NaHSO_3$.

2.Remainders are dipatched by closed truck to a fermentation facility in Germany: Rhaderreisted.

3.Truck arrives too late and stays overnight outside the gate (150 mtrs from the entrance).

4.The next morning (ca. 6:00 am) unloading of 25 tons of waste into a pit takes place. The driver opens pressure release truck.

5.The pit (100 m^3) contained 20% sticked material. Previous unloading consisted of animal waste and lactic waste.

6.Unloading did not taken place through the air tight valve connection but through an open cover: => malfunction of a hoist to move the heavy metal doors which normally cover the pit.

7.The air exhaust and the stirring device were in operation.

8.Large quantity of H_2S was emitted !

9.Acidity of the waste:

•On dispatch: pH= 8.5-8.6

•After unloading in the pit: pH= 5.6-5.9

11. Temperature:

•On dispatch: T= 60-65 ºC

•During unloading: T= ? (no thermal insulation of the truck)

12.Operator collapses during unloading.

13.Truck driver and other personell rush in for assistance.

14.Outcome: 4 fatalities and one seriously ill in hospital.

Scenario:

1.Possible origin of Sulfur:

•Intestinal membranes

•Stabilizer $NaHSO_3$ (1.5%)

2.Acidity:

•Lowered by the presence of products from a previous load (20%) => dairy material (containing lactic acid).

3.Escape of H_2S gas:

•Possible because using an opened cover during unloading.

4.Operator does not know the possibility of H_2S release (hazard assessment) .

5.Concentration of H_2S is too high to be noticed by smell.

6.No detection / alarm/ measurement equipment present.

7.No emergency training means that those trying to help were killed too. 1st rule of First Aid is that the helper is not endangered.

ACTIONS TAKEN

Investigation of the site took place by the Dutch inspectorate: Visiting the site and communicatiion with local personnel and local authorities took place.

Research questions were given to a research institute (Rivm a.o.) about the correlation pH and H_2S-release with stabilisized and non stabilized waste. Results are expected mid 2007. The research is doen because It is likely that similar accidents may occur with other kinds of wastes in fermentation facilities, large and small, industrial and on farms. When proven the licensing authorities will be informed.

LESSONS LEARNT

1.Lack of caution with a familiar, but not well understood issue: smelly waste.

2.Do not take rescue actions without thought.

3.Knowledge is important about possible generation of H_2S .

•Hazards •Safety measures •Measurements

4.Always assess possible chemical reactions.

5.Good maintenance. Malfunction = non-use!

6Measuring equipment H_2S and pH should be available.

7 Research should be done to find a alternate stabilizing agent (non S). At the moment the agent is obligatory for the farmaceutical process of extracting heparin from the membranes. Within about 10 years the heparin wil possibly be produced synthetically and the agent will not be nescesarry for this application any more.

8 The accident could possibly also occur with other types of fermentation facilities that don't have proper equipment and procedures.

Release of toxic gas from a vacuum truck at an installation for treating hazardous waste

29 December, 2005

Stuttgart - Germany

Toxic release
Hazardous waste
Vacuum truck
Safety management

THE INSTALLATIONS IN QUESTION

The hazardous waste treatment facility is located in the commercial port area of Stuttgart. The facility receives a wide range of hazardous wastes in a variety of containers. Some wastes can be treated on-site and others must be transported to other facilities to be treated.

THE ACCIDENT, ITS BEHAVIOUR, EFFECTS AND CONSEQUENCES

The accident:

On 29th December 2005 an accident took place in a hazardous waste treatment facility in which an employee was killed and six others (two employees, two members of the emergency services, and two employees of contact companies) suffered injuries and required hospital treatment.

The cause, based on current knowledge, was the release of hydrogen sulphide (H2S) from the tank vent of the vacuum-truck whilst liquid wastes were being pumped from steel drums into the vacuum-truck. A fork-lift truck driver who happened to be in the immediate vicinity was found dead near by; the cause of death being the toxic effects of hydrogen sulphide. Five of those treated in hospital were also suffering from the health effects of hydrogen sulphide.

The fire-brigade could not identify any hazardous gas concentration on arrival at the scene. The fire-brigade then left the site. To secure the scene for the police investigation, the police ordered that the contents of the suction hose should be drawn into the vacuum-truck. The vacuum pump was restarted and once again hazardous sub-stances were released from the tank vent. This process led to the collapse of the vacuum-truck driver. As a result the police ordered that the operation should cease and the fire-brigade and an emergency doctor were called to the scene.

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 of the index concerning the quantity of dangerous materials released (in the meaning of the SEVESO Directive) expresses the small quantity of toxic substance (H2S) which was released (parameter Q1).

The level 2 given to the human and social consequences is due to the one fatality and the number of people suffering from the effects of the toxic substance (H2S) (parameter H3, H4 and H5).

The economic consequences was not evaluated.

Finally, there is not any noticeable consequence regarding environmental consequences.

ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

The immediate cause of the production of toxic gas was the combining of liquid wastes which on mixing react together releasing H2S. An organo-sulphur (thio) compound was mixed with an organic, acidic compound leading to an unexpected liberation of hydrogen sulphide.

The indications are that the organisational measures which had been taken were not adequate to prevent this event.

The operator was not able to demonstrate that adequate measures for the identification, assessment and documentation of the hazards of the individual containers of hazardous waste received. The hazardous wastes which were received in drums and brought together in a vacuum-truck were to be transported from the waste treatment facility to another location because they could not be treated on site. The operator was not able to demonstrate that adequate measures were in place to regulate how the drums should be pumped into the vacuum-truck (order, ruling out of any hazardous chemical reactions). There were no adequate measures for the safe discharge of gases vented from the vacuum-truck.

ACTIONS TAKEN

As a result of this incident there is a criminal investigation which is ongoing. This is also a reportable incident under Seveso II.

The mixing of hazardous waste in the vacuum-truck is no longer carried out and the operator transports the drums of waste, untreated to another location.

Operators and inspectors need to be made aware that vacuum trucks have potential hazards relating to their operation and that under no circumstances should it be tolerated that chemical reactions be carried out in the tank of the vacuum-truck. The treatment of hazardous waste should be carried out in a controlled manner in designated reactors with suitable monitoring equipment.

Vacuum-truck operations may be carried out at a number of sites; therefore the State Institute for Environment, Measurement and Nature Conservation Baden-Württemberg issued the following recommendations to the regional governments of Baden-Württemberg.

Prevention measures:

1. Problematic wastes, that is, wastes which either have hazardous characteris-tics themselves or on mixing with other substances may release hazardous sub-stances must receive special consideration.

2. The safety critical parameters / characteristics for these wastes must be de-fined.

3. The safety critical characteristics which have been defined for the identification of the waste and which regulate the further treatment, e.g. pH, must be tested for every container (drum, IBC, tank) which is delivered, documented and confirmed with a signature.

4. Procedures must be defined for the handling of containers which deviate from the criteria.

5. If more than one container of problematic wastes are to be combined (in a vacuum-truck), then a list of the containers together with their hazards, and the safety critical parameters is to be made and the operation assessed as to its feasibility. Following this a mixed-sample of those wastes which are to be combined is to be taken. The order of mixing is to be noted.

6. If it becomes apparent that a combining of the wastes is only possible under compliance with a particular order of mixing, then this order is to be laid down in writ-ing and the adherence to this order is to be controlled and documented.

7. Before initiating the pumping process the tank vent of the vacuum-truck is to be connected to a suitable exhaust gas system. If this is not possible, then the location and orientation is to be chosen so as the vapours may be vented safely at all times.

8. Access to the area in which the vacuum-truck and pumping operation are lo-cated for persons not involved in this procedure is to be prohibited. The area is to be clearly marked and cordoned off.

LESSONS LEARNT

- ✓ Operations involving the use of vacuum-trucks may lead to the release of hazardous gases / vapours.
- ✓ Where ever possible, measures need to be taken to avoid the release of toxic (or flammable) vapours from the vent of the vacuum truck tank and to prevent the exposure of employees and others to such hazards.
- ✓ Vacuum trucks are not suitable for processes involving the mixing of hazardous wastes which may lead to a chemical reaction and the subsequent release of hazardous gases or vapours.
- ✓ The treatment of hazardous wastes requires a robust safety management system with:
  - ✓ Clear definition of responsibilities for all operations within the treatment facility
  - ✓ Definition of and testing for safety relevant criteria and characteristics (e.g. pH, Temperature, colour, viscosity, odour, phase separation) to enable hazardous wastes to be accepted and treated or transported safely,
  - ✓ Documentation of the .whole process from the acceptance of a hazardous waste to its disposal including all safety critical criteria and characteristics.

Tank failure in a bitumen storage unit of a refinery

8 September, 2004

Italy

Refinery
Storage unit
Tank
Bitumen / hot-oil
Failure
Overpressure
Victims

THE INSTALLATIONS IN QUESTION

The site:

The refinery is located in the centre part of Italy, and is strategically situated in the middle of the Adriatic coast to cover a large area of eastern Italy. it is part of one of the top 20 private industrial groups in Italy.
It has been operating since 1950, and has about 500 employees. It has a production capacity of 3.9 million tons/year, and represents nearly 5 % of national refining capacity. Its storage capacity is over 1.500.000 m3 of oil products in 128 tanks.
The plant, cover 70 ha of area, and is located in an urban site (Fig. 1), near the city, the motorway, the railways, the port (slipway) and the airport.
The plant is under Seveso II Directive (upper tier plant).

Fig. 1 Photo DR

The unit concerned:

The unit consists 12 fixed roof tanks, 8 loading arms and 6 pumps for transfer/loading of bitumen, 1 heat-exchange for possible additional heating of stored bitumens.

The accident took place in the cylindrical atmospheric tank of bitumen (TK145), operative since 1970 and extended in the near loading/unloading areas. With 1200 m^3 of capacity, 12 m of height, the tank was equipped with an internal heating coil, positioned at the bottom, in order to assure an internal temperature of 170℃. The coil was feed with hot-oil at 280℃.It was also equipped with level indicator, temperature indicator, and a mixing stirrer.

There were about 592 m^3 of bitumen inside the tank, and about 150 m^3 of hot-oil inside the heating circuit, at the moment of the accident.

THE ACCIDENT, ITS BEHAVIOUR, EFFECTS AND CONSEQUENCES

The accident:

At 07.25 a.m., a catastrophic tank (TK145) failure occurred: the shell and roof tore off the foundation were projected in vertical direction, and were moved laterally 15 m away. Along the way, they broke some pipe rack, at about 5 m of height, and then fell and on a 2nd bitumen storage tank, causing a massive total leakage of bitumen (about 550 t) and hot-oil (about 120 t) at 170°C, and their spreadin g all over the areas.

The missile-tank exploded fell down on a 2nd bitumen tank (TK166) of 8000l of capacity. The missile roof entered in the TK166 shell, then squeezed itself into the TK166 basin (Fig. 2,3).

A pool-fire was then ignited in the TK145 basin, other fires followed involving equipments in sight, with domino effect on others tanks and on some tank-trucks under loading, located in the area. The fire was then fed by the hot-oil releasing from the heating circuit, due to the tear of the circuit lines connected to the tank coil.

At the moment of the accident, there were 8 tanker in the area, ready to loading/unloading operations and 9 persons in the site: 7 drivers, one internal shift operator and the site-head which is inside the building located in the area, and had just finished the line preparation for tanker n°1 loading from the TK145. The operator was monitoring the TK252 level, installed on the basin wall in common with the other bitumen storage tanks (TK251, TK252, TK253 e TK328).

The emergency alarm started and the internal emergency measure, cooling and spread-foam systems activation, were immediately applied. The internal fire team's intervention was immediate, involving 6 fire-men and 2 fire-trucks.

After 25 minutes from the internal emergency alarm, the external Fire Brigades arrived. All the units area involved was put in safety condition.

After about 3 hour the fire was controlled, and the emergency was closed.

The consequences:

The accident caused effects to people and to environment, and did non lead to significant off-site consequences, even if the accident generated distress in the population, which was taken into account by the media and the public authorities.

Human effects

One driver burned by bitumen and projected inside a tank basin, where his body was found 3h later the fire extinguished. Three other drivers differently injured by the contact with the hot bitumen: 2 hospitalised and 1 treated and released.

Environmental effects

The bitumen released expanded in a vast area of about 13.000 m^2 (2% whole refinery area). Part of the product (6-34 t) involved the external site, releasing in the sea through an internal ditch of the refinery.

The effects of the smoke plum on the near city population were judged at low impact by the Regional Agency for the protection pf Environment.

Consequent to the accident, the central scientific research institute for the sea performed a series of controls in the sea, and recovery operations of spread bitumen. Moreover, sanitary local authorities conducted some shellfishes analysis.

Limited quantities (some hundred of kg) of bitumen were recovered in the sea near the establishment, or in the seaside beach for 8 km far away.

Economic consequences

According to a preliminary costs estimation made by the society:

-3 millions of euros for structural losses

-0.5 millions of euros for emergency

-3 millions of euros for clean up

-31 millions of euros for response and restoration of the establishment

-25 millions of euros for production loss (for 1 year, which is the time estimated for the bitumen plant activity recovery)

Fig. 2 Photo DR

Fig. 3 Photo DR

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.

About 120 tons of hot-oil (classified as dangerous for the environment R51/53) have been involved (5% of 500 tons Seveso threshold) justified the level 3 for "dangerous materials released" (parameter Q1).

With one person death and three other injured, the parameter "human and social consequences" reached the level 2 (parameter H3).

The level 3 for "Environmental consequences" is explained by the pollution of the seaside beach for 8 km far away (parameter Env14).

The production losses, estimated at 25 M€, explain the level 4 for the "economic consequences" (parameter €16).

ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

The two principal hypotheses assumed based on a preliminary analysis conducted by the society, are:

- an internal overpressure in the tank caused by explosion of light flammable hydrocarbons, wrongly introduced in the tank

- an internal overpressure in the tank caused by rapid phase transition of water, wrongly introduced in the tank, (internal temperature 170°C)

Further following investigations lead to consider the first one, related to the wrong introduction of light flammable hydrocarbons compounds during unloading to the tank of bitumen in excess present in tank-trucks.

ACTIONS TAKEN

Emergency measures:

Internal fire-team immediately was activated, followed 30 minutes later, by Fire Brigades (15 trucks and 35 fireman).

The external emergency plan was activated with:
- interruption of railways traffic, which runs inside the plant
- interruption of the near roads traffic
- reduction of the near airport activity, without practical consequences
- blockage of electrical feeding of 132 kW line which runs along the railways
- start-up of the mixed advanced coordination centre
- start-up of the procedure for the information to population.

Fire was handled through water and foam, while tanks and browsers involved were been cooled (Fig. 4, 5, 6).

After about 2 hours the fire was under control, and the railways traffic was opened 3 hours later.

The emergency was concluded with the put in safety of the plant, according to the dispositions of the judicial authority, who sequestrated the whole area.

Fig. 4 Photo DR

Fig. 5 Photo DR

Fig. 6 Photo DR

Actions taken:

A detailed investigation is still in course, to understand the causes of the accident.

The regional technical committee immediately disposed to the operator after the accident:

- detailed technical report of the accident, containing the design solutions adopted in similar bitumen plants
- request of a new SMS inspection
- adoption in short/medium period of the following measures acted to move the loading ramp away from the storage area and verify the safety conditions of all the hot-oil circuit of the refinery
- improve the internal emergency plan, in particular the time to evacuate operators, and the interface between internal and external fire-teams.

LESSONS LEARNT

The accident put in evidence some SMS issues that had an important role in the event occurred. The table here below explains, for each SMS issue identified, the principal corrective actions taken or planned.

Description	Actions taken	Actions planned
Operating procedures and instructions in normal, abnormal and emergency conditions	More attention for process parameters monitoring, providing a temperature controller of bitumen inside, and blockage in case of over temperature max. The same for temperature and flow of hot-oil in the coil.	Realization of temperature control systems for bitumen in the tanks, with heating system blockage and bitumen feeding blockage Realization of blockage system of hot-oil line to tank coils, in case of over temperature Realization of blockage system of hot-oil flow-rate, in case of different flow-rates in input/output from plants
Emergency team organization. Alarm systems and communication and support to the external intervention	Difficult communication among fire teams. Need of a more rapid recognition of possible persons missing. Need of an improvement in information exchange between the emergency centre (in the offices) and the operators in site. Need of a more integration between the internal fire team and the Fire Fighting	Internal emergency plan improvement, in particular for the involved personnel control and census, and for the operative emergency procedure of internal fire team
Controls and verifications of the management of emergency situations	2 bitumen tanks involved didn't have the cooling system active	
Identification of substances and processes hazards; definition of safety requirements and criteria. Emergency management	Plant lay-out, storage area too close to loading area, few space available for emergency team intervention….	Remove the loading platforms from the storage area
Planning and updating of technical and/or managerial solutions for the reduction of risks	Need of a more congruency between safety analysis, operative procedures on normal, abnormal and emergency conditions, and actions for risk reduction. The safety analysis should consider a possible introduction of lights compounds by unloading the bitumen from the overloaded tank-truck	realization of automatic system for tank-truck loading, equipped with weigh at prefixed load, too-full detectors and systems "at present man", to avoid or limit overloading prohibition of direct unloading of overloads to bitumen tanks adoption of management and technical measures to avoid water and lights introduction in bitumen tanks provide an explosive atmosphere presence monitoring inside the bitumen tanks
Maintenance procedures	Necessity of systematic control of restoring and washing for the tank-trucks	Adoption of system to verify the presence of the recovery and clean-up certificates for the tank-trucks

Rupture of a crude oil storage tank

25 October, 2005

Kallo – Belgium

Rupture
Flammable liquids farm
Storage tank
Crude oil
Corrosion
Periodic control
Thickness measurements

THE INSTALLATIONS IN QUESTION

The oil storage terminal contains 7 storage tanks in one large bund made with earth dikes. Between the tanks there are lower inner dikes.

- ✓ 4 crude oil storage tanks with a content of 40 000 m^3 each: D1, D2, D3 and D4;
- ✓ 2 storage tanks for the multifunctional storage of crude oil or rainwater contaminated with crude oil, slop oil, with a content of 24 000 m^3 each: D10 and D11;
- ✓ 1 small tank D26, with a content of 730 m^3 which is out of service.

The crude oil is delivered by pipeline from the port of Rotterdam and after some storage at the terminal at the left bank of the river Scheldt the feedstock is pumped by pipeline to a refinery, which is situated at the right bank of the river, where it is further processed.

The oil storage terminal was licensed by a decision of the Permanent Executive of the Province of East Flanders on February 7th, 1991 for a period expiring on February 6th, 2011.

The establishment falls within the scope of application of the Seveso II Directive because of the presence of more than 50.000 tonnes automotive petrol and other petroleum spirits. The license allows the company to store 208.000 m^3 of crude oil. For that reason the terminal is an upper tier establishment.

On September 12th, 2005 a minor incident occurred at the storage tank D3. During this incident crude oil leaked from the bottom of the tank. In October 2005 the exact cause of this incident was not yet known, because the tank bottom was not yet fully cleaned to start the investigation of the incident. At the moment the major accident occurred with tank D2 cleaning operations for storage tank D3 had just started in order to inspect storage tank D3.

The storage terminal is permanently manned during daytime. In the evening and at night inspection rounds are performed by an external security company. The permanent supervision of the terminal (by means of cameras) and the filling and discharging operations of the storage tanks are completely managed from the control room at the refinery.

THE ACCIDENT, ITS BEHAVIOUR, EFFECTS AND CONSEQUENCES

The accident:

On October 25, 2005 around 18.15h a major leak at tank D2 was detected. The operators in the control room of the refinery were alerted by a low level alarm for tank D2. Storage tank D2 contained almost 37 000 m^3 crude oil before the release. The level history in the control system situated in the control room of the refinery indicates that after a short period of increasing leakage almost the full inventory of storage tank D2 was released within 15 minutes.

The accident has been considered a ‘major accident’ according to the criteria set in Annex VI of the Seveso II Directive.

The consequences:

Consequences for the installation

Because the content of the storage tank was released in such a short time, an enormous crude wave was created. This wave moved in the direction of the several meters high earth dike, which fortunately resisted against the power of the wave. The released crude oil filled the whole bund (40 000 m^2 large) with crude up to a height of 1 m.

After the release the storage tank was leaning forward and a part of the foundation of the storage tank had disappeared.

Consequences for the environment

- ✓ *Air pollution:* the enormous amount of crude oil that was captured in the bund caused strong odour pollution in the wide surroundings of the depot. Odour pollution was reported close to the border with the Netherlands due to the very strong wind in Northwest direction that evening. Although the company took several measures to fight the odour pollution (like covering the bund with sand and foam), odour complaints were reported during several days after the accident. Another series of odour complaints occurred two weeks after the accident at November 11th 2005, at the moment that the floating roof of the tank has landed by which means the function of the seal of the floating roof was lost.
- ✓ *Surface water pollution:* There was a very slight contamination of surface water in the surroundings. Due to the height of the dike only a small amount of crude oil (approximately 3 m^3) was ejected out of the bund. This caused a confined pollution of the polder ditch which is situated at the outside of the terminal.
- ✓ *Soil pollution:* the upper layer of the bund is a clay-layer. In the past a layer of sand of approximately 50 cm was placed above this clay-layer in the area of the bund where there are no tanks. Under this layer, about 1,2 m deep, there is a sand layer. Samples of the soil were taken to determine the soil pollution. These samples showed that the clay-layer stopped the pollution. The part above the clay-layer was polluted over the whole area of the bund, the depth of this pollution varied from 10 cm up to 1 m.

  Also on the other side of the road near the terminal samples of the soil were taken because of the presence of a nature area. Due to the accident some of the grass in this area was covered by a mist of crude oil. Analysis of these samples showed that no soil pollution occurred in this area.

Figure 1 shows a picture of the situation in the bund the morning after the major accident happened.

- ✓ *Groundwater pollution:* analysis of the groundwater showed that there was no groundwater pollution due to the accident. First some increased concentrations of benzene were measured near tank D2, but after the removal of the polluted soil the situation was normalised.

Consequences for the people : There were no injuries caused by this accident.

European scale of industrial accidents:

By applying the rating rules of the 18 parameters of the scale made official in February 1994 by the Committee of Competent Authorities of the Member States which oversees the application of the 'SEVESO' directive, the accident can be 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 level of the dangerous substances index is 4 because approximately 30.000 tons of crude were released (parameter Q1).

The level of the human and social index is 0 because there were no injuries.

For the environmental consequences the index is 3 because the surface area of soil requiring cleaning is 4 ha (parameter Env 13) .

The index for the economic consequences is 5 due to the high cleaning costs (€ 18).

ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

History and construction information of the storage tank D2:

The storage tank was an atmospheric storage tank with an external floating roof and with a cone-up bottom. The storage tank had a diameter of 54,5 m and a height of 17 m. Because of the cone-up bottom the present water in the crude oil flowed towards the shell of the storage tank, where one water sump system was installed. The storage tank also contained two mixers, to put a part of the sludge back into suspension.

The foundation of storage tank D2 consisted of a crushed rock annular ring. The rocks had a diameter between 50 mm and 150 mm. The crushed rock annular ring had a height of approximately 120 cm of which a part was below the ground level. The crushed rock ring had a width of approximately 340 cm at the bottom and 100 cm at the top. The shell was situated in the middle of the width of the crushed rock ring. The inner part of the annular ring was filled with compacted sand. Above this sand there was a layer of 5 cm consisting of oiled sand, to avoid external bottom corrosion. Figure 2 provides a schematic view of the foundation of storage tank D2.

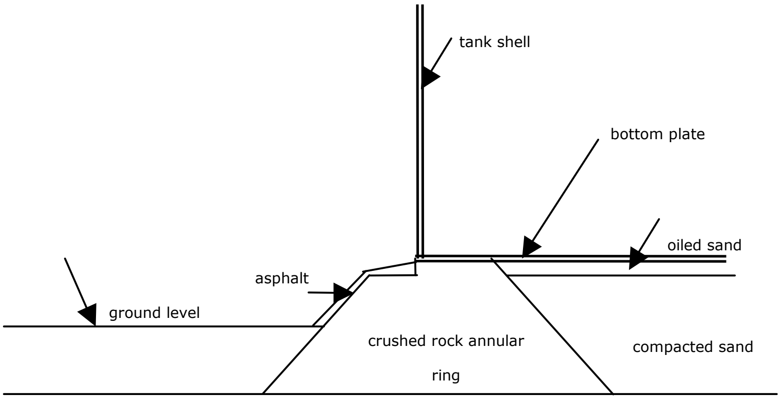


Figure 2: Schematic view of the tank foundation

The annular plates, these are the bottom plates on which the shell of the storage tank is welded, have a design thickness of 12,7 mm. The other bottom plates are designed with a thickness of 6,35 mm.

The underground of the storage terminal existed of a soft clay layer with a thickness of 1 m with a sand layer of 3 m underneath.

The storage tank was built in 1971 according to specific construction standards code API 650. At that moment the storage terminal belonged to another owner. In 1990 the storage terminal was sold to the refinery. At that time all the storage tanks were fully inspected and repaired if necessary. Storage tank D2 was fully inspected in 1990 and was put into service in 1991.

Since 1994 each 3 years external inspections were performed on storage tank D2. The reports of these inspections showed almost no remarks. A full inspection of storage tank D2 was scheduled for 2006, after the full inspection of D1 had been finished. Each three years foundation settlement measurements were performed on the storage tanks. The latest measurements were performed in 2004 and showed no abnormal results.

Findings after the tank rupture:

The investigation of tank D2 showed that the bottom plates in a long, small circular band at approximately 1,5 m from the shell of the storage tank were extremely weakened due to internal corrosion. In this band the thickness of the bottom plates was nearly reduced to zero. This band had a length of approximately 35 m and a width of approximately 20 cm.

In this band the bottom of the tank formed a gutter. In this gutter uniform, internal corrosion was found and no pitting corrosion.

The bottom plates showed no external corrosion in the long, small band. The other bottom plates indicated no extreme corrosion.

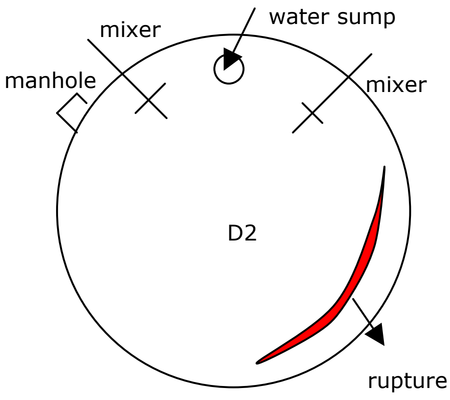


Figure 3: Schematic view of the bottom of storage tank

Primary causes:

During the exploitation of storage tank D2 a gutter was formed in the bottom of the tank. This gutter is situated at a distance of 1,5 m from the tank shell. Due to the formation of the gutter the present water could not longer flow to the drain water system to be removed. The accumulation of stagnant water in the gutter caused strong corrosion which strongly reduced the thickness of the bottom plates in that area.

The major release initially started with a small leak. Due to this small leak the compacted sand underneath the tank bottom was saturated with oil and a kind of quicksand of oil and sand is formed. This small leak has not been visually detected because the crushed rock annular ring had a lot of holes, which were initially filled with crude oil. In the second phase of the accident the resistance of the foundation under the tank was locally strongly reduced (due to the fluidisation of the sand bed) and due to the hydrostatic pressure of the crude oil on the tank bottom, the bottom has ruptured over the length of the gutter. The force of the discharged crude oil was that large that it destroyed a part of the tank foundation and swept away a part of the underground.

Underlying causes:

As mentioned before, a gutter was situated in the tank bottom at a distance of 1,5 m from the tank wall. This is just beyond the annular plates on which the tank shell is welded. The first normal bottom plates after the annular plates were cracked during the accident. The gutter has been formed due to settlements in the tank foundation, which at that place consists of compacted sand. The gutter has probably been formed during the first hydrostatic tests on the storage tank. The moment a storage tank is loaded for the first time, the compacted sand settles. In the neighbourhood of the crushed rock annular ring, which consists of coarse rocks, it is difficult to compact the sand bed in an appropriate manner during construction. At the moment the storage tank is loaded for the first time, the sand in that area will be more compacted, but because of the existing holes in de crushed rock annular ring a part of the sand will disappear in the holes between the coarse rocks. Due to these phenomena a gutter is formed in the bottom plates nearby the crushed rock annular ring. Calculations based on a finite element method showed that based on the information about the foundation of the tank in combination with the underground under the tank foundation and the size of the storage tank, the forming of the gutter could be predicted.

The gutter in the bottom plates has not been detected during the internal inspection of the storage tank in 1990-1991, probably because of the used inspection technique and the fact that inspections are performed when the storage tank is unloaded, in which case the elastic deformation can partially hide the gutter in de bottom plates. During the internal inspection in 1990-1991 all the bottom plates were visually inspected on pitting corrosion and ultrasonic thickness measurements of the bottom plates were performed at some places of the tank bottom. These thickness measurements were performed on all bottom plates situated on two perpendicular axes over the whole diameter of the tank (measurement in cross-bandage). The places in the bottom where pitting corrosion was detected have been repaired. The ultrasonic thickness measurements on the bottom plates gave good results for the thickness of the tank bottom.

In the gutter in the bottom of the tank, the present water could not longer flow towards the water sump. This situation of stagnant water in the gutter enabled very fast corrosion in the gutter with the rupture of the tank bottom as the major consequence.

After this incident the bottom plates of all other storage tanks in the terminal have been accurately inspected. All tanks showed the same gutter forming in the bottom plates at 1,5 m from the tank shells. For some storage tanks the length of the gutter was only a few meters long, while other storage tanks showed exactly the same phenomenon as the ruptured tank D2. The visibility of the gutter was different from tank to tank. Ultrasonic thickness measurements in the gutters indicated that locally the thickness of the bottom plates was reduced. In some storage tanks even small perforations in the bottom plates were found, while for storage tank D1 the thickness of the bottom plates in the gutter was never lower than 4 mm.

The inspections on the full tank bottoms of the other storage tanks had to be performed in a very accurate manner. Thickness measurements of the whole tank bottom of storage tank D1 by means of a so called “floor scan” initially did not detect that locally (in a gutter) the thickness of the bottom plates was more reduced. Only after a surveyor made a topographic map of the tank bottom, a small gutter was detected. Ultrasonic thickness measurements indicated that, as mentioned above, in this gutter the thickness of the bottom plates was reduced to 4 mm.

These inspections proved that the leak in the storage tank D3, which happened on the 12th September 2005, had the same causes as the rupture of storage tank D2. In contradiction to storage tank D2, the gutter in tank D3 was much shorter. After some time the leak has stopped, probably because sediment in the crude oil closed the perforated places in the bottom plates.

ACTIONS TAKEN

Emergency measures:

The fire brigade of the refinery, the fire brigades of the surrounding communities and civil protection started a massive intervention. Initially the intervention team started to cover the bund with fire fighting foam. Directly a large amount of fire fighting foam, 214 ton, was gathered from the refinery, other (petro)chemical companies, the fire brigade and civil protection to cover the very large bund area with foam. Due to the very strong wind that evening and the largeness of the bund they did not succeeded to cover the whole bund with foam. On the other hand the strong wind was in favour for not achieving an explosive atmosphere above the spill. The crude oil did not ignite. The release of the crude oil caused a lot of odour pollution in the wide surroundings. The rupture of the storage tank got al lot of attention from the national media.

After the major accident all the crude oil stored at the terminal was immediately pumped to the refinery and the contents of the bund was pumped to the storage tanks D10, D11 and D4 by using the existing drain water pump system. Immediately measures were taken to perform all cleaning activities in the storage terminal in a safe manner.

In the afternoon of October 27th, 2005 the major part of the bund was empty. On October 28th, 2005 activities were started to reduce the smell. The smell was effectively reduced by covering the entire bund with sand. Where possible the sand layer was placed by trucks and bulldozers. Between the tanks the sand layer was placed by blowing sand in these areas. This operation lasted for about two weeks.

The stability of all storage tanks was periodically measured. The stability of storage tank D2 on the place where the foundation was blown away, was achieved by hanging the storage tank on 4 large cranes (figure 4).

The intervention was only formally stopped on 18th of November 2005 when the storage terminal was completely free of product.

Figure 4: Major cranes stabilising tank D2

Corrective actions taken by the company:

After the major accident the company inspected all other storage tanks in the terminal. These inspections indicated that the gutter forming and the strong internal corrosion of the bottom plates in that gutter, which were the two main causes of the rupture of storage tank D2, were also found in the other storage tanks.

The storage tank D2 had been totally demolished.

The parts of the bottom plates of the other storage tanks of which the thickness and/or the deformation do not fulfil the prescriptions of the standards API 653 shall be repaired. The foundation of the other storage tanks was investigated to control if they still have enough stability (during the accident they were drawn in crude oil) to restart the exploitation of the storage tanks.

Before start-up all crude oil storage tanks shall be coated with a lining to stop the internal corrosion of the bottom plates.

The water at the bottom of the crude oil tanks is drained on a regular basis. After the accident the company decided to analyse the corrosive character of this drain water (by measuring the pH-value of it).

The company also decided to adjust the inspection program of all vertical storage tanks. Between two internal inspections acoustic emission measurements will be performed. Based on the results of these acoustic emission measurements, the next date for the internal inspection shall be adapted if necessary. During the internal inspection of the storage tanks the condition of the bottom of the tank is visually inspected. From the moment there is any doubt about the condition of the bottom plates, ultrasonic thickness measurements will no longer be performed in a cross banded pattern, but the whole bottom of the storage tank will be fully scanned. If a floor scan is performed, 5 additional ultrasonic thickness measurements will be carried out on each bottom plate.

In order to detect leaks in an early stage the company has decided to install a detection with alarm on abnormal level changes on crude oil tanks. Such systems were already available on product tanks in the refinery. Besides these measurements the company is still evaluating to install an on-line oil detection system under the storage tanks.

The company took several measures for cleaning and rehabilitation of the environment. As a result of the soil samples that were taken an area of about 4ha was excavated to a depth varying from 10 cm to 1m. This contaminated soil (including the sand that was used to cover the bund) was removed for further treatment. Several odour catchers were installed around the terminal to prevent possible odour pollution during the cleaning operations. The released crude oil, which was contaminated with 214 tonnes of foam, was recovered from the bund. The polder ditch at the outside of the terminal was cleaned. Several extra gauge wells were installed to establish possible groundwater pollution and to ensure further monitoring of the groundwater quality in the future.

LESSONS LEARNT

Detection of the problem:

Just as for each process equipment with risks for major accidents, the phenomena which can lead to a degradation of the containment, in this case the storage tank, should be identified and analysed.

This accident indicates the possible risks as a consequence of the presence of non mixable phases which can settle out. An investigation of the possible presence of such phases should form a part of the identification of possible corrosive phenomena. If necessary chemical analyses should be performed to determine the corrosive behaviour of these phases (chemical composition, pH,…).

This incident further shows that in the bottom of storage tanks gutters can be formed. In those gutters corrosive products can accumulate, what can result in local, uniform corrosion. In the case water and/or other corrosive products can induce corrosion of the tank bottom, it should be investigated if there is also a problem of gutter forming in the bottom.

Gutter forming in the bottom of storage tanks is induced by a combination of the size of the storage tank, the local compressibility of the foundation and a relative elastic underground. The gutters are not always visible by the eye. They can be mapped by performing a topographic investigation. The topographic maps are achieved by a surveyor who measures the bottom of the storage tank with a laser.

The local uniform corrosion which is a consequence of the gutter forming is not easily detected. The local reduction of the thickness of the bottom plate can be overlooked if ultrasonic thickness measurements are only performed on a cross banded pattern. If the risk of local corrosion due to gutter forming in the bottom exists, suitable techniques should be used to investigate the bottom plates. These techniques are described below.

Possible solutions:

If local, uniform corrosion induced by gutter forming is a problem, the company should take suitable measures to avoid a loss of containment as a consequence of the corrosion. In the next paragraph some different possible measures are listed according to the place they take in the prevention hierarchy. In function of the specific situation it can be necessary to take multiple measures, if necessary completed with additional measures which are not described here.

1. Avoiding or limiting the presence of corrosive products that can settle out.
2. Avoid that products settle out (mixing the different phases)

   Mixing of the products in the storage tank can avoid or limit that insoluble phases settle out. To achieve good results the effectiveness of the mixing is important.
3. Removing of settled out products

   It has to be assured by a procedure that settled out products are periodically removed. But note that the draining of settled out products does not guarantee that settlements are removed out of gutters in the bottom.
4. Avoiding the formation of gutters in the bottom

   Existing storage tanks can be lifted up and the foundation underneath can be restored. In this case it must be kept in mind that by performing a hydrostatic test it is possible that new settlements can take place. For existing tanks there is also the possibility to analyse the foundation and the underground under the storage tanks in order to gather enough information to perform calculations. These calculations can indicate if the risk of gutter forming exists or not. For new storage tanks a detailed calculations of the foundations can be performed during the design phase to reduce the risk of gutter formation.
5. Lining

   A lining is applied on the tank bottom and the first shell course. A lining which is well attached will largely reduce the corrosion velocity. A badly adjusted lining will still reduce the uniform corrosion but will promote pitting corrosion underneath the lining. A good attachment of a lining depends on a lot of parameters such as moisture, temperature, kind of lining, not stepping on a not fully hardened layer, … To achieve guarantee about the thickness of the lining and the attachment of the lining it is necessary to perform measurements on the thickness of the different layers, to perform a conductivity test and to perform a non porosity test. The code API 652 "Linings of aboveground petroleum storage tank bottoms" describes the advantages and disadvantages of different kind of linings.
6. Planning of internal inspections based on the corrosion velocity

   The intervals between internal inspections have to be defined based on the estimated corrosion velocity. This is a general principle that can be found in the API 653 standard "Tank Inspection, Repair, Alteration and Reconstruction". Normally the corrosion velocity of the bottom plates is the most important one. In the case of major local corrosion, it will be this higher, local corrosion velocity which is determinative for the inspection interval.

   The internal corrosion velocity can be determined by analysing the settled out products. Based on graphics which indicate the overall corrosion velocity of the construction material as a function of the corrosive character of these residues (e.g. pH-measurement), the corrosion velocity can be estimated. Based on the corrosion velocity it can be determined how long the storage tank can be safely used before a next internal inspection is necessary. Standards API 653 describes what minimum plate thicknesses have to be measured to use a storage tank safely. If it is expected that large differences can occur in the chemical composition and the properties of the residues, these analyses and the calculation of the inspection interval must be periodically repeated. The analysis of the bottom products can be used to trace other corrosion phenomena (e.g. bacteriological corrosion).
7. Adapted internal inspection techniques

   Internal inspections in which case ultrasonic thickness measurements are only performed in a cross banded pattern (just to achieve a general impression of the thickness of the bottom of the storage tank) are not sufficient to trace local, uniform corrosion.

   In order to achieve an entire image of all changes in the thickness of the bottom of a storage tank the bottom must be totally scanned. Floor scans are very useful to measure sudden volume changes in the floor (e.g. pitting corrosion). They can however also be used to trace gradual changes in the thickness of the bottom plates. To guarantee that a floor scan generates accurate information on the state of the entire bottom of the storage tank, certain conditions have to be satisfied.

   It must be checked if the presence of a lining has an influence on the results of the floor scan.

   Before the inspection it must be clearly discussed with the performers in which state the storage tank must be presented to achieve good measurements. In some cases the entire bottom of the storage tank must be sand blasted before measurements can be performed. In this case it is necessary to discuss the criteria for the sand blasting in advance. It is also favourable that the contractor who will perform the floor scan inspects the cleaning conditions of the bottom plates.

The signal that is generated by the floor scanning apparatus can suffer from drift. This phenomenon is not necessarily a problem if the floor scanning is used to detect pitting corrosion. The moment pitting corrosion is detected, the signal changes so much that even with some drift on the signal, the pitting corrosion is detected. The drift on the electric signal has however a much larger impact when floor scanning is used to detect gradual changes in the bottom floor. To solve this problem it is useful to perform a few ultrasonic thickness measurements on each bottom plate. The signal from the floor scanning apparatus can be gauged for each bottom plate in order to achieve accurate measurements on gradual changes in the bottom thickness.

8. Additional external inspection techniques

In addition to the above described internal inspections, intermediate external inspections can be performed in order to gather additional information on the corrosion status of the storage tanks. These inspection techniques, which can be applied when the storage tanks are in duty, are especially useful when there is large uncertainty on the corrosion phenomena and/or on the corrosion velocity.

A first technique uses acoustic emission measurements. Microphones are placed on the shell of the storage tank to receive sound waves coming out of the tank. Each sound wave is stored and the source of the noise is calculated by software. The sounds that can be associated with a general corrosion activity have a very high frequency. The data are processed in order to map the places where corrosion activity is found and to determine the density of the corrosion activity. The technique makes it also possible to determine different grades of corrosion activity, going from grade A (very small) to grade E (high corrosion activity). As a function of the established corrosion activity it can be decided to perform immediately an internal inspection on the storage tank (in case of grade E), to reschedule the next internal inspection to an earlier date or to repeat the acoustic emission measurements after a certain period.

The acoustic emission technique also allows to detect leaks. These leaks are detected at other frequencies than the frequencies at which the general corrosion activity is detected. This technique makes it possible to detect small perforations in the tank bottom.

Another technique to achieve an indication of certain corrosion phenomena is “long range ultrasonics”. This technique admits to achieve a qualitative image of the status of the annular bottom plates (not from the entire tank bottom) by using guided waves.

These external inspection techniques do not gather (quantitative) information about the corrosion velocity and can‘t be used to enlarge the inspection interval that is based on the corrosion velocity.

9. Applying leak detection techniques

Several techniques can be applied to detect a leak in the bottom of a storage tank while the storage tank is in duty.

A possible leak detection technique exists of cables placed in the underground at fixed distances. The conductivity of these cables changes if a product is detected in the underground.

Larger leaks can be detected by looking for abnormal deviations in the fluid level in the storage tank. If a continuous level measurement is installed on the storage tank, it is possible to install an extra alarm in the control program. The alarm is generated when the fluid level decreases when there are no pumping activities out of the storage tank.

Toxic release in a frozen food warehouse

23 April, 2005

Nemours – [Seine-et-Marne]

France

Toxic leak
Food industry
Refrigeration / Ammonia tank
Organisation
Training
Work
Emptying

THE INSTALLATIONS IN QUESTION

The company and the administrative context:

The company concerned by this report stores, packages and distributes food products. It operates several hundred frozen food stores.

Located in the Nemours industrial estate near the A6 motorway (Nemours rest stop), the establishment employs 236 people and consists of 2 buildings separated by a public thoroughfare:

- ✓ A "Distribution Platform" built in 1979 and expanded in 1984, which houses a packaging workshop and a cold room using a halogenated refrigerant.
- ✓ A "Storage Logistics Warehouse and Workshop", built in 1987, which houses a laboratory and a cold storage facility coupled to a refrigeration installation operating with ammonia (NH_3); these installations contain a maximum of 2 tons of NH_3.

The public is received in a 360-m^2 store reserved for frozen food products.

The Nemours establishment is governed by a prefectoral order dated October 15, 2003, authorising it to continue operating its installations. This order clearly stipulates the provisions of the Ministerial Order of July 16, 1997 relative to refrigeration installations using ammonia as a refrigerant.

The installations concerned:

The equipment responsible for the accident was a pressure tank, identified as No. 0935. Its rated capacity is 450 kg of NH_3. Its maximum service pressure is 32.5 bar and its operating temperature between -20 ℃ and +50 ℃.

The tank was equipped only with filling and drainage valves and was not equipped with any pressure accessory such as a "pressure gauge" or "safety valve" (see photo).

The tank was rented from a chemical product importer/distributor by the service provider in Nemours. This order did not require that a tank filling procedure be provided. The service provider was however required to attend certain internal training programs held on the distributor's premises.

According to the equipment log, the pressure tank had undergone hydraulic testing less than 5 years ago, in compliance with the provisions of article 13 c (bis) of the order of dated July 23, 1943.

THE ACCIDENT, ITS BEHAVIOUR, EFFECTS AND CONSEQUENCES

The accident:

Safety improvement operations on the refrigeration installation were scheduled April 20 to 26, 2005 in order to replace the condenser and the valves on the cold production system in which the NH_3 circulates under pressure.

In order for these operations to take place in the proper conditions, part of the NH_3 had to be emptied from the installation. The operation took place on Friday, April 22nd. Of the 2 tons of fluid in the circuit, 500 kg remained isolated in the "evaporator" portion not concerned by the operations, 1,500 kg of NH_3 at - 18°C being transferred into four 450 kg tanks rented by the subcontractor specialised in maintaining and monitoring refrigeration installations.

Three full tanks and a fourth half empty were then stored outside the warehouse under guard.

One of the tanks burst Saturday, April 23, 2005 at 11.50 am, releasing 450 kg of NH_3. None of the tanks had been handled during their storage period.

The consequences:

A toxic cloud effected roughly one hundred people in the industrial estate, including 21 warehouse employees, and third parties parked in the rest area 200 m from the tanks.

The internal contingency plan was initiated at 12.15 pm.

Significant human and equipment resources were put into action: including roughly one hundred firemen, forty vehicles and 2 helicopters. The rescue services reported 52 victims, 28 of which were hospitalised that evening for analyses, 5 being more seriously effected: 2 *gendarmes*, 1 truck driver in the warehouse and 2 individuals suffering from asthma.

A security perimeter of 150 m was set up, a road was blocked off and lighted sign messages indicating "rest area closed, close car windows and stop fans" were set up on the motorway.

Firemen equipped with PBA diluted the NH_3 fumes with ""peacock tail" fire nozzles, one near the ruptured tank and a second directed toward the road to shield the nearby rest area. In order to maintain a sufficient retaining capacity during the operation, the dilution water collected in a 300-m³ basin were released into the network after its pH had been controlled (8 to 9); 550 m^3 of water was used and released after the pH check. The NH_3 tanks still intact were transferred to the refrigeration unit.

The rest area was reopened at 9.26 pm. The rescue services ended their intervention at around 10 pm. The store resumed its activities Sunday, April 23rd.

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 450 kg of ammonia released into the atmosphere represent 0.23 % of the corresponding Seveso threshold (200 t), or level 2 of the "quantities of dangerous materials released" index according to parameter Q1 (0.1 to 1%).

Three parameters are used to determine the rating of the "human and social consequences" index: H3, H4 and H5.

Parameter H3 is 0, no deaths occurred as a result of the accident.

Parameter H4 is also level 0, no one was seriously injured.

Parameter H5 is level 4, 28 members of the public were effected and hospitalised as a precaution.

As a result, the overall "Human and social consequences" rating is 4.

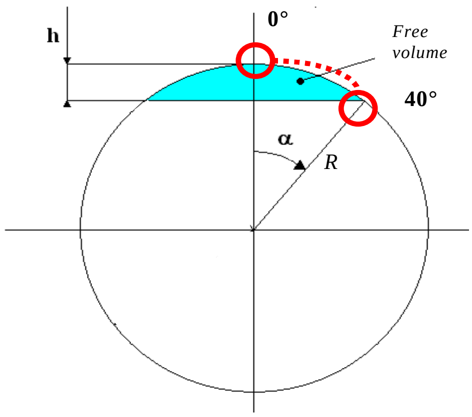
ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

The rupture of the pressurised tank was the result of abnormally high pressure in the tank as a result of overfilling.

Considering the significant variation in temperature during the storage period of the NH_3 drained from the refrigeration installation, the dilation of the liquid contained in the tank increased the pressure and ruptured the tank.

These "multipurpose" tanks and their filling method may be the cause. These tanks were actually designed to store liquefied gas or liquids. The filling rate is thus able to vary between 85 and nearly 100%.

The coefficient of 85% is obtained by aligning one of the 2 painted marks with 40° angle on the side o f the tank. The operator can thus position the eduction pipe (built into the tank) allowing the NH_3 to discharge before the entire available volume is filled up. The tank's positioning is thus extremely important as shown in the following diagram:



It was noted that, due to the design, the end of this discharge tube is a variable distance from the cylinder wall: It cannot thus fulfil its role with precision.

Next, one must admit that the volumetric method used to transfer product cannot adequately guarantee filling of tanks more than 430 kg. This quantity is very close to the tank's maximum quantity, particularly during filling operations at very low temperatures (-18 °C).

Furthermore, the procedure provided did not correspond to the tank model used, and thus to the marks indicated on the body of the tank.

Finally, the probability of error was increased by the multitude of various types of position marks (corresponding to various operating modes: filling, transfer, storage or drainage) without documents being provided explaining their meaning, and thus their use.

Furthermore, accidental mixing of incompatible substances cannot be fully excluded between 2 successive uses. In this case, just the presence of water after possible rinsing and insufficient drying is incompatible with the "refrigeration quality" (minimum purity 99.95%) of the anhydrous NH_3 or R 717.

ACTIONS TAKEN

Administrative and penal actions:

Following this accident, the Prefect required the operator to conduct the following within a period of 2 months:

- complete its danger study with a precise evaluation of the possible consequences of a similar release with a proposal of measures to reduce the consequences of a similar leak
- reinforce its internal contingency plan
- review its procedures concerning its filling operations

Next, within the scope of regional action, the prefect initiated a complementary order outlining organisational and technical provisions intended to reduce the probability of an accident. In compliance with the conclusions of the *Pôle National d'Expertise des Appareils à Pression*, the quantity of NH_3 introduced into the tank must be weighed when the operation is not performed in a confined environment.

Finally, a legal procedure must determine the levels of responsibility of the players involved in the accident.

Technical actions:

The operator, after having considered several provisions designed to reduce the distances of effects in the event of a similar accident, built a dedicated NH_3 storage facility adjoining the machine room, capable of resisting heat flux and equipped with appropriate detection equipment. In case of a similar maintenance operation, the NH_3 tanks shall be placed in this facility. In the event of a leak, the toxic releases shall be automatically directed to the machine room stack via a trap, thus reducing the exposure of personnel, and allowing the toxic plume to be channelled and sufficiently diluted.

From the organisational point of view, the operator reinforced its internal contingency plan and reviewed its maintenance procedures by paying particular attention to greater formalisation of the NH_3 tank filling and draining procedures.

LESSONS LEARNT

This accident highlighted certain procedures for handling liquefied toxic gas which could present significant dangers, and not explicitly outlined by the Ministerial Order of July 16, 1997 or by good practices.

From the equipment point of view, one could question the use of simple "multi-purpose" tanks, not equipped with a safety valve or other pressure or fill limiting device and which is not maintained in a safety position by a metal frame (as the majority of NH_3containers).

From the organisational standpoint, it would appear that this type of handling requires much stricter procedures than those currently in place.

At any rate, this feedback has lead the Ile-de-France DRIRE to propose a additional requirements at the regional level regarding prefectoral orders, requiring that operators comply with a certain number of organisational and technical provisions aiming to reduce the probability of a similar accident, notably by weight a container to ensure the quantity of fluid introduced in the tank as soon as the operation is not performed in a confined environment.

Sudden fracture of a pipeline immediately upstream of an oil terminal

13 December, 2004

Nanterre – [Hauts de Seine]

FRANCE

Soil contamination
Pipeline
Gas oil
Dismantling
Safety management systems
Mapping
Successive operators

THE INSTALLATIONS IN QUESTION

The site:

The operator was the owner of a 20,500 m^2 stretch of land, on which another company had run a lubricant manufacturing and packaging activity until June 1995 and was subject to the classified facility legislation.

Site clean-up operations under the supervision of the operator were underway since July 2000.

As part of the operations termination procedure, an additional prefectoral decree of 11 June issued within the framework of site rehabilitation set out the objectives of the site clean-up operations.

Further to these operations, the dismantling of the building and the facilities was initiated at the end of the 2004.

An oil depot classified top tier SEVESO facility, another lubricant storage unit, as well as a T22 pipeline terminal with its transport pipes were located inside the industrial area close to the site. The "Paris - Le Havre" pipeline cut across this industrial area and ended at the T22 Terminal. Downstream from this T22 terminal, three distinct pipelines transporting gas oil, domestic fuel and petrol were operating.

This segment of the "Paris - Le Havre" pipeline was constructed in the early 1950s to supply the Nanterre petrochemical complex (lubricant and fuel depot).

THE ACCIDENT, ITS BEHAVIOUR, EFFECTS AND CONSEQUENCES

The accident:

As part of the ongoing dismantling of a lubricant depot, a subcontractor disassembled surface pipes, as well as their concrete foundations on **Monday 13 December 2004**. During these operations, the removal of one of the blocks led to severing a segment of underground pipe that neither the site operator nor the subcontractor knew about. In reality, this pipe was one of the three pipes supplying oil products to the Nanterre depot from the T22 terminal of the company operating the pipeline.

The site being dismantled was located just downstream from the terminal of the company operating the pipeline, and at 100 m upstream of the oil depot.

This fracture had no immediate consequence since there were no liquid hydrocarbons being transported at that time. The works contractor considered this pipe to be one of the numerous old decommissioned pipes of the site.

On the morning of December 15 around 11.00 a.m., a gas oil delivery intended for this depot was conveyed through the pipe that had been partially severed 2 days earlier causing an oil spill in the site being dismantled. The construction superintendent of the works company noticed this hydrocarbon spill and promptly informed the oil depot manager. After arriving on site, the oil depot manager ordered an emergency shut down of the transfer. The leak lasted for about 40 minutes.

At 11.55 a.m., the Paris fire department and the police arrived on site to implement the first emergency measures (danger area, pumping, floating boom at the docks, etc.).

Around 2.15 p.m., two specialised companies came to pump the hydrocarbons. At 4.00 p.m. the Paris fire department left the premises.

The consequences:

✓ Nearly 370 m^3 of gas oil was spilled on the stretch of land being dismantled. The hydrocarbons seeped into the soil to reach the water table that is 4 meters deep. However, no immediate or medium term pollution was observed in the neighbouring docks of the Seine. Pumping equipment was set up by the various players involved and the operation was coordinated by the fire department right from the afternoon of 15 December on the site being dismantled and in the nearest drainage network. On the evening of 16 December, the pumping equipment helped in recovering 55 m^3 of spillage. About three months following the accident 70% of the products had been recovered.

Photo operator

✓ The supply of oil products (gas oil, domestic fuel and petrol) by the pipeline to the SEVESO oil depot was suspended for about a month until the three 9 inch pipes running from the pipeline terminal to the oil depot were made compliant again.

ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

The three pipes supplying the depot were installed in 1952 during the construction of the oil terminal. Their diameter was 9 inches and the pipes were directly buried in the ground without an underground warning mesh. During site clean-up and dismantling operations, the external company designated by the site owner was in possession of a work order, an excavation order and had previously sent a formal notification of intent to commence works to the concerned bodies (mainly the neighbouring oil depot, the company operating the pipeline, the Nanterre Town Hall, etc.) in compliance with the regulations in force.

Unfortunately, the existence of these transport pipes was not clearly mentioned in the administrative and technical files drafted on the occasion of the works.

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 quantity of dangerous materials released is set at level 3 because of the 370 m^3 gas oil spill (parameter Q1 - 312 t rejected i.e. 1.25% of 25,000 t of SEVESO top tier).

Level 1 is attributed to environmental consequences due to the 2,500 m² of polluted soil requiring cleaning and excavation of nearly 1,800 tons of polluted soil (parameter Env 13).

The economic consequences rating is set at 4 and includes cost of damaged external material that stands at 550 k Euros for the overhaul of the 3 pipeline segments (parameter € 17); the total cost incurred is 1.5 million euros and that includes site clean-up operation, production losses and material damage.

Lastly, there are no known human and social consequences.

ACTIONS TAKEN

By the classified facilities inspection authority:

- On the one hand, an emergency prefectoral order notified on 21 December 2004 required the last operator of the site to:

- ✓ Submit a new hydrocarbon pollution diagnostic study of the site (soil, sub-soil, underground water)
- ✓ Inspect thoroughly the water table on a weekly basis
- ✓ Supervise the site by designating a site guarding company
- ✓ Draw up a detailed inventory of underground pipes before proceeding with any new excavations.

- On the other hand, perform detailed inspections on the safety management systems especially for 2005 on the "pipeline-oil terminal" interface, as well as 2006 on external companies carrying out operations in top tier SEVESO facilities.

By the authority in charge of inspecting pipes:

- ✓ An inspection of the three pipes by a competent body in compliance with the guidelines indicated by a professional body in the oil industry to check the pipes for scratches, sinking, tensile stress or unacceptable buckling except in the severed segment
- ✓ Replacement of the severed pipe segment and X-ray inspection of the tie-in welds
- ✓ The technical analysis of the operating mode of the three pipes with a view to re-commission them and the drawing up of a technical and administrative file to prove the facility's compliance with the safely requirements of 1 October 1959 or 21 April 1989 depending on the case.

By the Nanterre Town Hall:

- ✓ A motion to appoint an expert at the administrative court.

LESSONS LEARNT

The lesson to be learnt from this incident is more of an organisational kind than a technical one.

The inspection must have observed that the hydrocarbon pipes between the terminals of the operating company and the oil depots were likely to run through private or public property without the owners or the concerned authorities being aware of their existence.

An efficient document management system e.g. plans of facilities at risk is an important criteria when dismantling and excavation operations are carried out on an old site by external companies.

The successive changes of operators in a very old site operated since the 1930s, as well as the transfer of the oil depot between the two operators in 1995 resulted in a loss of information among the various parties in question.

There was a serious lack of communication and information among the various parties involved (land owner, pipeline manager, oil depot operator, external company, etc.).

Apart from the administrative and organisational aspect, the Inspection of Classified Facilities as part of the inspection of safety management systems as of 2005 played an active role in furthering the monitoring capacities of the automatic reception of oil products by pipelines inside oil terminals of top tier SEVESO facilities as well as the interface between the transporter and oil depot.

After this inspection campaign, oil depot operators were asked to improve and reinforce their monitoring capacities right from the filling phase of a tank upon reception of product to detect any leak under pressure.

The following proposals were made to improve the facilities and make them compliant:

On the technical level:

- ✓ Installation of hydrocarbon detectors at the manifold of the transporter terminal.
- ✓ Ensuring air tightness of transfer zones (above-ground transport pipes) and reception zones (transporter terminal manifold).
- ✓ Installation of additional technical equipments such as sound/visual remote alarm in the operating premises of the oil terminal that indicates the start of the tank filling phase.

On the organisational level:

- ✓ Reviewing organisational procedures related to monitoring reception by pipeline during and after working hours with a focus on the critical tank filling phase, e.g. :
  - o Increasing the frequency of inspection rounds.
  - o Continuous monitoring and traceability of tank level readings by technicians or the guarding company.
- ✓ Drawing-up of a formal protocol defining the roles and responsibilities of the transport pipeline and oil terminal operators.

Conclusion

Denis Dumont

Head of the Bureau for Analysis of Industrial Risk and Pollution (BARPI)

After two days of interaction and discussions, our seminar has come to an end and I have the honour of giving the closing address

First of all, may I underline that with this 7th edition bringing together 230 participants, and 23 States and presentations made by 7 countries, our seminar has attained a certain level of maturity. The IMPEL network has truly acquired a full-scale European dimension.

I would like to thank all those who contributed to the success of this event and especially the German, English, Belgian, Italian, Dutch, Swedish and French participants who agreed to make a presentation. The high-quality and pertinence of their speeches were greatly appreciated. Through our publications, these presentations will contribute to the awareness campaigns for all players in the risk prevention sector.

I would also like to thank the Chairpersons of the sessions, as well as all participants, who, by way of their questions, view points and the discussions that naturally followed contributed to furthering our thinking.

May I also thank DRIRE Ile de France, its regional Director Philippe LEDENVIC and his team, in particular Jane SILVERT, Fabienne RAGACHE, Romain LAUNAY and many others who have made endless efforts to welcome us in such excellent conditions.

Last but not the least, I also thank the BARPI staff: Adèle HEUDIER, Christel ROBERT, Marie-José TRUCHOT, Gérard CARTAILLAC and other project managers for having prepared the documents on the resemblances with other accidents in the ARIA database.

The typologies of accidents are rarely new. Accidents tend to draw from human organisational errors to repeat phenomena that are often already well-known.

Without recalling the numerous aspects that contributed to furthering our discussions, I would like to emphasize a few topics:

- Persistence of major hazards
- Aging of industrial facilities
- The importance of the human factor in accident mechanisms
- The special place of work done on facilities these mechanisms

1° THE PERSISTENCE OF MAJOR HAZARDS

Accidentology examined during these two days confirms that the operation of dangerous processes inevitably comes with the probability of a major accident. Even if this risk is brought down to a strict minimum, it can never be totally eliminated. This is due, on the one hand, to the energy and toxicity potentials in the facilities, and on the other, to the limitations in human organisation with regards to our unclear position in the sequence of events triggering the accident and taking effective, timely action.

The crop protection product fire at BEZIERS, the petroleum product fire at BUNCEFIELD, the BLEVE of tank trucks at DAGNEUX and on another scale, the rupture of the ammonia container at NEMOURS have taught us the lesson.

Despite the efforts made in reducing risks, we must always be aware of the quantity of dangerous material in our processes. This is an unavoidable dimension in risk management. From this arises the logical question: does our society need to foresee other major accidents and prepare itself accordingly?

Engineers and technicians must not only have an unfailing sense of determination to reduce the frequency and severity of accidents but also have a sense of modesty when it comes to accepting the limitations of their actions and doing their duty of informing the civil society of the ever present residual risk.

2° AGING OF INDUSTRIAL FACILITIES

The cases concerning the sudden failure of facilities were the highlights of our seminar even though the topic was raised with much restraint in danger surveys due to the low probability of occurrence. Several alarming cases of facility destructions that were not properly supervised and maintained were discussed in our previous seminars.

These cases are not as rare as we would like them to be and affect SEVESO facilities just like others:

- Bursting of a petroleum tank at GONFREVILLE in 2004, at KALLO in 2005 and more recently at AMBES last January,
- bursting of a phosphoric acid tank at GRAND-QUEVILLY in 1999,
- corrosion of gas pipes at LA MEDE in 1992,
- as well as cereal silos that collapsed under the weight of the contained matter.

It is advisable to be cautious of aging facilities; time takes its toll on the initial safety margins. Inspection and maintenance programmes directly influence the awareness and restoration of these margins. They help players in positioning themselves in the sequence of events resulting in the collapse of these facilities.

This is undoubtedly a critical aspect in the inspection of old facilities.

3° THE IMPORTANCE OF THE HUMAN FACTOR

Managing safety also implies managing the complexity of processes and the related preventive measures. This calls for appropriate “adaptation” of these measures by managers, operators and possible sub-contractors.

Whether it is the non-compliant execution of plans, or non-observance of operating procedures or guidelines or lack of communication between the involved players, the “human and organisational” factor is omnipresent in the accident chain. This is illustrated by the MARTIGUES, ND

GRAVENCHON, SAINTE MARIE de la REUNION and GOTEBORG accidents to name a few.

On this account, the European directive Seveso emphasises the need to rectify basic failures observed on site before they become serious enough to lead to a major accident.

In France, this initiative is stipulated by the order dated 10 May 2000. It is based on a process aiming at constant improvement that consists in

- detecting these basic failures at their origin
- recording and analysing them with a view to optimise the technical and organisational operations and their follow-up in time.

All this tends towards promoting better communication and management in companies and ensuring the on-site application of the SGS regulatory provisions.

4° THE PROBLEM OF WORK DONE ON FACILITIES

Whether it is the un-commissioning of the “chlorine transport pipe” at CHAMPAGNIER, valve replacement on the grease box circuits at ST–AVOLD, assembly of a temperature sensor during the major shutdown at ND GRAVENCHON or dismantling of pipes at NANTERRE, the problem of work done on facilities is very manifest in the accidents examined. It is a recurring weakness in risk prevention.

This problem accounts for 30% of fatal casualties recorded in the ARIA database whereas the work phases are far from representing 30% of the service life of facilities.

The most frequently identified weaknesses include:

- poor prior assessment of risk,
- sharing conclusions of this analysis among managers, operators and sub-contractors,
- organisation and supervision of work site,
- un-commissioning and re-commissioning of facilities,
- commissioning of work,
- as well as precautions to be taken during re-commissioning.

The work done on the facilities constitutes a significant area for SGC inspection.

* *

*

I hope that this two-day seminar has provided you with useful guidelines for inspecting facilities and examining danger studies but also spreading general awareness on the realities and limitations of risk prevention.

The IMPEL network helps us stay better informed when faced with commonly encountered problems and be more efficient in carrying out our day-to-day jobs. I hope that we will be able to further this exchange without having to wait for our next seminar at the end of 2008. I look forward to welcoming you in large numbers.

I thank you for your attention and the cordial atmosphere enjoyed throughout these two days.

Thanks

List of the persons having contributed by their documentation, their participation and their assistance to the good progress of the seminary and to the elaboration of this document :

Claire BASTY (DRIRE Réunion), Wilfried BIESEMANS (Environmental Inspection – Belgium), Karine BIZARD (DRIRE Lorraine), Pierre BOURDETTE (DRIRE Ile-de-France), Fabien COUDOUR (DRIRE Pays-de-la-Loire), Fausta DELLI QUADRI (APAT – Italy), Elisabet DIMMING (County Administration Board of Vastra Götaland - Sweden), Laurent FELBER (DRIRE Picardie), Thierry FERNANDES (STIIIC), Philippe FRICOU (DRIRE Rhône-Alpes), Mark HAILWOOD (Environment Agency Baden-Wurttemberg – Germany), Fred HUISMAN (Ministry for Environment – Netherlands), Jean-Christophe JUVIN (DRIRE Ile-de-France), Romain LAUNAY (DRIRE Ile-de-France), Chrystèle LECHAUX (DRIRE Pays-de-la-Loire), Isabelle LE CRONC (DRIRE Ile-de-France), Emmanuel LEPRETTE (INERIS), Célia MARTIN (DRIRE Haute-Normandie), Medhy MELIN (DRIRE Ile-de-France), Martine MORTIER (Labour and Social Dialogue – Belgium), Astrid OLLAGNIER (DRIRE Provence-Alpes-Côte-d'Azur), David PASCOE (Inspector of Health and Safety – United Kingdom), Nicole PETIT (DRIRE Ile-de-France), Sébastien PREVOST (DRIRE Picardie), Fabienne RAGACHE (DRIRE Ile-de-France), Christophe RIBOULET (DRIRE Auvergne), Colette RZESKI (DRIRE Ile-de-France), Gilles SAULIERE (DRIRE Languedoc-Roussillon), Jane SILVERT (DRIRE Ile-de-France), Virginie TEISSIER (DRIRE Franche-Comté), Joep VAN DEN BRINK (Ministry for Environment – Netherlands).

Analogies

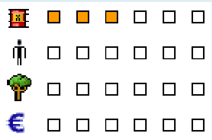
The studies of the 19 accidents made by the inspectors of the IMPEL network and the lessons learnt from them are written down in reports produced in the previous chapter. They enabled to touch different recurrent issues of the industrial accidentology.

For each one, the European inspectors could refer to synthesis illustrated on technical and organizational levels with a number of similar accidents recorded in the ARIA database. The corresponding synthesis are given in the following pages.

Explosion of a chlorine pipe in Champagnier

ARIA 29864 - 05/21/2005 - ISERE (38) - CHAMPAGNIER

24.1E – Manufacture of other basic inorganic chemicals



An explosion ripped through a pipeline transporting gaseous chlorine between a chemical platform (producer) and an elastomer manufacturing plant (user).

The piping, built in 1961 to transport hydrochloric acid (HCl), was being used to convey deoxygenated and dried Cl2. Measuring 200 mm in diameter and 3,600 m in length, the painted, lagged steel pipe was equipped with an external skin effect heating system and operated at 4 bar (relative) and 30 °C. Production operations h ad been stopped the day earlier for a 10-day maintenance shutdown period, and the pressure in the 'chloroduc' had been lowered to 0.25 bar.

The explosion occurred 150 m from the delivery point, in an area outside the user's site. The pipe ruptured in 4 locations along a 70 m section and showed traces of internal shock waves. The accident did not claim any victims despite a large amount of pipe debris projected in a 150 m radius. An estimated 475 kg of Cl2 was released following the explosion. The damage observed (helical rupture, pressure wave...) indicates the explosive character of the accident. The 4 other pipes on the aboveground rack (dia. 100 mm) suffered extensive damage: the 2 nitrogen lines (13 bar, 2 to 3,000 m^3/h) were deformed although were not leaking, and their pressure as reduced to 10 bar; the oxygen line (10 bar), was also damaged and was drained. The last line was no longer in use and was kept under N2 at atmospheric pressure.

Analysis of the accident showed that an H2/Cl2 explosion caused the damage. The formation of H2 (20%) can be explained by the combination of several elements: The accidental introduction of humidity into the piping during a previous maintenance operation may have led to hydration of the ferric chloride present in the pipe's environment. According to the operator, the change in the deposit's crystalline phase due to excessive heating of the pipe (80 to 90 °C) promoted corrosion in the steel pipe (by the hypochlorous acid) and the formation of H2. This heating caused a temperature sensor to lose its electrical power supply after a cable on the user's site was broken when a slab protecting the structure was poorly handled, just 3 days earlier.

In fact, the proportion of hydrogen (20%) released in the gaseous chloride contained in the pipe, which was capped at each end and kept at low pressure (0.25 bar), formed an explosive mixture requiring very little initiation energy to ignite (in the order of a dozen microjoules or so).

The operator cleaned the inside of the structure (2.5 to 3 t of mineral and organic residues were extracted), and had planned to install temperature sensors every 500 m with upper and low safety devices, refurbish and secure the electric (heating) tracing, and perform regular endoscopic inspections...

Faulty lock-out procedures during maintenance/servicing operations

The explosion of the Champagnier 'chloroduc' once again illustrates the risks associated with work involving this product, whether it be maintenance, installation modification or dismantling of production units or plants. It's particularity, however, despite its spectacular and dangerous nature, is that it was caused by a combination of errors committed during maintenance operations performed a more or less long time ago (influx of humidity, a damaged electrical circuit on the temperature sensor), as well as problems relative to the locking out of equipment.

Shutting down and securing a production facility prior to maintenance/servicing is not limited to the habitual **draining, degassing, cleaning, and valve closing operations**… even these tasks are essential, and must not be neglected as they can be considered a high "accident-risk" (Nos. 21034, 29425, 30365, 30516, 31934, 32402, 32690).
A proper lock-out procedure requires that the risks be analysed in proportion to the actual stakes involved, taking the unit concerned by the works into consideration, as well as any units they may be associated or located nearby (No. 6227), le **shared facilities** (No. 23893, 27516), **common measurement or measuring or safety chains** (No. 2684)… in order to ensure the safety of both the installation and its environment, as well as that of the personnel or subcontractors.
The few examples of accidents taken from the ARIA database and presented below illustrate the difficulties sometimes encountered in ensuring efficient lock-outs, notably when complex systems are involved.

As the work grows in scope and the number of people involved in the operations increases, extreme care must be taken in their preparation. It is thus essential to establish a works **schedule** and to **coordinate,** and even differ certain interventions, notably when they concern personnel from different departments or companies (No. 20656), in order to avoid possibly dramatic consequences. In Ribecourt-Dreslincourt (Oise-60), the replacement of a electrical power generator during a reactor cleaning operation caused automatic valves to open that had been previously closed, resulting in the death of a maintenance technician (No. 5989). On this occasion, the operations habitually conducted during 2 different periods were being performed simultaneously.

This accident also shows the importance of having complete control over the **electrical power supply** of the equipment being worked on. Securing the installation by disconnecting the electrical power supply must also include measures designed to prevent the power from being restored by either human intervention or automatic means (No. 6093 – *The change from the "off-peak" period of the electrical installation of a brewery energised 2 pumps and a valve that had been off load, causing ammonia to leak from the valve that had remained open)*. In addition, special attention must also be given the **PLCs** controlling the locked out unit, as their involuntary reset may create risks (No. 16072).

Heating or tracing equipment must also be locked out when operations are being prepared. In certain cases, the heating can be maintained or stopped. Here again, only a risk analysis will allow a proper diagnostic to be drawn up (No. 2684 – *the shutdown of the heat tracing on an ammonium nitrate production facility being worked on led to the formation of ammonia condensation which altered a sensor resulting in the release of 5 t of NH3 through a valve that was opened automatically*; No. 24436 – *the heating of a poorly locked out chemical reactor resulted in an explosion and fire*).

The efficiency of these preparations determines the success of the actual repair work or modification of the installations. Deficiencies in these areas invariably lead to an accident. Once the work has been successfully accomplished, the care afforded to risk prevention must remain constant as installation restarting operations can still be a source of an accident. The partial or incorrect lifting of programs specifically established for the operations (No. 32692) or lock-out defects on obsolete equipment (No. 26895) are only just a few examples among other causes of accidents during the restart phase (the lack of or an improperly conducted acceptance inspection…).

The accidents for which the ARIA No. is not underlined can be consulted at
www.aria.ecologie.gouv.fr

ARIA 2684 - 10/24/1992 - PAS DE CALAIS (62) - BULLY-LES-MINES

24.1J - Manufacture of fertilizers and nitrogen compounds

At around 6.30 pm, 5 t of ammonia (NH_3) was released over a 15-minute period from 2 valves at a height of 7/8 m on equipment used to manufacture an ammonium nitrate solution. Individuals located approximately 1,100 m to the north-east of the unit were effected by the pollution; one person had to be hospitalised.

Ammonia condensation occurred following a shutdown prior to performing work on the unit itself and the steam tracing system. The measurement of this altered parameter caused a valve to open automatically. The NH3 overflowed via an evaporator through a gas line. A high-level security was not operating independently.

ARIA 5989 - 12/01/1994 - OISE (60) - RIBECOURT-DRESLINCOURT

24.1J - Manufacture of fertilizers and nitrogen compounds

A 3-man maintenance crew was cleaning a reactor in a granulation unit of a fertilizer plant whose automatic and manual feed valves had first been closed. The replacement of a power generating unit caused the automatic valves to open, releasing the ammonia contained in a pipe between the automatic and manual valves into the reactor.

Two workers were seriously intoxicated, one of whom died 6 days later. The 3rd employee was only slightly injured and was able to leave the hospital during the day. The accident had no notable consequence on the environment.

Poor coordination of the operations was blamed for the accident.

ARIA 6093 - 12/02/1994 - BAS RHIN (67) - HOCHFELDEN

15.9N - Manufacture of beer

A leak of 30 to 40 kg of ammonia occurred in a brewery at 9.15 am while a suction manifold on a refrigeration unit's compressor was being replaced. Three subcontractors, wearing masks, exited the machine room and were hospitalised for a few hours. The leak stopped 15 minutes later after the suction system valves were closed in a room next to the hall.

At 7.15 am, the manifold had been isolated (by 3 valves) and purged, but the valve on the return line of fermentation tanks' cold circuit was not closed. The error had not been detected as the 2 pumps and a 1 valve on this circuit are off-load during periods of peak electricity consumption. The leak occurred when they were re-energized.

The environment was not effected, although 100 people were evacuated.

ARIA 6227 - 11/11/1994- UNITED STATES - LAKE STE CATHERINE

11.1Z - Extraction of hydrocarbons

An explosion occurred on an off-shore gas drilling platform while 4 employees from a subcontracting company were removing a motor. While using blow torches to cut metal parts near tanks used to store hydrocarbon wastes located under the platform's deck, the workers managed to explode one of the tanks that was nearly empty. The tank had not been degassed.

One employee was reported missing, while the 3 others were only slightly injured. The firemen allowed the fire to burn out until extinction as it was confined to the storage area.

ARIA 16072 - 03/09/1999 - DROME (26) - PIERRELATTE

24.1A - Manufacture of industrial gases

At a site producing industrial gases (O_2, N_2), a valve opened on a vaporised O_2 circuit supplied by a liquefied oxygen tank (LOX). The unit had been shut down (a high energy consumption day) and the customer supplied on line was scaled back. The LOX vaporisation station maintained the O_2 pressure in the network. During the day, the operator replace his FOXBORO software which drives the unit with a compatible "Year 2000" version.

At around 7 pm, with the unit still shut down and without the operator's knowledge, the restart of the system stopped a water pump used to vaporize the LOX. An hour later, the temperature of the O_2 from the vaporisation pool was too low, causing the safety system to be triggered: a valve closed downstream from the vaporisation bundle, the LOX pump shut down and the FOXBORO software alerted the supervisor on duty. The trapped LOX vaporised, and one of the unit's 2 valves opened. The noise alerted a local resident living nearby. The police and fire department arrived at the scene and the incident was brought under control in 15 minutes.

ARIA 20656 - 03/29/2001 - SEINE MARITIME (76) - LE HAVRE

40.1E - Distribution and trade of electricity

An accidental release of 100 to 200 m³ of iron oxide-charged effluents in a thermal power plant in one of its port basins. The release was detected during a security round (brown colouration of the water). During the shutdown of a plant unit, the combustion air heaters of the steam generators were being cleaned as they had become clogged by flying ash deposits. This operation is conduced every two years. For this purpose, the heater's inspection hatches are opened and the equipment is cleaned with water sprayed at high pressure (no cleaning products are used). The effluents are exceptionally conveyed to an internal tank (SNM) prior to their elimination in the effluent treatment station of the smoke desulphurisation installation. The tank is equipped with 2 screw conveyors which, during normal operation, drain off the overflow from the residual tank to the tank on the port.

During the works, the screws should have been locked out (off), which was not the case. Several organisational malfunctions were noted: lock-out was requested for the following day; an interface problem between the 2 structures concerned was noted (shutdown and lock-out management); the job site was under maintenance's responsibility although the effluents were monitored by another department; continuous operations at the job site (night/day) with rounds performed only during the day (thus the delay in detection).

ARIA 24436 - 04/17/2003 - SEINE MARITIME (76) - OUDALLE

24.6L - Fabrication of industrial chemical products

An explosion followed by fire occurred at 3.20 am in a SEVESO plant's lubricant additive manufacturing facility located in a harbour-based industrial zone. The unit, experiencing an operational shutdown for the last 3 days, appeared to be empty of all additives at the time of the accident. The establishment's internal contingency plan was initiated. The company's firefighters brought the fire under control before the external rescue services arrived. The situation was brought under control at 4.30 am and the internal contingency plan was called off at 8.15 am.

The explosion was due to a lock-out defect associated with the simultaneous presence of a combustible, an oxidant and a heat source: 200 kg of enriched mineral oil-based product remained, left over from the last fabrication run in the esterification reactor's outflow cone. The possible decomposition of the oil, or even the synthesis of peroxides above 150 °C for several hours was considered: tests were conducted by a third party company. Oxygen was present in the reactor following a ventilation operation by the personnel in order to service the reactor of the parallel line. The heating system used by the reactors of both lines were started to test the boiler, without by-passing the reactor that had been shut-down. The empty tank was thus heated for more than 24 hours: the internal temperature reached 150 °C for several hours and 200 °C for 2 hou rs. The reactor parameters (T, P and level) were indicated in the control room, but during the accident, as the unit was shutdown, no one was monitoring the instruments.

Property damage was limited to the production unit (6.5 M euros); the associated storage facilities were not damaged. However, the activities of the site's other units were shut down and would resume subject to prefectoral authorisation (operating losses estimated at 4.5 M euros). No atmospheric or water pollution was detected; the quality of the water in a nearby canal was checked every 30 minutes. The barriers of a nearby bridge were lowered accidentally 4 hours after the accident and remained down for 30 minutes. An official statement was issued to inform the administrations, communities and local media outlets, and the industries in the zone.

Corrective measures included the implementation of a heating control system with alarm at 210 °C and a utomatic shut-down when agitation is stopped, an increase in the frequency of parameter measurements, review of the heating procedures, and monitoring of parameters in the control room even during shut-downs…

ARIA 26895 - 01/21/2004 - NORD (59) - AUBY

27.4G - First processing of lead, zinc or tin

Zinc-laden water from a metal manufacturing plant was released into a canal during restart operations following periodic maintenance of the lixiviation and electrolysis shops. The establishment is equipped with a polluted rainwater network, connected to a sump enabling it to be transferred to a 5,500 m³ storage tank and a neutralisation-settling tank that had been commissioned the previous year. The sump's older pumps that discharge directly (without treatment) into the canal were kept in place to be used in exceptional situations (precipitation in excess of the decade rainfall level or a long-term malfunction of the neutralisation station) and provided that the quality is satisfactory for the release. On the day of the accident, leaks on the lixiviation exchangers began flowing into the rainwater network then, due to a pumping error, were released without treatment into the canal for 3 days; 700 kg of zinc were thus released into the natural environment.

An inquiry revealed that the operating error was possible owing to the fact that the older pumps were kept locked. The Inspectorate also noted a malfunction of the leak detection system and the process control transmission chain to the central computer. This accidental release appears not to have had a notable impact on the environment. The operator undertook the following measures: replacement of the exchangers, displacement of the conductivity measurement and recycling of the condensates from the evaporators, physical locking or electrical lock-out of the older pumps and implementation of a procedure concerning their use. A prefectoral order relative to additional requirements, notably requiring the pumps to be locked, was also proposed to the prefect.

ARIA 30365 - 07/25/2005 - PAS DE CALAIS (62) - DESVRES

27.1Y - Manufacture of basic iron and steel and of ferro-alloys

At 11 am in a steel mill specialising in galvanising, an explosion ripped through a sheet preheating furnace that had been shut down the previous evening for annual maintenance work. The zinc crucible's draining operations was completed and the hydrogen purge operation (hydrogen is used with N2 to form the furnace's reducing atmosphere), which had been started 6 hours earlier, was underway when the accident happened. The 4 employees present were not injured, although were hospitalised for hearing tests. No impact outside the site was reported.

The blast was attributed to the valve on the backup H2 tank and the by-pass on the furnace's supply line not being closed; hot points ignited the explosive atmosphere. Following the accident, the operator modified the procedures concerning these operations (blinding of the by-pass and leak test, modification of the valve of the back-up H2 circuit to allow lock-out capability...) and completed the intervention procedure.

ARIA 32692 - 11/10/2006 - SEINE MARITIME (76) - GONFREVILLE-L'ORCHER

24.1L - Manufacturing of plastics in primary forms

A 200 kg leak of liquid propylene occurred at around 1 am on a copolymerisation reactor being restarted in a primary plastic materials plant. The resulting cloud that formed was detected by the unit's network of gas detectors. The workshop's interlocks isolated the section of the unit concerned, stopped the leak and initiated the shutdown of the unit. Operators wearing personal breathing apparatus isolated the circuits. The event lasted just a few minutes. The unit's N2 circuit would then be purged as a precaution.

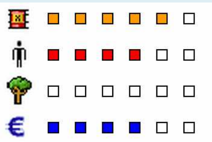
Within the scope of maintenance on the installations since October 28th, the reactor had been placed under a nitrogen atmosphere with a 60 cm hose connecting it to the site's N2 network. Before restarting the unit, a round was conducted the day before to disconnect all hoses from the "N2 injection points". One of the 3/4" hoses had been forgotten during the checks and cracked when the installations were restarted, causing the leak. The procedure used to remove the N2 lines did not include a check-list, but simply a drawing indicating the N2 injection points within the unit. During a cursory visual check, the "taut" hose concerned may have been confused with a fixed line. Its short length may have prevented it from forming a loop, contrary to the other hoses that were not forgotten. The crew that installed the hoses was not the same as the one that removed them.

Also following the previous rupture of a branch connection on 500 kg propylene tank leak on 10/28/2006 (ARIA 32611) and an intervention by the Classified Installations Inspectorate on November 15th, the operator proposed several corrective technical and organisational measures: insertion of a "check-list" in the procedure outlining the removal of hoses prior to the restart of the unit to avoid any forgotten elements, replacement of the existing hoses with hoses capable of resisting the reactor pressure, use of longer hoses for better visual recognition of the permanent piping...

Phytosanitary products catch fire in Béziers

ARIA 30269 - 06/27/2005 - HERAULT (34) - BEZIERS

24.2Z - Fabrication of agrochemical products



A fire was reported at 3.05 am, during the night from Sunday to Monday, in one of 4 buildings (A/B/C/D) adjacent to a SEVESO site producing agro-pharmaceutical products (powders, granulates) and storing finished solid and liquid products. The installations were shut down at the time of the accident.

Less than an hour after conducting his round, the security guard sounded the alarm upon confirming that there was a fire in zone D1. The executive on duty and the director made their way to the plant. The firemen noted that 3 of the buildings were on fire upon their arrival at 3.27 am. The utilities were disconnected and the internal contingency plan was initiated, followed by the special intervention plan at 4.22 am. A confinement perimeter of 400 m was set up around the site. A flour silo and lightweight structures were sprayed with water to protect them. The firefighting water (500 m³/h) was recovered in a retaining basin at the lower portion of the site through the use of inflatable balloons. Following a malfunction of the lifting pump, part of the firefighting water was pumped and removed by trucks from a specialised company or transferred to a hermetic reservoir (10,000 m³) provided for this purpose after a mobile backup pump had been set up. Roughly one hundred firemen brought the fire under control by late morning; 5 had been injured or otherwise effected (burns, nausea) during the operation.

The 4 buildings (7,500 m²) and a stock of 1,700 tons of phytosanitary products were destroyed. Property damage and operating losses were estimated at 40 M euros. A sharp odour was noticeable several dozen kilometres away, and 3,000 people were invited to stay at home or their place of work. Although no serious sanitary impact was feared, the smoke caused discomfort among the residents and personnel of companies in the industrial estate. An analysis of the smoke revealed the presence of sulphur compounds (H_2S, CS_2, SO_2) and HCN. Although the concentrations of CS_2 exceeded the toxicity level (OEL 10 ppm) above the fire, none of the various pollutants exceeded the level at the site's borders. Several companies within the industrial estate had to suspend their activities on the day of the accident. The firemen monitored the slow combustion of the chemical products with the release of fumaroles for several days. A mobile measuring station located 200 m downwind from the site monitored the concentration of sulphur products in the air. As the cause of the fire was unknown, a judicial inquiry was conducted and the insurance company appointed a claims expert. The Prefectoral Order of June 29th suspended operations at the site and required that all safety equipment be overhauled prior to the restart of all equipment not damaged in the fire.

Accidents and phytosanitary products

Numerous phytosanitary products are used extensively throughout the world to combat "organisms" that destroy cultivated plants or adversely affect their growth or reproduction : herbicides, fungicides, insecticides, acaricides, molluscicides, nematicides, rodenticides, taupicides, corvicides, bactericides, virucides, repellents, growth regulators, and sprout suppressants… The Béziers accident illustrates the risks incurred by humans and the environment when such substances are involved in a fire: intoxication and pollution by the pesticides themselves or their degradation products (dioxins, H_2S, CO_2…). The release of these substances can result from their ***self-ignition*** (Nos. 5608, 32277, 32541), a ***fire*** (Nos. 58, 892, 4997, 5187, 5530, 5608, 5697, 5747, 5993, 6044, 11374, 22083, 27615, 29618), an ***explosion*** (Nos. 58, 892, 5993, 15602), a ***runaway reaction*** (No. 5620), a ***spillage*** (Nos. 65, 28745), or a ***leak*** (No. 9393, 30103)…

These events can also result from ***procedural modifications***: the use of certain types of packaging and self-ignition of phytosanitary products (Nos. 5608, 32277, 32541), a reaction placed on stand-by and agitation shut down resulting in a runaway reaction with the formation of dioxins (No. 5620)… Checks and tests can be conducted to detect the presence of impurities (No. 58) or check the stability of finished products (No. 892). Problems regarding ***design*** (Nos. 6329, 28745) and the ***training*** of personnel (n°15602, 31023) are listed among orga nisational malfunctions (No. 30103). The handling of powders, during both the fabrication and bagging processes, requires the use of specific equipment for ***ATEX*** (explosive atmospheres) and the consideration of the possible "static electricity" hazard (Nos. 5993, 27615, 29618).

Despite a malfunctioning of lifting pump, firefighting water can be recovered before being released into the environment. Unfortunately this was not the case at Mulhouse where a 3 km stretch of river was polluted (No. 892). ***Fire protection resources*** (hose stations, water reserves, retaining catchpits) must thus be correctly dimensioned to collect the firefighting water : the pollution of the Rhine River could have been avoided during a fire in Switzerland (No. 5187). The fire system must also be operational before a plant is commissioned (No. 5993)!

The accidents recorded also feature ***releases of pesticides into the atmosphere*** (Nos. 5747, 6044, 15602), ***soil*** (Nos. 6708, 11374) ***or water*** (Nos. 28745, 30103, 31023) and their toxic effects on the ecosystem. At Meda, 200 ha were contaminated by the release of dioxins (No. 5620). The crops next to agro-pharmaceutical plants disappeared (Nos. 6329, 6708, 11374). The pollution of a river and the Italian coastline by dimethoate required special precautions with regard to the consumption of fruits and vegetables (No. 58). The Rhine was "devastated" several times (No. 65), sometimes even all the way to its mouth in Holland (Nos. 563, 5187). Another major river, the Rhone, was polluted over more than 100 km with extensive mortality among fish (No. 4997). An exceedingly high level of DDT, well above the standard, led the Italian authorities to prohibit fishing and the consumption of fish (No. 9393). In Russia, 600,000 people were deprived of drinking water following the release of phenol by an agrochemical plant (No. 1858)…

An information program for residents and the surrounding companies is essential in order to outline possible major accident scenarios and the action to take in the event of an accident (No. 5697). In certain cases, a release of phytosanitary products into the atmosphere can lead the authorities to confine (Nos. 892, 5187, 5530, 15602) or evacuate (Nos. 5620, 5697, 5747, 11374) the surrounding populations.

Governments constantly develop their regulations based on the lessons learned from certain serious accidents; such was the case with the Seveso Directive after the contamination of humans, fauna and flora following a catastrophic release of dioxin (No. 5620). Following extensive pollution of the Rhine during a fire in a phytosanitary product warehouse, Switzerland dictated several criteria regarding the operation of warehouses: floors must be sealed to prevent infiltrations, rainwater downspouts outside of the storage building to prevent all accidental pollution of the rainwater drainage network… The instructions relative to the dimensioning of retaining catchpits (5 m^3/t of products stocked) shall be included in French regulations.

Feedback is an essential component in the continuous improvement of industrial safety.

The accidents for which the ARIA No. is not underlined can be consulted at

www.aria.ecologie.gouv.fr.

ARIA 58 - 07/17/1988 - ITALY - MASSA CARRARA

24.2Z - Fabrication of agrochemical products

A tank containing ROGOR (dimethoate in solution in cyclohexanone) exploded and caught fire. Two fragments passed through the unit and control room, injuring 2 employees. The fire was rapidly brought under control and the population, worried about the potential consequences, began to flee the area. Although 6,000 m^3 of firefighting water was recovered in the storage unit's retaining catchpit, the accident nevertheless polluted a river and the coastal area, leading authorities to restrict swimming over 15 km. Precautions were taken with regard to the consumption of local fruits and vegetables. This accident was caused by the instability of the products.

ARIA 4997 - 06/15/1985 - ISERE (38) - ROUSSILLON

24.1E - Fabrication of other basic inorganic chemical products

At around 10.15 pm, a fire engulfed a 1,600-m^2 warehouse containing finished chemical products. Despite rapid intervention, the fire menaced a nitric acid production unit, thirteen 1-ton containers of dimethylsulfate (DMS) and ammonia tanks. The metal framework and the roof collapsed after 45 min., hampering firefighting efforts with foam. At 11.40 pm, the firemen were informed of the exact nature of the products stored: 369 t of pyrocatechine, 88 t of oxadiazon (herbicide) and 80 t of diphenylpropane (DPP). In order to protect the stock of DMS and the nitric acid unit, firefighting and cooling operations were continued with full knowledge of the consequences; part of this firefighting water polluted the Rhone. Approximately 200 t of pyrocatechine and an unestimated quantity of oxadiazon and DPP flowed into the Rhone; 70 t of dead fish were recovered along 75 km of the river, downstream from the discharge point. The water supply was disrupted for 2 days over 200 km along the Rhone. Damages within the company were evaluated at 36 MF and operating losses at 3 MF. The Court sentenced the operator to pay a total of 2.6 MF in damages to roughly fifteen fishing companies and associations. Following this accident, the establishment was required to reinforce its prevention program in 4 main categories: reinforcement of the fire monitoring and detection system, continuous monitoring of aqueous releases in the workshops, in the sewer mains and in the plant's general effluent, construction of a 10,000 m^3 catchpit for water accidentally polluted (10 MF) and modelling of accidental toxic effluent spillage into the Rhone (DISPERSO program).

ARIA 5187 - 11/01/1986 - SWITZERLAND - BALE

24.2Z - Fabrication of agro-chemical products

On Nov. 1, 1986, a fire broke out in a phytosanitary product warehouse located south of Bâle, Switzerland. After the emergency services had already been fighting the blaze for 20 minutes, specialised firefighters from neighbouring industries came to assist. The flames reached heights of 80 meters and were visible in a radius of 10 km. The mercaptans released a characteristic rotten egg smell. The Rhine River and the atmosphere were seriously polluted. According to certain sources, the 50 m^3 catchpit built on the site was unable to contain the 10,000 to 15,000 m^3 of firefighting water resulting from the millions of litres of water sprayed to put out the fire flowed for approximately 28 hours via the wastewater drainage system into the river which took on a pinkish tint. This water carried approximately 30 tons of toxic products and completely destroyed all aquatic life over more than 250 km. The period of time between the start of the fire and when the population of Bâle and border countries created a high-degree of indignation among the population. Since the accident, local operational centres have implemented a local procedure. A new group safety/environmental organisation was foreseen: human and equipment reinforcements at the operational division level. On November 12, the Ministers of the Environment of the surrounding countries met in Zurich to convince Switzerland to adopt legislation similar to the Seveso Directive and finance the restoration of the river. Switzerland has adopted legislation similar to the European Seveso Directive, thus reinforcing the safety of industrial sites and improving the exchange of information between neighbouring countries in the event of an accident. On October 1, 1987, the International Commission for the Protection of the Rhine (CIPR) adopted an ambitious plan to restore the quality of the Rhine: the Rhine Action Program (PAR) 2000: The CIPR now operates 6 alert centres which continuously monitor a section of the Rhine and 2 others for the Moselle. This environmental catastrophe resulted in the creation of land-use and water management plans (SDAGE) and water management and development plans (SAGE).

ARIA 5608 - 06/22/1985 - ISERE (38) - LE PONT-DE-CLAIX

24.6L - Fabrication of industrial chemical products

A fire broke out in a bagging workshop at the base of a row of pallets containing fungicide (manganese dithiocarbamate produced from carbon sulphide, ethylene diamine and manganese salt). The plant's firemen fought the blaze with foam to avoid sending polluted water into the sewer system. It took 30 minutes to bring the fire under control. As the stock of fungicide tended to burst back into flames, it was removed in metal bins and kept under surveillance. The use of microperforated bags, which replaced hermetic paper bags just a few days earlier, was determined to be the cause of the fire. These microperforated bags could lead to sufficiently high temperatures resulting in the self-ignition (100°C) of the carbon sulphide, p roduced from the degradation of manganese dithiocarbamate. Reoxygenation of the mass contained in the bag facilitated by the microperforations and better filling of the bags (greater settlement) explains the phenomenon that lead to the fire.

ARIA 5620 - 07/10/1976 - ITALY - MEDA (SEVESO)

24.4 - Pharmaceutical industry

A chemical plant that had stopped its production for the weekend released a toxic cloud containing 2,3,7,8-tetrachlorodibenzodioxin into the atmosphere: 6½ hours earlier, at the end of the shift, the production cycle of 1,2,4,5-trichlorophenol had been stopped while only 15% (instead of 50%) of the solvent (ethylene glycol) had been distilled. Agitation was stopped and the vacuum broken. No water was added to the mixture. The unit was left unsupervised for the weekend. At 12.37 pm, the safety valve, calibrated at 3.8 bar, ruptured due to the increase in temperature and pressure in the reactor. The heating of the reaction mixture's surface at rest initiated the secondary exothermic reaction forming the dioxin. It was only the next day that the company informed the authorities that a release of herbicide had occurred. Two days later, crops were declared unfit for consumption. The company reported the dioxin release only 10 days later. In all, 11 communities were effected, including 2,000 ha contaminated. 3 zones were defined: zone A ($C > 50\ \mu g/m^2$) covers 110 ha, its 736 inhabitants were evacuated; zone B ($5 < C < 50\ \mu g/m^2$) covers 270 ha, children and pregnant women were evacuated during the day, agriculture and animal husbandry were prohibited; zone R ($C < 5\ \mu g/m^2$) measuring 1,430 ha. More than 250 case of chloracne were diagnosed, and 220,000 people were exposed to the pollution. In all, 81,000 animals were kill or had to be put down. The quantity of dioxin released has been evaluated between 200 g and 40 kg. The decontamination of the zone began 6 months later and lasted 5 years. The topsoil of the contaminated zones, the demolished constructions and the remains of the contaminated animals were buried in 2 pits, in zone A. Wastes and materials from the plant were placed in drums for subsequent incineration. One year later, 511 people from zone A returned home and zone R returned to agriculture. Zone A was decontaminated and zone B was again declared fit for construction in 1984. The installation was dismantled. In 1985, the plant's management was sentenced to suspended jail sentences ranging from 2.5 to 5 years. The company paid more than $240 M in damages to the residents and communities concerned. The epidemiological studies have not established a concrete link with all long-term pathologies (cancers, deformations...). Only an increase in the proportion of female births in relation to male births was observed.

ARIA 5697 - 04/12/1994 - PAKISTAN - HAWKSBAY ROAD

24.2Z - Fabrication of agro-chemical products

A major fire started in a phytosanitary product warehouse. The fire destroyed 50 to 60 tons of products including profenofos, cypermethrine and monocortophos (insecticides), triasulfuron and turbutryn (herbicides), and metalaxyl and mancozebe (fungicides). The fumes spread into the surrounding environment for 3½ hours. Evacuation instructions were issued to the unprepared population and neighbouring companies with little success. The companies were not inclined to stop working. Part of the products entered the sewers and was recovered in drums and destroyed before entering the natural environment. Numerous individuals, including 7 firemen, were intoxicated and received hospital care at the company's expense (4 people were able to leave the hospital the next day).

ARIA 5747 - 04/04/1987 - UNITED STATES - MINOT

63.1E - Non-refrigerated storage

A fire broke out in a parathion and methyl-parathion storage facility. Fifteen people were intoxicated and 10,000 others evacuated due to the formation of a toxic cloud. The cloud passed over the area, then was pushed by the wind over the Canadian border and totally dispersed approximately 100 km from the release point.

ARIA 5993 - 11/02/1994 - GARD (30) - SALINDRES

24.1J - Fabrication of nitrogen products and fertilisers

In a factory packaging agro-pharmaceutical products, an insecticide (LANNATE) fell from a hopper on a packaging line while employees were changing the valve at the base of the machine. The building was evacuated owing to the presence of toxic dusts. A slight explosion occurred slightly thereafter (electrical incident -> sparks). A fire broke out and spread to neighbouring packaging (fertilizer…) and to the building (2 levels-1,600 m²); 130 firemen intervened (3 were effected), 40 employees and local residents were evacuated. A neighbouring site and a childcare centre were instructed to confine themselves. The community was isolated. The firefighting water was collected in a 8,500 m³ catchpit. Certain difficulties were encountered during the intervention: the plant had been commissioned recently and the firefighting network was not yet operational, building inaccessible, fire doors closed, no executive personnel was had knowledge regarding the hazards at the site, slightly swirling wind, light rain and low ceiling, no map and products poorly known… Property damage was evaluated at 20 MF.

ARIA 6708 - 10/03/1994 - RHONE (69) - VILLEFRANCHE-SUR-SAONE

24.2Z - Fabrication of agro-chemical products

In an agro-chemical plant, a mono-product workshop, dedicated to formulating a liquid herbicide, was being used for the salt formation process of another acid. Three days after production had started, market gardeners noted that 40 ha of crops began to wilt. The plant's management was informed 10 days later. The pollution was caused by weed-killer dusts released into the atmosphere. The frame of the filtration system, part of which was slightly warped, was not hermetic and the filter had not been inspected prior to or during the production period. The workshop's activity was shut down. External damages were evaluated at 3.5 MF.

ARIA 28745 - 12/10/2004 - AUDE (11) - PORT-LA-NOUVELLE

24.2Z - Fabrication of agro-chemical products

In an insecticide manufacturing plant, between 50 l (according to the operator) and 250 to 500 l (according to the rescue personnel) of soluble ethyl chlorpyriphos / hydrocarbons mixture spilled from a 34 m³ storage tank used as a buffer tank for packaging of the insecticide in 200 l drums. Located just a few meters from the production building, the tank was connected by means of an open-top buffer tank to an overhead stainless steel pipe. The installation was not equipped with level sensors, so an operator was in charge of monitoring the filling and transfer of the toxic solution. At the time of the accident, the buffer tank overflowed and spilled into the poorly maintained catchpit: catchpit breached (2 cm hole), concrete facing in poor condition. The substance that escaped from the catchpit seeped through low wall, also in disrepair, separating the establishment from a neighbouring company, then made its way to a rainwater drain and into an underground trench near the catchpit which then flowed into a stream 50 m further away. Dead fish were found in the canal and at the mouth of the fishing port, where birds were at risk. Samples taken from 3 piezometers at the site confirmed the traces of iridescence. A floating barrier was set up at the mouth of the port and a bladder was used to block the piping. Active carbon was poured into the water near the damns the next day and the pipe was plugged 4 days later. Production operations were stopped and the tank involved was drained into drums. Absorbent products were spread throughout the polluted area. The plant manager acknowledged having used soda to neutralise 50 l of insecticide that had spilled that same morning. The pollution was discovered at 7 pm. The layer that formed above the clay loam protecting the underground water table below the catchpit released the substance several days following the accident. A Prefectoral emergency order was signed December 11th, and a second order stipulated the conditions required for the plant to resume activities, and the necessary environmental monitoring and preventive measures. External companies were called in to clean up the site: pumping, core sampling, dismantling of the tank and catchpit, and the removal of polluted soil.

ARIA 32541 - 09/20/2006 - BAS RHIN (67) - LAUTERBOURG

24.2Z - Fabrication of agro-chemical products

A batch of phytosanitary products was placed under supervision in an agro-pharmaceutical plant after it was noted that 300 t of mancozebe in big-bags intended for shipment to a company in the Rhone region. Having noted that the heating phenomenon had continued the following day, the operator contacted the customer, informing them that they should monitor the last big-bags delivered. The latter had also noted the self-warming phenomena and the progressive increase in temperature (see ARIA No. 32277), and decided to initiate the establishment's internal contingency plan and flood the batch by placing it in tanks of water. The big-bags still at the supplier's site were isolated in a special location and monitored. The manufacturer recovered the batch that had been treated on the customer's premises for progressive recycling. Analyses and tests determined that the self-heating phenomenon was the result of recent modification in the packaging process at the customer's request. The product's decomposition was promoted by the product's increased contact with the air. The customer decided to return to the initial packaging. Manufacturing operations resumed after several days.

Emission of ethylene in Saint Avold (Moselle-57)

ARIA 30920 - 07/21/2005 - MOSELLE (57) - SAINT-AVOLD

24.1L - Manufacturing of plastics in primary forms

A rupture disk in a plastics factory opened on the medium pressure return (MPR) line of a compressor due to a pressure increase on discharge side of the primary compressor, resulting in the release of 3.2 t ethylene into the atmosphere.

On 07/10, a leak was detected on a line serving the polyethylene workshop at the level of the filling valve of a grease cylinder (MPR) which had been cooled pending repair. The line was to be shut down August 20th at 4 am for maintenance, and then placed back into service at 6 pm.

The operator started the primary compressor according to the normal procedure with automatic monitoring of the rising pressure. The pressure measured at the inlet of the secondary compressor was in excess of 300 bar, even though a valve on the discharge side 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. The operator noted the abnormal increase in pressure and switched to manual mode. The operator's belated action was unable to prevent the pressure from rising to 310 bar and the rupture of the disk.

The primary compressor was unable to stop due to partial clogging of the pressure increase regulating gauge ($P_{measured} < P_{true}$). The valve malfunction was attributed to a maintenance error: the valve had been replaced by an inappropriate model (Calibration pressure > 310 bar). The fouling of the MPR section resulting from several days of production without being purged of greases accentuated the pressure increase kinetics.

The check valve, obstructed by low polymers was cleaned and checked, the safety PLC and the primary compressor's standby sequence were tested. The rupture disk and valve were replaced. Other measures were also taken: shut-down of the compressor in automatic or manual mode with a fail-safe pressure measurement, review of grease cylinder operating rules to prevent clogging of the MPR, additional training for the personnel, and consideration of this clogging phenomenon in the installation's danger study.

ARIA 31232 - 09/21/2005 - MOSELLE (57) - SAINT-AVOLD

24.1L - Manufacturing of plastics in primary forms

Around 6.15 am, a rupture disk at a chemical site opened on a grease cylinder of the medium return pressure system (MPR) on one of the lines in the polyethylene workshop that had been shut down for programmed maintenance; 1.4 t of ethylene was subsequently released into the atmosphere. The cloud dispersed at altitude upon leaving the stack.

The shut-down procedure included the rinsing and purge of the reactor 3 times, each flushing operation being performed in 2 phases: the reactor is filled to 600 bar with the secondary compressor and depressurised via the MPR circuit. The rupture disk opens during the depressurisation of the 1st flushing operation. The line is cleaned, the blocked valves of the 2 MPR circuits are checked, the remaining greases are purged and the disk is replaced. The presence of a considerable greater quantity of grease in the MPR circuit than during normal operating regime, notably at the check valves, remains unexplained.

A clogged valve on a neighbouring line had already led to the release of 3.2 t of ethylene on 07/21/05 (ARIA 30920). The design of these valves, which promotes blockage of the MPR circuits, should be studied in order to reduce the probability of grease accumulation at these locations. Their removal was also considered in late 2006, following a prior risk analysis owing to the role they play in installation safety (check valve).

The installation of an additional preventive barrier on the MPR will be discussed within the scope of an additional danger study. Since proper cleaning of the installation has a certain impact on its safety, procedures must be formally drawn up regarding the nature and frequency of cleaning operations as well as the traceability of the controls performed. Performance indicators must be implemented to determine the efficiency of these cleaning operations. The causes can generate a significant quantity of grease and must be identified. The impact of the phases leading to significant pressure discontinuities must be analysed (shut-down, rinsing phase...).

Clogging and fouling of equipment

Both of the accidents presented involve excessive fouling of equipment: in the 1st case, a partially clogged pressure control gauge indicated an incorrect value. The fouling of the medium pressure return line accentuated the pressure increase kinetics, causing the disk to rupture. Low polymers were also blocking the check valve. A maintenance error was also reported in which a incorrect valve had been used as a replacement. This accident can be attributed to an organisational failure as the necessary controls were not taken into consideration in the clogging risk associated with the process. The operator foresees reinforcing its personnel training program. The 2nd accident, 2 months later, was essentially a repeat of the first involving the blockage of check valves on the medium pressure lines.

Equipment clogging and fouling is the cause of numerous accidents on record in the ARIA database. Excessive fouling of **instrumentation** upstream from or in equipment such as sensors (level, temperature, pressure…) can lead to erroneous measurements that can prevent the entire installation from operating normally: accidents No. 18339 (IMPEL Reims, June 12 and 13, 2001), Nos. 22211 and 30726.

This type of failure on **inlet or outlet pipes** can lead to deviations in control parameters and accident situations. Clogging can be attributed to various factors: formation of a product derived from the reaction itself, or a secondary reaction (Nos. 32172, 10163, 22495 and 24761), residual fire extinguishing products (No. 14987)... Clogging or fouling creates an increase in pressure within the equipment (No. 32172, 14987, 22495, 30175 and 48626), or in other equipment when product flows back into the equipment (Nos. 19323 or 10163). The consequences can be quite serious, as in Balan (No. 10163) where the clogging of an ethylene exhaust stack caused it back flow via the extruder; the ethylene then ignited and exploded claiming 2 victims. When such products form inherently in a process, it is desirable that procedures be implemented regarding the inspection and cleaning of sensitive zones (branch connections, sensors, piping...). It may also be necessary to ensure that there are no areas within the pipe system likely to promote the accumulation of substances (elbow, abandoned channels…). In this respect, two accidents presented at IMPEL 2001 and IMPEL 2002, respectively (No. 19351 and No. 22 062) where butadiene polymerised in an anarchic manner forming a sort of "popcorn" that clogs the piping. Clogging can also prevent a chemical substance from entering a reactor or mixer and lead to a dangerous situation, notably if this substance is a stabilising agent (No. 130297). Finally, the meteorological conditions (low temperatures) can assist in the solidification of substances in a pipe as demonstrated in the Chalampé accident presented at IMPEL in November 2003 (No. 23839). In this accident, the solidification of cyclohexane caused a rupture in a pipe that was insufficiently protected from the cold.

Also worth mentioning is the **partial obstruction of a valve** which caused it to close 1 second slower, leading to the rupture of a burst diaphragm and the release of ethylene into the atmosphere which ignites shortly thereafter (No. 24891). What was responsible for this? An insect next! The case is not unique: on an unloading station, 2 safety valves used to isolate the truck fro mother installations were out of service. Investigations revealed that this malfunction was caused by the presence of a mud dauber wasp nest (No. 28388). Undesirable hosts can also enter cooling loops, such as the obstruction of this type of equipment by molluscs (No. 4924)...

And finally, we can also mention obstructions of **atmospheric venting** devices such as vents which can cause a reverse vacuum phenomenon on certain tanks not designed to resist strong pressure differences in relation to atmospheric pressure. Large tanks can thus be easily crushed if the relief vent cannot fulfil its role in balancing pressures. The "Process Safety Beacon" newsletter (February 2007) fully illustrates this type of "vacuum" event, in which plastic film was deliberately installed to prevent humidity from entering the tank. This newsletter also describes vents plugged using was or bee's wax, and even a tank crushed when its gaseous atmosphere cooled rapidly following a thunderstorm. In this case, it was naturally the vent's "useful diameter" that is to blame, whether it was under-dimensioned or partly clogged. It is thus important to regularly check that the vent of tank in operation is not closed or even partially clogged.

Accidents for which the ARIA No. is not underlined can be consulted at

www.aria.ecologie.gouv.fr.

ARIA 4924 - 11/25/1993 - SEINE MARITIME (76) - GONFREVILLE-L'ORCHER

24.1J - Manufacture of fertilizers and nitrogen compounds

The blockage of a cooling loops by molluscs, caused a pneumatic vent valve to open on the temperature control system of an ammonia storage unit. At least 100 kg of ammonia was released into the atmosphere. At the same time, an individual located approximately 1,000 m away reported smelling ammonia. There remains, however, a doubt as to the connection between this perception and the release of ammonia. The accident had no consequence on the environment and claimed no victims.

ARIA 10163 - 03/28/1983 - AIN (01) - BALAN

24.1L - Manufacturing of plastics in primary forms

A leak occurred in a high-pressure polyethylene synthesis unit, releasing ethylene into the confined atmosphere of the extrusion facility. The ethylene ignited which caused the gas cloud to explode (CVCE: Confined Vapour Cloud Explosion). Two employees were killed and the upper and medium pressure sections of the unit were destroyed. The leak was caused by clogging in the ethylene exhaust stack followed by its backflow into the extruder.

ARIA 14987 - 09/11/1991 - BOUCHES DU RHONE (13) - MARTIGUES

24.1G - Manufacture of other basic organic chemicals

An explosion ripped through a chlorine production site during the restart of an installation. The hydraulic seal had apparently become blocked by fire extinguishing products following a fire on the hydrogen exhaust system. The blockage caused the pressure to increase in the hydrogen manifold and the passage of flammable gas into the chlorine through the diaphragms. The Cl_2/H_2 mixture then entered the Cl_2 desiccation unit before exploding. The explosion was probably initiated by a discharge of static electricity or UV radiation. The internal contingency plan was put into action. The accident did not claim any victims although the desiccation towers were destroyed and the chlorine manifold was damaged. The increase in the chlorine's hydrogen content had been detected by an on-line analyser 15 minutes prior to the explosion. The accident demonstrated the inappropriate hydrogen firefighting means or insufficient with regard to the detection of overpressure in the hydrogen manifold and the analysis of this gas in chlorine, as well as inappropriate operating procedures with regard to the intervention procedures in the event of excessive H_2 pressure or chlorine gas polluted by flammable gas. Corrective measures were implemented: Elimination of the causes of pressure build-up in the H_2 manifold, reinforcement of hydrogen overpressure detection systems and the presence of hydrogen in the chlorine, adaptation of the initiator operating procedures (H_2 overpressure and chlorine polluted by hydrogen).

ARIA 18339 - 07/22/2000 - OISE (60) - VILLERS-SAINT-SEPULCRE

24.1L - Manufacturing of plastics in primary forms

At 10.40 pm, during a styrene/acrylonitrile copolymerisation reaction in a plastics manufacturing plant, the operator in the control room detected an abnormal temperature increase to 125 °C on one of the 75-m³ reactors. The visual display screen in the control room confirmed the request for cooling. An operator then went to the cooling tower to check the water level in the pool, and noted that the water was at the "very low" level: the industrial make-up water supply was no longer operating.

The operator was unable to reprime the cooling pumps. The control room operator initiated the emergency procedure in case of reactor runaway: 3 loads of cold water, 2 m³ each, were introduced into the reactor in an attempt to bring the temperature to 121 °C maximum. The procedure proved to be inefficient, each load lowering the temperature only 0.7 °C. The reactor's volume prevented any additional water from being added. As stipulated in the emergency procedure, a reaction inhibitor was then introduced to prevent the product from solidifying before the reactor was completely emptied into the "dump" tank placed below the reactor, i.e. 65 t of styrene-acrylonitrile mixture. At the time of emptying, the limits of the process had been reached (a temperature of 140°C, pressure of 5.2 bar). The thermal runaway of the reaction was due to a lack of water in the reactor's jacket circuit connected to a low level in the water-receiving tank associated with the atmospheric cooling tower. The operator inspected the tank and noted that 2 vibrating blade sensors were fouled. The failure of the "low" level sensor did not allow the tank's water makeup valve to open automatically. As regards the "very low" level sensor, its fouling was such that the control room alarm was not triggered. Authorisation for the starting of the manufacturing cycle was therefore not blocked during the preliminary tests carried out on the reactor. Initially, the reactor in question was locked out while the operator had the level sensors cleaned. A maintenance procedure was established: the condition of the sensors will be checked during each reactor cleaning operation, performed every 15 days. A series of tests of the "low" and "very low" level sensor alarms will also be initiated before each production cycle. The operator also intends to install level sensors with different technologies. The installation in question was re-started on July 26th, in late evening, after being subjected to the checking programmes and tests defined above.

ARIA 19323 – 10/14/1993 - BITTERFELD, GERMANY

24.1J - Manufacture of fertilizers and nitrogen compounds

The blockage of a drainage line on a thin layer vaporiser (separation of dimethoate by distillation of the azeotrope dichloromethane-water mixture in continuous operation) leading to the discharge pumps and the malfunction of the radiometer measuring head caused the dimethoate to flow back into the vaporiser facility. This led to overheating and spontaneous thermal decomposition of the dimethoate. A rupture disk burst and 25 kg of dimethyl decomposition products, as well as 3,500 litres of organic sulfur compounds were sprayed 15 m into the air. The foul-smelling cloud drifted eastwardly and 10 individuals were hospitalised for discomfort and nausea after inhaling mercaptan. The entire unit was shut down and the sector was secured.

ARIA 22211 - 04/12/2002 - HAUT RHIN (68) - HUINGUE

24.1C - Manufacture of dyes and pigments

In a plant manufacturing dyes and miscellaneous additives, a hydrogen and butyl acetate release caught fire on the vent of a hydrogenation reactor. The accident occurred when a safety valve opened; the roof vent was equipped with a flame arrestor. The increase in pressure inside the reactor was due to excess hydrogen resulting from a faulty pressure measurement which was brought on by a clogged pressure tapping on the reactor itself. The rector's hydrogen supply and the injection of nitrogen in the installation were stopped. During a post-accident inspection, the Classified Installations Inspectorate reported that the operator had not defined an explosive zone in the area around the vent despite the presence of electrical equipment in the immediate vicinity (lighting, ventilation, air conditioners). Some of this equipment was explosion-proof, although it could not be established with certainty whether or not the class of gasses, for which this equipment was designed, includes hydrogen. The Classified Installations Inspectorate also noted that the opening of the valve and the release of gases and flammable vapours were detected belatedly. The operator was required to implement a safety improvement program: technical and organisational measures to prevent such an event from happening in the future, designation of explosive zones (under the terms of the ministerial order of March 31, 1980) around all vents in the building likely to release flammable gases or vapours into the atmosphere and to search for such zones in the site's other installations, and verification of the compatibility of the explosion-proof equipment near the vent involved with the hydrogen. Several technical provisions were undertaken before the workshop was restarted: doubling up of safety devices to disconnect the supply of hydrogen in the event of overpressure, improvement of the pressure tapping and implementation of preventive maintenance for this device.

ARIA 24891 - 04/05/2003 – AIN (01) – BALAN

24.1L - Manufacturing of plastics in primary forms

A black cloud was released on the polyethylene production line No. 1 at a basic plastic materials plant. The plant had resumed operations on March 31 following a ten-year inspection lasting 4 weeks, only to be shut down due to an incident after just 4 days of production. The unit restarted April 5th at around 2.20 pm. At 4.49 pm, overpressure on the unit's medium-pressure separator led to the emergency shutdown and then the opening of a rupture disc. A cloud of gas and black particles located within the separator (roughly 310 kg) were released. Actuated simultaneously by the automatic sequence, the reactor's safety valves opened in order to decompress it. The ethylene released by the reactor's 2 stacks caught fire; the 2 torches formed were smothered by the water injection system and the incident was brought under control in less than 10 minutes by the operating crew on site. There was no property damage. Only a loud noise (caused by the opening of the rupture disc, then the ethylene catching fire) worried the local residents who alerted the external rescue services. The unit was shut down at 6.10 pm, decompressed and inerted with nitrogen. Several operations were then performed: a pressure-reducing valve was removed for inspection (a polymer of normal colour at the valve's inlet and black at the outlet); the primary separator of the apparatus' bottom trap was removed to purge the residual polymer; removal and replacement of the rupture disc of the medium-pressure separator. All the inspections conducted on the various elements (seals, safety devices…) showed no sign of anomaly. The findings relative to the pressure-reducing valve show that it had opened although it was slowed down slightly (~1 sec) due to the partial obstruction of the pneumatic exhaust by an insect next. As the temperature of the gas at the stacks' outlets were less than the ethylene's self-ignition temperature, it is probable that it was ignited by incandescent soot released through the chimney from the rupture disc or by the residual gases in the event of insufficient cooling. Several measures were taken: the valve was protected against insect intrusion, recording of valve parameters in the event of a replacement for at least one week, temperature recorded before and after the valve, and a valve repair log.

ARIA 28388 - 10/07/2004 - INDRE (36) - LE BLANC

51.5A – Wholesale of combustible products

During security testing conducted by the operator in the presence of the Classified Installations Inspectorate, 2 shut-off valves did not operate at the tractor-trailer unloading station of an LPG depot. In the event of an anomaly, these positive safety valves enable the truck to be isolated from the other installations. The operator shut down the station until the installations could be refurbished. After verification, the problem was found to have been caused by the presence of a wasp nest that had been built inside the air system's depressurisation solenoid valve, preventing it from operating. Additional checks, conducted on the site's other solenoid valves of the same type, turned up additional nests in another device but did not prevent it from operating. The operator had mesh netting installed to prevent insects from entering the device.

ARIA 30726 - 03/18/2004 - JURA (39) - TAVAUX

24.1E – Manufacture of other basic inorganic chemicals

The sudden shutdown of a halogenated organic product incinerator in a chemical plant lead to the formation of an aerosol cloud that did not disperse at altitude. This malfunction caused the degassing flows to the scrubber to be saturated in organic amines. The scrubber receives acid and halogenated gaseous effluents to be processed. The neutralisation operation normally performed prior to the release to the atmosphere did not take place. The emission point at the scrubber outlet is located 8.7 m above the ground. The gaseous emissions lasted 43 minutes, from 5.23 am to 6.06 am, and formed an organic amine halide aerosol cloud (mist) estimated at less than 5 kg. The accident had no human consequences or property damage. The cause of the accident was attributed to a faulty maximum level sensor on the separator of the degassing circuit before entering the incinerator, leading to the undetected presence of organic liquids. The malfunction was caused by the lack of periodic verification to sure that the separator's max. level measurement was operating correctly, even though it is subject to fouling caused by the presence of organic amine halides. The incinerator is shutdown several dozen times a year.

ARIA 32172 - 05/10/2006 - LANDES (40) - CASTETS

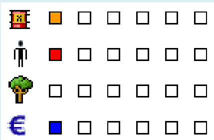
24.1G - Manufacture of other basic organic chemicals

In a chemical plant, rising pressure in a recovered sodium acetate storage tank caused the tank to rupture and its cover to be thrown nearly 20 m. No other consequence was reported. A safety perimeter of 50 m was established, the content of the tank was transferred into tanker trucks for removal. The accident took place while the plant's sodium acetate transfer piping was being flushed with nitrogen. The increase in the tank's pressure was caused by vents that were blocked by a crystalline deposit generated by a secondary reaction. The possible formation of these crystals had not been brought up during the risk analysis of the process. Various measures were adapted to prevent this type of accident from happening again: installation of a weighted cover on the tank, the vent's diameter increased, modification of the piping purge mode (using water then expanded nitrogen), verification of the unit's valves, periodic inspection of the vent and cover, and installation of purges on the supernatant organic phase...

Sulphur dichloride leak in Catenoy

ARIA 31691 - 04/26/2006 - OISE 60 - CATENOY

24.1G - Fabrication of other basic organic chemical products



In a chemical plant, a sulphur dichloride leak (SCl_2) occurred on a pipe equipping the distiller of a distillation column hydrolysed causing a significant release of hydrogen chloride (HCl). The column was located in a metal building forming a sort of confined space.

The establishment's internal contingency plan was initiated. The plant's internal emergency services set up water curtains and the external firemen were called. A 50 ppm concentration of HCl was measured in the building (irreversible effects for 1 hour of exposure = 60 ppm). This was nevertheless below the detection threshold outside. Three internal firemen were placed under observation in local health care centres. The water used for the water curtains (100 m³) was recovered in the site's firepond.

The accident occurred during maintenance on a pressure sensor. The sensor had been identified as faulty after indicating a pressure of 108 mbar on the distiller's outlet (upper alarm threshold = 100 mbar), thus trigging the closure of the SCl_2 supply valve and the steam control valve of the distiller's heating system. Before replacing the sensor, the distiller containing 50 kg of SCl_2 had to be drained after the discovery of glass from the downgraded distillation column. This clogging had been identified 3 weeks earlier without any action being taken. In addition, the pressure sensor's shut-off valve, which could not be removed due to seized bolts, could not be closed; the operator was required to remove the entire assembly, thus leaving the ND25 branch connection exposed to the open air. As the sensor was not fail safe, when disconnected electrically the steam control valve opened and the distiller heater, whose temperature rose from 24 to 120℃ in 30 minutes, resulting in the release of SCl_2.

The measures taken with regard to the feedback notably concern the monitoring and intervention procedures in downgraded mode, the "failsafe" principle on the unit's entire functional safety chain...

Hydrolysable materials

Hydrolysable substances are materials that react more or less violently with water. This decomposition reaction, especially in an accidental context, can create significant hazards as demonstrated by the selection of accidents presented below.

Numerous chemical products are hydrolysable although accidentology places the blame on only a limited number of substances involved in a large number of accidental hydrolyses, sometimes just through contact with the humidity in the air. This primarily includes:

- certain **halogenated, chlorinated or fluorinated compounds,** such as titanium tetrachloride (No. 1402), phosphorous trichloride (No. 2900), boron trifluoride (No. 30725), and methyltrichlorosilane (No. 5460)…
- **alkaline metals** such as potassium and sodium (Nos. 23953, 22215), which react violently in the presence of water with strong exothermicity.

Furthermore, thermodynamic phenomena can be assimilated with these hydrolyses which occur when water is added to fuming sulphuric acid or **oleum,** the exothermicity of this phenomenon leading to the release of sulphuric cloud (Nos. 4605, 9467 – *the cloud of H2SO4 generated by an oleum leak led to a massive collision of three vehicles on the nearby motorway*).

If, by definition, water initiates the hydrolysis reaction; polar solvents and methanol, as well as acids and bases (by providing the H^+ or OH^- ions) can also lead to the same effects (No. 22170).

The associated risks are different depending on the reagents present and the products generated:

- The latter are also gaseous and can cause **overpressures** (Nos. 22170, 25818) when the reaction takes place in a confined environment. The chemical equation of a hydrolysis reaction (that of titanium tetrachloride, for example) explains this phenomenon very well:

  $$TiCl_4 + 2H_2O \rightarrow 4\ HCl + TiO_2$$

  Here, 4 moles of gaseous hydrogen chloride (HCl) are produced from a single mole of $TiCl_4$; the reaction between these liquid substances generates 4 moles of gas, which, in normal temperature and pressure conditions, produces 4 x 22.4 = 89.6 litres of gas for 190 g of TiCl4 that reacted.
- Hydrolysis reactions can also generate **toxic compounds**, most commonly sulphur dioxide (SO2) and hydrogen chloride (HCl) but sometimes other chemical species such as hydrogen fluoride (HF), which is also **corrosive** (No. 9542 – *vehicle corrosion after the release of chlorofluoride antimony salts which spontaneously hydrolyse on contact with humid air*). This type of toxic release is also increasingly encountered in accidents involving chlorinated products used to treat swimming pools (Nos. 17986, 18060, 20133, 27719, 32396), as the primary function of these substances is to be easily hydrolysable… to generate chlorine!

  A toxic hazard also exists for aquatic fauna, highly sensitive to the NH_3 molecule which can be generated, for example, during hydrolysis of urea in an industrial environment (No. 28625) or subsequent to the release of effluents containing nitrogen (feedlot runoff).
- **Ignition hazards** are also possible when the hydrolysis reaction is very exothermic in the presence of combustibles (solvents, packaging…) (Nos. 20133, 22215) or leads to the formation of flammable gases (No. 12159 – *hydrolysis of calcium carbine produces acetylene*).
- And finally, **explosion hazards** must not be forgotten from the moment when hydrolysis leads to the formation of hydrogen (H_2), as is the case with alkaline metals, for example.

It is thus essential that all addition of water be properly controlled when hydrolysable compounds are involved. Generally speaking, this "water" can come from humid air (No. 9467) and possibly complicated by the installation's ergonomics (No. 5137), accidental inclusion (tank bottom poorly dried (No. 25818), unloading error, cleaning operation (No. 5460) or operations by the emergency services (No. 29085).

Anyone working in close proximity of these substances (operators, maintenance technicians, emergency services…) must thus be informed of the specific risks involved with hydrolysable products in order to ensure their proper management or take the appropriate action in the event of an accident. Measures are to be taken, not only concerning the implementation of these substances or their wastes, but also with regard to their storage in locations that are protected from humidity (rain, flooding…)

The accidents for which the ARIA No. is not underlined can be consulted at

www.aria.ecologie.gouv.fr

ARIA 1402 - 06/16/1989 - CANADA - VARENNES - QUEBEC

24.1 - Basic chemical industry

A leak on a pipe released 400 l of titanium tetrachloride. The product hydrolysed in contact with the air, creating a plume of toxic fumes which drifted 1 km. The employees were evacuated and the population had to remained confined indoors for 2 hours.

ARIA 4605 - 07/26/1993 - UNITED STATES - RICHMOND, MICHIGAN

24.1E - Fabrication of other basic inorganic chemical products

During an unloading operation, the rupture disk on a tank car used as temporary storage and loaded with concentrated oleum burst at 3.8 bar even though it was calibrated at 7 bar. Upon hydrolysing in contact with the air, the SO3 formed 13 km-wide and 300-m thick cloud of toxic H2SO4 aerosol that remained over the sector for 4 hours.
Schools were evacuated. The population was confined indoors and traffic was stopped. An estimated 8,000 people were effected by the respiratory and skin problems after having inhaled the cloud's toxic fumes. Of these people, 6 284 were admitted for examination at local hospitals. Only 7 people were hospitalised more than 24 hours. A worker managed to plug the leak 4 hours after it started.

ARIA 5137 - 02/15/1988 – HAUTS DE SEINE (92) - GENNEVILLIERS

24.4A - Fabrication of basic pharmaceutical products

In a fine chemistry workshop, a flash occurred on a pilot reactor in which the condensation of ethyl carbon in a methyl-tertio-butyl-ether solvent environment (MTBE) and in the presence of sodium to obtain a ceto-ester. It was the first time the procedure was being tested. An operator was injured in the face and a bag of hydride being loaded caught fire upon falling. The employees were able to bring the hydride fire and the fire in the reactor under control.
The accident could have been caused by a ventilation duct, near an open manhole, and a drop of condensation water falling onto the hydride or hydride dusts drawn into the solvent vapours and the ambient humidity. The safety airlock was not in place during the reactor loading operation. The accident had no visible consequence on the environment.

ARIA 5460 - 06/02/1994 - ALPLES MARITIMES (06) - ANTIBES

24.2Z - Fabrication of agro-chemical products

Water was poured into a drum containing 30 litres of methyltrichlorosilane during cleaning operations in workshop at an industrial establishment. A cloud of hydrochloric acid formed, requiring the hospitalisation of 19 people. A severely effected employee, as well as an adult and 3 children passing near the company, remained under medical supervision as a precaution. A mobile chemical response unit monitored the chemical reaction (hydrolysis) initiated in the drums.

ARIA 20133 - 12/06/2001 - INDRE ET LOIRE (37) - AMBOISE

24.1E - Fabrication of other basic inorganic chemical products

During his daily inspection, the production manager observed fumes emanating from one of the masonry 2-hour fire boxes located outside of buildings at a plant manufacturing and packaging swimming pool treatment products. The boxes contained drums (50 kg) filled with sweeping residues and dusts from organic chlorinated products collected from the packaging shops' environment vacuums. The wastes consisted of highly volatile trichloro-iso-cyanuric acid (TCCA) and derivatives, likely to be contaminated by inorganic materials recovered from the floor or by the ambient humidity. These wastes are normally retreated 2 to 3 times/week depending on the stocks. The employees sprayed down the fire and the manufacturer requested that the establishment next door confine themselves as a preventive measure. The firemen were called and arrived 15 minutes later. It took 10 minutes to bring the accident under control. No abnormal concentration of chlorine was detected in the ambient air. The firefighting water (1.5 m³) was collected in a 150 m³ catchpit.
The contents of a poorly sheltered drum had spontaneously hydrolysed in contact with rainwater, releasing HCl, etc. The wooden pallet supporting 2 residue drums caught fire as a result of the exothermic reaction. The operator reviewed its danger study (scenarios), permanent security of the site was started at night and the dusts will no longer be stocked but treated on a daily basis.

ARIA 22170 - 02/05/2002 - VAL D'OISE (95) - PERSAN

24.1G - Fabrication of other basic organic chemical products

During cleaning operations at a chemical site that had ceased its activities, hydrogen chloride was released for a few minutes when a tank containing 11.7 tonnes of benzoyl chloride was being drained. The substance was no longer used and had been stocked in the tank for 3 years. Draining tests conducted a few days earlier proved unsuccessful owing to the presence of a solid decomposition product: benzoic acid. Laboratory dissolution tests with methanol showed no abnormal reaction, and tank drainage operations were planned using 2 m³ of methanol injected into the tank by a pump. At around 9.30 am, an employee began the operation with a fireman from an outside company. Slightly thereafter, 200 l of methanol had already been introduced into the tank when the pump malfunctioned. The operation was suspended and spraying equipment was placed into operation. At 10 am, a weak explosion was heard, most likely associated with overpressure, followed by a gas cloud released from between the flanges of a manhole due to a faulty seal. A water curtain was set up and a fire nozzle was used to dissipate the cloud that was drifting north of the site toward a residential area just 150 m from the tank.
A few local residents were effected by the cloud. An elderly woman was hospitalised for testing and remained under observation for 24 hours.
Hydrochloric acid was involved and its highly exothermic hydrolysis leads to the formation of benzoic acid and HCl. A chemical reaction with alcohols leads to the formation of esters and HCl; the accident was a result of this reaction, 90 kg of HCl (55 m³) were likely released with high heat release for the 100 l of methanol added.
Several alarms were triggered in the guard's shack who then alerted the internal firemen. The neighbours informed the public emergency services. Only 2 plant employees were present besides the subcontractors. No production manager or plant representative was at the site at the time; the site's internal contingency plan was initiated only at 3.15 pm. The Classified Installations Inspectorate recorded several anomalies: the accident was not declared, a misunderstanding of the dangers associated with the substances stocked and certain installations, disregard for labelling rules, poor internal organisation and security not in place after business hours... This accident highlights the importance of removing unused chemical products within a reasonable period of time to prevent new hazards (degradation of products, equipment condition, loss of information).

ARIA 22215 - 03/11/1987 - SAVOIE (73) - SAINT-MARCEL

24.1E - Fabrication of other basic inorganic chemical products

A fire broke out in a sodium (Na) packaging workshop at 6.45 pm on valves on top of a tank having a potential capacity of 52 t of Na which was fortunately empty at the time. This tank was located next to another tank containing 15 t of Na. These buffer tanks are pressurised at 7 bar in order to transfer Na to the chemical plant and the empty tank, which was to undergo regulatory ten-year testing, was in its finally cleaning stage prior to being flushed with nitrogen.

Three firemen emptied roughly twenty powder extinguishers located in and near the workshop, then threw 40-kg sacks of anhydrous sodium carbonate onto the two torches formed, but the fire was not extinguished. They then attempted to drain the oil system (4 m³) into a buffer tank, but the process could not be completed due to the geometry of the piping. External emergency rescue services arrived in several waves. Attempts were made to place a massive quantity of sodium carbonate on the fire, now several meters high, but were unsuccessful. Fire nozzles were used to project nitrogen on the fire in an attempt to rarefy the oxygen locally. A platform was installed on the tank at around 9.30 pm in an attempt to retain the carbonate. The system was finally purged 30 minutes later by means of a small pipe and the fire's intensity dropped rapidly. Although the fire remained contained, firefighting operations lasted 3 hours and 20 minutes.

The considerable amount of heat generated ruptured part of the facility's roof made of eternit and damaged plastic elements at the centre of the workshop. At daybreak, an external rescue team member used a tarp to cover the sodium present in the hall.

The fire was caused by the ignition of hot oil sprayed from a leaky seal. The leak was caused by excessive pressure in a thermal oil coil heated by exothermic hydrolysis of the residual Na in the tank in contact with steam from the cleaning operation. No notable pollution of the natural environment was observed. The operator undertook the following measures: modification of the tanks' ten-year review procedure (water replaced by a different fluid...), study of the complete drainage of the oil circuits, reorganisation of the internal emergency services (internal contingency plan).

ARIA 25818 - 10/29/2003 - HAUTE GARONNE (31) - TOULOUSE

24.1G - Fabrication of other basic organic chemical products

At around 2.30 pm in a unit specialised in the synthesis of active species for the pharmaceutical industry, 600 kg of hydrogen chloride (HCl) was released into the atmosphere forming a 20 m² cloud visible from outside the site (westerly wind). The accident occurred while transferring acyl chloride (production residues) into a tanker truck. The acyl chloride was stored pending its incineration at an authorised waste disposal centre. The rapid hydrolysis of the chlorides 4-butyroyle and butyroyl, an exothermic reaction, increased the pressure in the tanker being loaded causing its safety valve (calibrated at 0.5 bar) to open.

The internal contingency plan was put into action. The safely service set up two "peacock" water curtains to neutralise the acid fumes. The firemen arrived at the site around 2.40 pm and installed a 3rd water curtain. As the dome of the tank was hot to the touch, a spray nozzle was used to cool down the tank. Measurements taken 2 m from the tank indicated an HCl concentration of 3 ppm (threshold limit value for the workers: 5 ppm). The gas drainage line was rerouted to a "cubitainer" filled with water, and constantly replenished. This system appeared to be efficient as the releases of HCl was limited to just a few fumes. The incident was finally brought under control around 3.30 pm. Monitoring of the tank and the "cubitainer" was continued until 10/31, at which time the contents of the tank was transferred into 6 "cubitainers" stored in a covered but open building pending new solutions to remove these substances. The polluted water was recovered in a 5,000 m³ catchpit

The incident also highlighted the existence of a leaking valve on the catchpit (approx. 30 m³/h) that led to releases into the Garonne River. The operator offered two 2 hypotheses regarding this incident: the presence of water in the poorly drained and poorly dried tank or water combined with the HCl in the residues. Compatibility tests of these products had not been conducted. Preventive measures were proposed: bulk mixtures of containing acid chlorides is prohibited (residues must first be treated in an appropriate installation), strict control of each tank to be transported prior to loading to ensure water is not present, drying certificate, determination of the compatibility between various residues.

ARIA 29085 - 02/02/2005 - ISERE (38) - LE PONT-DE-CLAIX

24.1G - Fabrication of other basic organic chemical products

A leak of pure phosphorus trichloride (PCl_3) occurred at a chemical platform during a transport tank unloading operation. Slightly after the unloading operation had begun, the operator noted a leak dripping from the tank's union connection. The flange was removed following various unsuccessful repair operations: closure of the valves on each side of the flange, then opening of the circuit without first draining that portion of the line. The small quantity of PCl_3 released (4 kg), corresponding to the volume of the section of line, hydrolysed spontaneously in contact with the humid atmosphere and wet ground, forming a cloud of hydrogen chloride inside the covered unloading station.

The platform's gas alarm was sounded as a precaution. The firemen sprayed down the puddle of water, thus amplifying the release of hydrogen chloride. The resulting cloud was driven outside the establishment by the northerly wind. The internal contingency plan was initiated and the personnel were confined indoors during the incident. Two employees from a neighbouring workshop complained of eye irritations and confined themselves inside their premises. The firemen conducted pollution measurements outside the platform. Although the measurements proved to be negative, they were confirmed by a post-accident study of the atmospheric dispersion The Internal Contingency Plan was lifted 30 minutes after it had been initiated.

The Classified Installations Inspectorate went to the site. The poor seal between the unloading arm and the tank was caused by poor alignment of the flanges prior to tightening, and product deposits forming on the surface finish of these flanges. The corrective measures taken include the development of a procedure for disconnecting the arm should unloading operations be interrupted (including decompression of the tank and drainage of the arm), implementation of a leak test under nitrogen pressure on the arm/tank connection prior to each unloading operation and the use of a new seal for each unloading operation.

Accidental release of propane in Donges

ARIA 30831 - 03/21/2005 – LOIRE ATLANTIQUE (44) – DONGES

51.5A – Wholesale of combustible products

Approximately 2 kg of propane were released into the atmosphere at an LPG filling centre (Seveso installation) and designed to supply customers throughout the region.

A tank car was moved while it was being loaded, causing a gas leak. Positioned at station P2, the tank car was coupled to a second tank car at the neighbouring station PB and for which the filling operation was nearly complete. When the loading operation was finished, the pump operator removed the tank car's yokes causing both tank cars to move a distance of 10 m (due to the sloped ground). This thus caused the loading arm to be ripped away from the tank car in position at station P2. The arm on the loading station side was closed by the rupture valve. On the tank car side, the arm was broken along the threads of the rupture valve. Back pressure on the tank car's bottom valve thus limited the leak. The station's level detectors did not trip due to the small quantity of gas released and the wind that dispersed the cloud.

The incident was attributed to a malfunction of several safety barriers (at both the technical and organisational level). The Classified Installations Inspectorate requested that the operator undertake several corrective actions: a feasibility study regarding the rehabilitation of the loading station site to ensure zero inclination of the track, verification to ensure that 2 chocks (or yokes) are present and identified at each tank car loading station, verification that loading arms were severed at the rupture valve level, awareness training for the operators regarding the formal procedures for installing anti-impact devices...

Loading/unloading station connections

Operations involving the loading and unloading of large quantities of product are frequently performed using a transfer arm. When correctly maintained and operated in strict compliance with the established operating procedures, a loading arm generally contributes to an overall improvement in safety during transfer operations between a mobile storage tank and a fixed storage facility.

The 11 accidents described below have been selected from the ARIA database to illustrate the human and organisational factors involved in accidents involving this type of equipment.

The condition of the equipment, most often exposed to inclement weather, is the primary potential cause for an accident: degradation caused by wear or corrosion and faulty maintenance of coupling elements on rigid pipe or flexible hose was responsible for a dramatic "BLEVE" (Boiling Liquid Expanding Vapour Explosion) accident in Riverview, Michigan (United States) (No. 20821) and in Perpignan (No. 6805), a defective threaded coupling resulting from repetitive incorrect manipulation causing a deadly flash-fire in Germany (No. 29590), damaged mating surfaces altering the clampability of flanges and the seal of a coupling in Pont-de-Claix (No. 29085), and premature ageing of a coupling resulting in a propane leak in Cournon d'Auvergne (No. 21859).

This type of equipment, subject to regular maintenance, must also be tested to ensure its overall seal in an operational context, and the correct operation of safety devices. Tests of this type were instrumental in the early detection of a leak on an ammonia-loading arm (No. 4320) and a faulty seal on a shut-off valve at the base of an LPG transfer arm (No. 28388) before unloading operations had started. Such tests can also prove useful prior to placing arms back into service following maintenance or servicing operations (No. 6786).

The automation of certain transfer station operations has not otherwise fundamentally modified the number of predominantly manual operations required to connect the arm to a mobile tank then to disconnect and store it after use. The operators, directly exposed to the effects of the products being transferred in the event of an accidental release (No. 7640, No. 28234, No. 29590), must remain vigilant (No. 6757) and conduct operations in strict compliance with the corresponding procedures.

Finally, the overall safety of transfer operations depends on the proper immobilisation of the mobile tank. The Donges accident is a recent example in the already long list of cases involving untimely movements (No. 5437, No. 948) causing the activation of rupture valves triggered by abnormal forces on the arm. Valve malfunction, attributable either to the arm's design (No. 948, No. 5437) or to neglected maintenance (No. 6135), is synonymous with a more or less significant release of product likely to generate a dangerous phenomenon (flammable cloud, toxic cloud) depending on its type.

The procedures specific to connecting operations at the loading or unloading station were drawn up by several organisations (UIC-Guides (loader), INRS–ED783, CNAM–R384…). It is also important for all players to be familiar with the lessons learned from events so that individual behaviours and the procedures governing these operations can be modified to ensure the safety of everyone involved.

The accidents for which the ARIA No. is not underlined can be consulted at

www.aria.ecologie.gouv.fr

ARIA 948 - 10/23/1989 - INDRE (36) - LE BLANC

51.5A – Wholesale of combustible products

Five tons of liquid propane leak occurred during transferring from a tank car to a propane sphere.

The leak was caused by a malfunctioning rupture unit on a loading arm in which only 2 of the 3 rupture blades ruptured. The 3rd blade bent, preventing the valves from operating normally. A gaseous cloud measuring 30 m in diameter formed, preventing all human intervention. After 8 minutes, the foreman entered the cloud without protection and pulled the turnbuckle's chain to stop the flow.

Three detectors detected the presence of gas. The accident had no visible incidence on the environment.

ARIA 4320 - 12/29/1993 - GIRONDE (33) - AMBES

24.1J - Fabrication of nitrogen products and fertilisers

An ammonia leak occurred during a test of a cryogenic ammonia loading arm used to supply ships.

The burst formed a toxic cloud affected the operators working on the quay and caused a vehicle to leave the road. The 3 passengers of the vehicle were slightly injured or affected by the gas.

All ship unloading operations were halted at the company during the search of the cause of the leak. The ammonia unloading procedure was reviewed, and now includes leak tests.

ARIA 5437 - 01/04/1987 - SLOVAKIA - VARIN

63.1E – Non-refrigerated storage

An impact followed by the movement of a tank car during an unloading operation at a pressurised liquid ammonia depot caused a rigid transfer arm to break and release 30 m^3 of liquefied ammonia. Considering the outside temperature (- 17 ℃), the ammonia spread a t ground level risking polluting the shallow water table. An employee was mortally burned or intoxicated by the liquefied product.

The installations and the operating procedures were modified (semi-rigid arm, instructions, etc.) and were subject to a safety audit 5 years later. The audit report recommended numerous improvements (removal of low point valves, etc.).

ARIA 6135 - 12/16/1994 - PAS DE CALAIS (62) - MAZINGARBE

24.1J - Fabrication of nitrogen products and fertilisers

At a chemical plant, leak occurred at 5.20 pm while a tank car containing 48 tonnes of ammonia (NH_3) was being unloaded. Twenty-seven tonnes of NH_3 were released over 37 minutes until the operator closed the tank's bottom valve by releasing the turnbuckle using a metal shim that had been thrown roughly fifteen meters away.

The internal contingency plan and special intervention plan were put into action (safety perimeter:). 5 km – 8,000 to 10,000 persons concerned), vehicles equipped with loudspeakers directed the population of 2 neighbouring communities to confine themselves indoors. A school and a supermarket were confined, and then evacuated after the cloud had dissipated. For 4 hours, 80 firemen intervened with 25 vehicles, ambulances and a mobile chemical response unit. The internal contingency plan was called off at 8.40 pm. The accident caused one child to experience respiratory difficulties, and who was hospitalised for 2 hours, and roughly fifteen people experienced discomfort. The ammonia odour was nevertheless detectable up to 8 km from the release point.

The accident was caused by the automatic disconnection of the unloading arm and the blockage of the 2 series-mounted safety valves in the open position: an unexplained failure of the anti-impact safety device (detection pedal) caused the transfer arm to disconnect, the turnbuckle actuating the tank car's bottom valve remained blocked (due to mechanical and automatic control problems) and the valve mounted on the transfer arm (tank car side) remained partially open as it was blocked by a foreign body (the origin of the bolt blocking the valve is unknown).

Following the accident, the corrective measures taken concentrated on the installation of positive safety type pneumatic turnbuckles, the limitation of arm disconnection scenarios, the replacement of disconnection pedals by rocker type stop cleats preventing all risk of accidental impact and the installation of a filter on the end of the unloading arm to protect the valves from the introduction of foreign objects...

ARIA 6805 - 07/22/1970 – PYRENEES ORIENTALES (66) - PERPIGNAN

40.1A - Electricity production

A violent explosion and fire broke out in a gas factory, i.e. an establishment producing manufactured gas and operating the site's related product distribution and storage activities and LGG brought in from outside the plant. While unloading 45 tonnes of propane from a tank car, a hose (dia. 50 mm) broke off flush with the tank car valve's disconnect coupling, causing a leak estimated at 8 kg/s. A mist formed (gas + droplets of liquefied gas).

At the time of the accident, there was a light wind (1 m/s) and the temperature was 25℃. Only 5 t of the product had been transferred at the time of the accident. The thick white cloud prevented the operator and 2 witnesses nearby from intervening. The cloud caught fire 4 minutes later as a locomotive was passing. Its 2 occupants were seriously burned and later died from their injuries. The irruption of the cloud caused several fires to break out, located several dozen meters downwind. The police evacuated residents living in a radius of approximately 200 m, notably a school and a home for the elderly. The fire menaced the site's 2 cylinders (100 m^3 each), 2 spheres (500 m^3 each), 2 gasometers (10,000 m^3 and 4,000 m^3), another propane tank car, and petrol storage tanks. The leak fuelled the fire and eventually engulfed the tank car that originally created the accident. Despite the efforts by the rescue services, the tank care exploded (BLEVE) 40' after the leak had begun.

Property damage was extensive: unloading terminals were destroyed, gasometers caught fire, and the heat lagging of the spheres was partially ripped away. The police extended the evacuation zone to 450 m.

The response teams were destabilised (among the team members hospitalised within 10 minutes, 17 suffered from burns) and resumed their efforts only an hour later. They attempted to move the petrol tank and the 2^{nd} tank car, and close the valves that were fuelling the fire. The various fires were extinguished approximately 4½ hours after the explosion. The accident left 2 dead and 49 injured, 11 among the personnel, 18 among the firemen (4 of whom were seriously injured), 23 passers-by and local residents (burns, fractures, flying glass, amputation of phalanges). Gas distribution was interrupted for 20,000 subscribers. Approximately 1,100 accident claims were established. Significant damage was located in a radius of 300 m around the tank car, with a lesser degree of damage in a radius of 500 m, while broken glass was observed 1,000 m away.

ARIA 7640 - 09/13/1995 - BAS RHIN (67) - REICHSTETT

51.5A – Wholesale of combustible products

During a truck loading operation in a gas depot, the wet hose slipped from the driver's hands while he was attempting to connect it, causing the arm's end valve to open. A release of gas was detected and the relay was secured automatically.

The retraction of the arm caused the driver to fall and injure his face on a sharp corner, for which he was hospitalised.

ARIA 21859 - 01/14/2002 – PUY DE DOME (63) - COURNON-D'AUVERGNE

51.5A – Wholesale of combustible products

A propane leak occurred on a loading station in an LPG depot that distributes product to trucks. The depot manager secured the site by pressing the emergency button, in accordance with the site's standard operating procedure. The emergency services were contacted as a preventive measure. The automatic devices associated with the emergency shut down operated correctly, including: automatic disconnection by closure of the valves, flooding by fixed sprayers (spray booms and monitors), disconnection of power supplies. The spraying systems are designed to dilute the cloud. The operator then went to the pump station and closed all the manual valves. No trucks were being filled at the time of the accident.

The leak was located on a purge line (VOC recovery) used to drain the hose after loading operations are complete. The line runs between the tank's manual valve and that of the loading arm and to direct the residual liquefied gas to the storage tank. This recovery function is fairly recent. The piping consists of a rigid part and a flexible part connected by an "olive" type screw connector. The piping is also equipped with valves, at the loading station, enabling it to be connected to either the pressurised LPG intake system (purge), equipped with a device in the pump house allowing it to be conveyed to the storage facility, or to the venting section (fumes), depending on how the valves are configured. The leak was caused by the rupture of union (due to ageing) between the rigid and fixed parts. In addition, owing to the position of the valves, the piping was connected with the product intake circuit: the leak was thus being fed, as the product system was not equipped with a device preventing its backflow through the purge.

The operator immediately implemented the following measures: the hose was replaced with an identical model, locking out of valves, temporary shut down of the recovery operation. Modifications were foreseen: the installation of hoses adapted to the stresses associated with product recovery, and automation of the purge system valves (with the system being secured when an alarm sounds or at the end of the loading operation). Additional investigations are planned in the long term (expert evaluation of all hoses, cataloguing of the installations having this device, identification of potential sources maintaining hoses under pressure...).

ARIA 28234 - 04/23/2004 - AUSTRALIA - NC

51.5A – Wholesale of combustible products

After having filled 2/3 of his truck with LPG, a driver detached the loading arm causing a propane leak to burst into flames. The driver was seriously burned to the 2nd and 3rd degree and was immediately transferred to the hospital where he died 12 hours later. This accident was most likely caused by a valve malfunction or the collapse of the loading arm.

ARIA 28388 - 10/07/2004 - INDRE (36) - LE BLANC

51.5A – Wholesale of combustible products

During security testing conducted by the operator in the presence of the Classified Installations Inspectorate, 2 shut-off valves did not operate at the tractor-trailer unloading station of an LPG depot. In the event of an anomaly, these positive safety valves enable the truck to be isolated from the other installations.

The operator shut down the station until the installations could be refurbished. After verification, the problem was found to have been caused by the presence of a wasp nest that had been built inside the air system's depressurisation solenoid valve, preventing it from operating. Additional checks, conducted on the site's other solenoid valves of the same type, turned up additional nests in another device but did not prevent it from operating. The operator had mesh netting installed to prevent insects from entering the device.

ARIA 29085 - 02/02/2005 - ISERE (38) - LE PONT-DE-CLAIX

24.1G - Fabrication of other basic organic chemical products

A leak of pure phosphorus trichloride (PCl_3) occurred in a chemical platform during a transport tank unloading operation. Slightly after the unloading operation had begun, the operator noted a dripping leak on the tank's sleeve connection. The flange was removed following various unsuccessful repair operations: closure of the valves on each side of the flange, then opening of the circuit without first draining that portion of the line. The small quantity of PCl_3 released (4 kg), corresponding to the volume of the section of line, hydrolysed spontaneously in contact with the humid atmosphere and wet ground, forming a cloud of hydrogen chloride inside the covered unloading station.

The platform's gas alarm was sounded as a precaution. The firemen sprayed down the puddle of water, thus amplifying the release of hydrogen chloride. The resulting cloud was driven outside the establishment by the northerly wind. The internal contingency plan was initiated and the personnel were confined indoors during the incident. Two employees from a neighbouring workshop complained of eye irritations and confined themselves inside their premises. The firemen conducted pollution measurements outside the platform. Although the measurements proved to be negative, they were confirmed by a post-accident study of the atmospheric dispersion The Internal Contingency Plan was lifted 30 minutes after it had been initiated. The Classified Installations Inspectorate went to the site.

The poor seal between the unloading arm and the tank was caused by poor alignment of the flanges prior to tightening, and product deposits forming on the surface finish of these flanges. The corrective measures taken include the development of a procedure for disconnecting the arm should unloading operations be interrupted (including decompression of the tank and drainage of the arm), implementation of a leak test under nitrogen pressure on the arm/tank connection prior to each unloading operation and the use of a new seal for each unloading operation.

ARIA 29590 - 04/23/2004 - GERMANY - NC

23.2Z - Petroleum refinery

A "flash" of LPG occurred a refinery during a transfer operation between a fixed storage tank and a tanker truck. On the day of the accident, a tanker was being loaded when the screw-type connection between the loading arm and the tanker began to leak. The resulting cloud caught fire, engulfing the driver. He was severely burned and later died of his injuries.

Analysis of the accident showed thread wear on both parts of the threaded union: on the arm, the threaded union of the brass bushing (ACME, 3¼"; female) was particularly worn (the initially trapezoidal section of the threads had become triangular). The threads on the tank's connector were also extremely worn: the end of the union was nearly conical and the threads themselves had visible flat portions. According to the local inspectorate, this situation could have been avoided by simply observing the prevention principles: regular document-based inspections and visual inspections of the unions, including the threads. German regulations require that a visual inspection be conducted 2 times/year. Furthermore, while certain users were tightening the bushing with a hammer (an apparently common practice), the practice is prohibited at the refinery and also not recommended by the German LPG association. This type of accident is not uncommon at these types of installations and warnings have been issued to this effect. It appears that the warnings were known at the site involved.

An extensive nation-wide thread verification program was conducted in Germany and revealed that a large number were in fact worn. In the six months following the accident, the situation was vastly improved and this type of problem appears to have been solved.

Accidental releases of hydrocarbons at Buncefield and Sainte-Marie

ARIA 31312 – 12/11/2005 - UNITED KINGDOM - BUNCEFIELD

23.2Z – Manufacture of refined petroleum products

Explosions followed by fire ripped through a fuel storage depot in Buncefield, England, located just 40 km north of London. The facility was storing 150,000 t of fuel (petrol, diesel fuel and kerosene) at the time of the accident. The 1st and largest explosion occurred at 6.01 am (measuring 2.4 on the Richter scale) and was heard 160 km away. The overpressure effects from the blast reached 700 to 1,000 mbar. Two other explosions occurred at 6.27 and 6.28 am. A gigantic blackish cloud containing irritating substances drifted across southern England, Brittany and Normandy December 12th, eventually reaching southwestern Spain. The authorities recommended residents living near the depot to remain indoors; 2,000 people were evacuated although were allowed to return to their homes the same evening. The M1 motorway connecting London to the Midlands was closed down for several days. The firemen were able to bring the fire under control after 60 hours, but the fumes from a tank initially spared by the flames caught fire on the morning of December 14th. During the most intense moments of the crisis, 180 firemen were mobilised along with 20 vehicles and 26 pump trucks. 786 m³ of foam concentrate and 68,000 m³ of water were used.

Forty-three people were reported injured, most of who were injured by broken glass. The 10 employees present at the site at the time of the blast were uninjured. The impact of the fire on water quality was closely monitored, notably due to the presence of perfluorooctanoic sulfonate (PFOS), a toxic and persistent product used in foam concentrate. The firefighting water that could be contained on the site was recovered then temporarily stored at several sites around the country; however, 800 m³ were inadvertently released into a treatment station then into the River Colne. Total cost has still to be established but it will be in excess of € 750 millions. Approximately 20 establishments employing 500 people were destroyed and roughly sixty employing 3,500 employees suffered considerable damage.

The accident was caused by the ignition of a flammable vapour cloud, which had extended over 8 ha, and formed from more than 300 t of lead-free petrol that had spilled over from the roof of a diaphragm float tank that was being filled (Dec. 11, at 3 am: the level gauge remained static while the output remained the same; 5.20 am: the tank began to overflow; 5.50 am: The filling of another tank stops and the output to tank 912 reaches 890 m^3/h; 6.01 al: 1st explosion). The ignition point, northeast of the depot, has not been precisely determined although hypotheses have been proposed: the pumping station, the heater in the emergency generator facility, car engines. Neither of the 2 alarm systems connected to the filling level detectors of tank 912 operated (level gauge + high level alarm). The supply was thus not stopped automatically and the malfunction was not reported by the supplier's system, as it should have been via the high level alarm.

Photo DR

ARIA 31227 - 12/30/2005 - 974 - SAINTE-MARIE

23.2Z – Manufacture of refined petroleum products

Following the transfer of Jet A1 jet fuel between the hydrocarbons depot of an airport (A) and an adjacent depot (B) on December 29, 2005, 2 connecting valves between the unloading booms and the tank were not closed. During unloading operation involving tanker trucks the day before, one of the semi-buried tanks was overfilled and its contents spilled out through the vents; 32,664 litres of fuel spilled onto the dome of the buried tank. Part of the fuel infiltrated the ground outside the catchpit and some spread into the adjacent parking area in the zone B. The parking area is connected to a petrol-intercepting trap that became quickly saturated (capacity: 600 l) and the jet fuel entered the rainwater network. The 2 depots operators quickly sealed off the rainwater network (between 8.40 am and 9.15 am) with sand and other oleophilic materials. However, after noting that jet fuel was present in the rainwater network, a depot B worker rinsed the network with a large quantity of water at 9.30 am, causing sand and jet fuel to be conveyed toward the sea. A drinking water supply well on property operated by the site B, 100 or 150 m from the tank that overflowed was stopped on the morning of the accident; the zone supplied by this well was temporarily interconnected to another network. Almost the entire polluted zone was covered with a tarp; 1,000 litres of jet fuel would be pumped in an opening of the tank and in the petrol interceptor trap of the depot B. Several measures were taken following the accident: excavation and treatment of the polluted soil by specialised means, installation of a piezometre between the tank concerned and the well, regular samples taken on the depot A piezometres and cleaning of the rainwater network. The three main causes for this jet fuel leak are as follows: human error in the handling of the valves, the position of connecting valves between the unloading booms and the tanks was unchecked and malfunction of the high level sensor on the tank concerned. The administration acknowledged the facts.

Photo DR

Tank overflowing

The overflowing of tanks, associated with problems regarding flow management within a depot or between two installations, is often initially attributed to human and organisational failures. The 21 accidents described below will illustrate various cases.

Accident analysis relates numerous overflow accidents caused by **failures or operational deficiencies of prevention systems**. The level gauges, the slaving of valves and information transmission systems, perfected and sensitive elements, must be subject to strict maintenance conditions. The malfunction considerably complicates the management of tank levels and can lead to overfilling (Nos. 22553, 25731, 29601, 30951, 31227 Sainte-Marie, 31312 Buncefield, 32693). These devices are generally "fail safe" enabling the transfer of liquid to be stopped in case they should go out of service. Nevertheless, there have been several cases of overflow caused by power supply failures: the operation of level detectors was interrupted following a power outage (Nos. 4695, 6449), a disconnected wire causing the valve of a purge tank to close (No. 15074). It is also important to ensure that level measurement equipment is adapted to the fluids and the storage conditions (No. 25731) and that they do not change under the stresses to which they may be exposed (overpressure,) (No. 26432), or otherwise they may transmit erroneous information.

The **organisational and human factors** are decisive elements of proper flow management. If no prevention system is present, it is essential that the ***information relative to the tank's receiving capacity*** be clearly indicated and immediately available: current accounting of the amount of fluid contained in each tank (No. 31342), information for the delivery man relative to the available volume prior to all filling operation (Nos. 30951, 31342) and, conversely, transmission of transport documents to the depot agent. Everyone's role, including the deliveryman and the receiving agent, must be clearly defined. Furthermore, during a product transfer, ***communication*** between these two individuals must be easy, reliable and organised. This mutual understanding is a priority when the successful completion of the transfer is based solely on direct exchanges between the supplier and the receiving station (29601, 30987).
Beyond good communication, the various parties involved must be ***informed and trained*** in the operation of fluid transfer and storage installations and the risks inherent to the transfer of fluids and the tank overflows, in order to prevent misinterpretation and anticipation errors (Nos. 26003, 31227). Operations must be set out in formal ***operating procedures***, clearly stating all steps of the operation: truck, boat or train receiving operations, pump flow rates and delivery time calculations (26981), preliminary inspection of supply line or unloading connections (No. 26003), valve position (Nos. 2778, 21868, 31227 Sainte-Marie) and the destination of the products (Nos. 27797, 29601).
During loading operations, operators must ensure close ***surveillance***: an agent from the storage site must be present to receive the delivery personnel and initiate transfer (30951) and loading operations (Nos. 7435, 26981, 32622) in order to detect anomalies as early as possible.
In addition, ***safety instructions*** must be established, issued and implemented should an accident occur. These instructions must include the reflexes one must have in the event of an alarm (Nos. 21868, 26003), how to stop an overflow, and the pollution prevention means to be used following a spillage (No. 31227 Sainte-Marie).
And finally, ***preventive maintenance*** of the transfer equipment and overfill detection and prevention systems (gauges, valves and control systems, information transmission systems, etc.) must be planned. Such elements must also be inspected regularly during rounds and tests to ensure that they operate correctly and when a malfunction is identified, its ***repair*** cannot be delayed (No. 25731).

The consequences of these events are often compounded by **confinement failures**. As spillages generally occur from vents, their design must allow products to be collected in catchpits or retaining basins (Nos. 7435, 30951, 31227 Sainte-Marie) which are the first line of defence (No. 30956). There are still many cases in which these structures are not hermetic or poorly dimensioned, leading to contamination of the soil and water through infiltration (Nos. 26432, 27797), spillage (No. 4695) or their incorrect use: catchpit full of rainwater or not isolated from the external environment (valve open or defective) (No. 4582). Although less common but nevertheless real are accidents in which the wind directs the liquids that spill from vents outside confinement areas (Nos. 2778, 22553).

In light of serious secondary accidents that could create tank spillages, such as a catchpit fire, an explosion of flammable gas clouds, the feedback argues in favour of the widespread use of adapted and correctly maintained spill prevention systems on storage tanks. On large sites, level gauges connected to valve control system and information and recording interface is a solution that should be considered. These devices, as sophisticated as they may be, cannot completely replace elementary instructions on how transfer operations are to be conducted (supply or distribution), and which can be considered fundamental when major product movements must be managed.

Accidents for which the ARIA No. is not underlined can be consulted at
www.aria.ecologie.gouv.fr.

ARIA 4695 - 08/27/1993 - BOUCHES DU RHONE (13) - VITROLLES

15.4C - Manufacture of refined oils and fats

Following a power outage that disrupted the operation of level detectors in an oil tank, sunflower seed oil spilled into the catchpit then overflowed into the rainwater system. This network is connected directly to the Cadiere from where the pollution spreads. The administration acknowledged the facts.

ARIA 22553 - 10/23/1999 - RHÔNE (69) - SAINT-FONS

24.1G - Manufacture of other basic organic chemicals

A 147 t leak of adiponitrile (ADN), used in the fabrication of nylon, occurred over the weekend at a chemical site. The installations include: a tank car unloading station, a main storage tank with a capacity of 8,900 m^3, a 2,500-m^3 buffer tank S2 which continuously supplies the production unit, piping with pumps and valves (manual V7 and motorised V8 pumps at the base of S1, manual V2 on the main pipe connecting S1 and S2, manual V3 on the unloading line and located between the main pipe and the small pressure surge tank S3) used to transfer the ADN to one of the 2 tanks or to perform transfer operations between these 2 tanks located in 2 separate catchpits. The tank car stations and the piping are equipped with hermetic zones and trenches connected to a remote pit. On Friday, an operator had performed a transfer operation between the two tanks. The enquiry revealed that V3 was not completely closed, that the mechanical key control system between V2 and V3 was inoperative (V2 remained open), as did the limit switch contact control on V3, controlling the closure of V8 whose position indicator light was out of service. The ADN flowed from tank S1 through V7 (normally open), V8, V2 and V3 by gravity and slowly filled up (2.6 m^3/h) tank S3 open to the atmosphere and finally spilling out via the latter's vent at a height of 4 m. Owing to the continuous wind throughout the weekend, 120 t of ADN did not flow into the trench under the tank, but onto the gravely soil nearby. This spillage was not detected by multiple rounds conducted by the weekend security team, certainly due to the low flow rate and the abundant rainfall that had partially filled up the catchpits, wetted down the installations and created numerous puddles on the ground. The leak was discovered the following Monday when the tank levels were recorded. The operators closed the valves and transfer pipes, pumped the substances still present on the ground and drained the catchpits into empty tanks that were available. The unloading instructions were modified (valve V7 systematically closed), the vent on tank S3 is connected to the trench leading to the remote pit. Hydrogeological studies were conducted. The polluted zone was evaluated at 1,600 m^2, and 4 piezometres were used to pump and draw down the water table level for several months.

ARIA 25731 - 10/10/2003 - RHONE (69) - GIVORS

63.1E – Non-refrigerated storage

At around 12.20 pm, in a fuel storage depot, an employee noted that a bitumen tank being filled was overflowing. Owing to its temperature, the product outside the tank began releasing vapours and insulating materials covering the tank caught fire. The site implemented its safety devices and the internal contingency plan was put into action as a preventive measure. The emergency services were informed and the depot was partially evacuated. The firemen set up two foam monitors and prevented the fire from spreading to the other tanks located nearby. The operator began extracting the bitumen from the tank concerned. The fire was brought under control at around 1.20 pm and the internal contingency plan was lifted at 2.00 pm. The leak remained confined in the catchpit. Property damage was minor. According to the operator's analysis, various parameters were united which led to the spillage from the tank: excess product, gauge well damaged not allowing proper flow, and the spillage went undetected. The excess product was attributed to the fact that the finished product manufacturing unit had being using less product, and thus tank contained an already large stock. The non-detection of the rising level in the tank, followed by the spillage can be attributed to: the level rule was unavailable as it had not yet been repaired (the repair operation would require that the tank be drained), incorrect operation of the very high level/vibrating blade device (not maintained, no technical file, adaptation/product measured?), 24-hour shift in the computerised stock monitoring application, no consultation of the information given by the local level gauge. The product most likely ignited because the tank was very hot, combined with the presence of pyrophoric sulfides. In terms of corrective action, the operator agreed to repair the rule, study and install a very high level detector. In terms of organisational planning, the operators were trained, for stock calculation purposes, in the application, development and implementation of a maintenance procedure with periodic verifications for managing all levels on the site. More generally speaking, the operator has organised a program to monitor the implementation of improvement actions (including corrective actions).

No. 26003 - 08/25/2003 - BOUCHES DU RHONE (13) - FOS-SUR-MER

24.1G - Manufacture of other basic organic chemicals

A phosphorus trichloride (PCl3) leak occurred in a chemical plant during an iso container filling operation. The operator stopped the loading operation when the control room noticed a cloud of PCl3 and hydrogen chloride (HCl) being released into the atmosphere. The establishment's internal contingency plan was initiated. The internal rescue services set up a water curtain. In the two neighbouring plants, the cloud of gas caused extreme irritation to the eyes and throats of roughly ten individuals. As the plant managers were unable to locate the source or nature of the gas, they decided to confine their personnel for approximately 20 minutes. The accident was caused by an inversion of the iso-container's supply and degassing lines. This type of container was being used for the first time at the site. After preliminary testing (including the verification of the automatic valves), the operator connected the degassing pipe on the valve equipped with a coupling identified as N2 and the loading pipe on the valve equipped with a coupling bearing an eduction tube symbol. The overfill capacitive probe was in place on the degassing branch connection. During the loading operation, the overfill probe alarm was triggered 3 times. Each time, the operator stopped the pump, closed the valves and checked the container. As nothing abnormal was detected, he acknowledged the fault and continued loading. After the 3rd alarm, liquid PCl3 overflowed via the degassing pipe even though only 3.45 m^3 of PCl3 had been transferred (container capacity = 14.6 m^3). Analysis of the fault tree showed that a marking error on the iso-container's connecting points was the cause of the accident: the couplings installed above the valves were reversed. The filling operation was thus performed via the degassing valve and as the tank was being filled, the pressure of the pump caused the PCl3 to return via the eduction tube attached to the filling valve connected to the degassing pipe. To prevent this type of accident happening again, various measures were undertaken: development of a receiving approval system for new packaging, a reliability study of the capacitive probe, PCl3 leak prevention procedures and start-up of the emergency fire-fighting unit... Henceforth, the neighbouring plants will be included in the site's internal contingency plan alert procedures.

ARIA 26432 - 06/11/2003 - BOUCHES DU RHONE (13) - BERRE-L'ETANG

24.1G - Manufacture of other basic organic chemicals

At a petrochemical site, an operator making rounds detected that a styrene tank had overflowed; approximately 10 m^3 of product had spilled from the atmospheric venting and was flowing along the wall. Provisional measures were rapidly taken to limit the consequences of the incident as much as possible: the transfer pump was immediately stopped, ground washed with water to make the styrene float which would then be pumped off and incinerated; the polluted portion of the soil would be excavated and incinerated; the water table analysed and purified by pumping. In the scope of corrective actions, the operator modified the level measurement so that it would be insensitive to pressure variations in the tank. The incident originated from slight overpressure in the styrene tank and led to a malfunction for the level measurement instrumentation and the transmission of erroneous information (low level in the tank) to the automatic styrene transfer system from a 3,500 t tank to the 60 t tank in question.

ARIA 26981 - 12/13/2002 - BELGIUM - BRABANT

23.3Z - Processing of nuclear fuel

A ship was unloading its cargo into a tank located in a petroleum depot. The handling operations were being carried out normally for the transfer. Suddenly, a warning alarm signaled that the first tank was nearly full. As the operator in charge of the operation was occupied with other tasks, the alarm went unnoticed: he was unable to switch over the valves in time. As a result, 5 m^3 of diesel fuel (3 m^3 inside the walls and 2 m^3 outside, on the ground) spilled into the tank's catchpits and outside. The disregard of strict compliance with the operating instructions and equipment use is to blame. While the fuel did not reach the canal, the Inspectorate noted that the company was in violation for the disregard of the operating conditions and requested that preventive and protection measures be implemented.

ARIA 29601 - 04/01/2005 - SAVOIE (73) - ALBENS

51.5A – Wholesale of combustible products

In a fuel storage depot, at around 3.30 pm during a delivery via a diesel fuel pipeline, 10 t of product spilled from a tank being filled (capacity: 2,100 m^3; internal floating diaphragm type tank) in a catchpit. Depot personnel initiated the site's emergency shutdown and the internal contingency plan was put into action. The operator transferred the product to the site's hydrocarbon separator and initiated pumping operations (that evening at 8 pm, 3 t of product had been recovered). The tank was equipped with neither a high level or very high level detector. The incident was partly due to an error during the delivery via pipe: the quantity to be delivered should have been distributed consecutively in two tanks (2X400 m^3) but was oriented into a single tank not having sufficient available volume. The operation was performed externally to the site by the transporter. Also, at depot level, the absence of high level and very high level detectors on the tanks with coupling of the supply valves did not allow the spill to be avoided. The Classified Installations Inspectorate recorded the facts and Prefectoral orders required that the site be backfitted to standards.

ARIA 30951 - 02/07/2005 - SAVOIE (73) - SALINS-LES-THERMES

51.5A – Wholesale of combustible products

An 80-litre leak of fuel oil through the vent of a tank being filled in a hydrocarbon depot spilled onto the road. The depot's manager intervened by using absorbent products to recover the spilled products. The delivery driver did not check if the tank was in fact able to receive all of the product delivered and the tank's vent was masked by another vehicle waiting delivery. The tanks at this installation are equipped with overfill protection devices but unit on the tank in question was faulty. Finally, the spilled products should have been directed to a retaining basin in the installation, demonstrating the installation's faulty design. The Classified Installations Inspectorate recorded the facts.

ARIA 30956 - 10/02/2005 - CHER (18) - RIANS

15.5C - Manufacture of cheese

At around 8.45 am, 10,000 litres of milk from a cheese factory spilled into the Ouatier River due to incorrect configuration of a diverter valve. The milk, being unloaded from a tanker truck, was directed to an already full storage tank that overflowed. As the tanks were located above a rainwater drain, the milk was directed directly into the river. The employee in charge of the unloading operation become aware of the problem and alerted the guard station. The guard and the technical supervisor on duty closed a gate valve to close off the rainwater network. A surface pump was installed near the gate valve to divert the dairy's internal rainwater network into the wastewater system. After drawing the pollution into these networks internally, the operator opened its clean water networks to increase the river's flow rate, raise the oxygen level in the water and limit the risk of asphyxiating the aquatic fauna. Corrective measures were implemented: reminder of the verification procedures relative to manual valve operations, securing of manual valve positions by electric control devices or PLCs, backfilling of the rainwater drain under the milk storage tanks.

ARIA 31342 - 08/24/2005 - MAINE ET LOIRE (49) - AVRILLE

24.1G - Manufacture of other basic organic chemicals

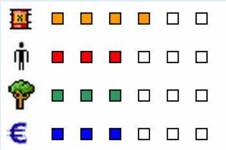
In a chemical plant, a tank containing used flammable liquids overflowed via the vent during the transfer of 3,500 litres of used solvent. Having witnessed the release, a member of the personnel closed the valve on the transfer station, and then alerted the operator in charge of the operation. The spillage involved 200 litres of solvents recovered in the storage facility's catchpit. The contents of the catchpit were pumped and transferred into a second tank dedicated to the storage of flammable liquids earmarked for destruction. The incident had no impact on the natural environment.

The accident occurred after the operator in charge of the transfer had checked the connection to the transfer station and registered the workshop to ensure that the volume present in the storage tank would allow the transfer without any risk of spillage. The register, however, was designed only to know the type of substances pumped into the waste solvents tank and not the available transfer capacity. Furthermore, the information regarding the fact that the tank was full was not transmitted to the operator when he came on duty, nor noted on the waste solvent transfer log; no written instructions concerning the workshop's transfer procedures to the storage tanks were available. This type of transfer lies entirely on the personnel; there is no overfill protection system on the tank and the level indicator does not have an alarm or report reporting capability. Several measurements are taken to prevent an incident of this type from happening again: implementation of a register of the contents of the tank near the transfer station, a warning panel indicating that the connection and the volume to be transferred must be checked, instructions drawn up regarding tank management procedures defining the responsibilities of the various persons involved, improvement of personnel training, and the implementation of overfill protection devices on the waste solvent storage facilities...

Accidental release of liquid and gaseous hydrocarbons at Châteauneuf-les-Martigues

ARIA 30406 - 08/07/2005 - 13 - CHATEAUNEUF-LES-MARTIGUES

23.2 – Manufacture of refined petroleum products



In a refinery, 10 to 20 t of gaseous and liquid hydrocarbons were released in 5 minutes starting at 4.46 pm by 3 of the 5 valves of the atmospheric distillation unit during restart operations.

At 6 pm, the firemen notified the Classified Installations Inspectorate which observed a deviation from the prefectoral order governing the site: The valves were not connected to the site's flare-stack network.

The accident was caused by a series of errors relative to the restart procedures and in the transmission of information between and within the shift crews: column normally full, numerous alarms ignored... underscoring violations and organisational deficiencies.

Partly owing to the strong mistral winds, part of the release fell on the vegetation, homes and the beach of the neighbouring community of Sausset-les-Pins; the traces left allowed the zone to be evaluated at 1 km wide by 8 km long. The 70 children at a holiday camp were restricted indoors, and 7 were examined by doctors. One person was effected by the product and subsequently hospitalised.

The Prefecture requested that samples and analyses be conducted on the fallout. The municipal authorities informed the population concerned by the fallout. The regional management of the group operating the refinery received 661 claims: 320 people were mobilised to clean 132 swimming pools, 563 homes and 726 vehicles. The consequences of this accident could have been much more serious if the cloud had ignited on one of the site's 2 flare-stacks or if the liquid part had fallen on the distillation unit.

The operator analysed the accident and the initial measures were taken: installation of a pressure sensor on the tower head to shut down the furnaces in case a high pressure threshold is met, shut-down of heating and closure of furnace supply line valves (shutting down the tower supply line) the pressure drop threshold in the column is exceeded (upper threshold difference between the pressure at the base and at the head of the tower). Costs of cleaning and compensations raised 1.7 million euros.

Due to the numerous complaints, Police Court fined the operator 10,250 € on June 8th.

Photo DR

"Overfilling" of continuously operating units

On March 23, 2005 at 1.20 pm, a violent explosion rocked a gasoline isomerisation unit when refinery staff attempted to restart it. The facility was the 3rd largest refinery in the United States, located in Texas City, Texas (No. 28598). A flammable cloud formed when approximately 28 m^3 of flammable liquid was released into the environment in less than 2 minutes. The liquid was overheated by the pipe of older design and not secured by a purge tank. The tank was supplied by the main pipe of a 50 m tall raffinate separation tower. The liquid inside the tower had reached a height of 42 m, roughly 20 times the normal level. The cloud was most likely ignited by an idling truck parked nearby. The ensuing blast killed 15 people and injured 180 others, causing extensive property damage. Beyond the presence of outdated equipment, the inquiry brought to light obsolete procedures leading the personnel to rely on their own procedures, faulty monitoring equipment and alarms, paving the way for a series of incorrect evaluations and errors committed by poorly-trained and weary operators on a site where the overall level of safety was tarnished by insufficient investments.

Two months later, in the French refinery at Grandpuits-Bailly-Carrois (No. 29903), rapid intervention by the internal emergency services was instrumental in containing a fire at the base of a gasoline stabliser after a faulty measurement resulted in it being overfilled and spillage of gasoline from the main valve on the wall of the tower and its ignition by a hot spot.

The accident on the atmospheric distillation tower at the Châteauneuf-Les-Martigues refinery (August 2005) has several points in common with the dramatic Texas City scenario six months earlier, although with less bodily harm. It appears that these three accidents occurred during the restart phase, and that the organisational deficiencies and human errors did not trigger alarms or other devices stopping the mechanism.

The context was nearly identical when a fire broke out in April 2002 on a vacuum distillation unit at a refinery in Feyzin (No. 22404), fortunately without significant human, environmental or economic consequences owing to the rapid action taken by the site's internal emergency services.

Other activities are also concerned by the equipment overfilling problem involving risks created by the potential hazards of the products involved or the configuration of the installations. Inappropriate equipment, insufficient instrumentation, restart operations and particularly the poor management of modifications and maintenance. The insufficiency or disregard for procedures can also be considered the main ingredients leading to the overfilling of a reactor or system and the subsequent cause of several accidents in the chemical or pharmaceutical industry. In Chalon-sur-Saône, a constant-delivery pump used for two different applications led to overfilling and spillage of phosphorous trichloride from a reactor being restarted, resulting in the intoxication of 19 people located essentially outside the site the effects up to 1,500 m. (No. 2900). A series of excessive sequential filling operations of several tanks on a production line being restarted caused the flare stack to release burning/liquid sulfur, burning 3 platform employees at Saint-Clair-sur-Rhône (No. 25247, No. 25248).

Other accidents taken from the ARIA database clearly illustrate this problem in other industrial sectors, all with fairly similar causes: an ammonia leak resulting from the disregard of a procedure during the restart of a cracking unit in a steel plant (No. 18135).

These accidents demonstrate that the order of events cannot be left up to chance or fate and that transitory phases (start-up, shut-down,…) are delicate steps that require special precautions involving risk analysis, maintenance, operator or subcontractor information, the respect for procedures, the control and correction of deviations, …as well as management's involvement on a permanent basis. All of these factors play an integral part in the "safety management system".

The accidents for which the ARIA No. is not underlined can be consulted at

www.aria.ecologie.gouv.fr

ARIA 2900 - 10/15/1991 - SAONE ET LOIRE (71) - CHALON-SUR-SAONE

24.1E – Manufacture of other basic inorganic chemicals

At 7.10 am, 300 kg of phosphorus trichloride (PCl3) spilled over from a measuring tank during a loading operation and hydrolysed in the sewers of a chemical plant. The day before, 1,320 kg of 2-ethyl-hexanoic acid was introduced into a reactor.

On the day of the accident, an experienced operator added 466 kg (293 l) of PCl3 from metering unit D2, located above reactor R2 and connected to a pump on a storage tank (22 m³) located roughly 20 m from the workshop. This pump is used to transfer PCl3 to the workshop's production lines and unload the storage tanks. The operator checked the level (using a glass tube and mirror), stopped the pump then adjusted the flow of PCl3 (10 l/min.) into the reactor. He returned to the ground level of the workshop and prepared to drain reactor R1 when he was sprayed with PCl3. He noted a release of white fumes and activated the pump's emergency stop button upon exiting the building. Another employee ensured that the pump was stopped by removing the fuses from the control circuit. The flooding of the sewer system lead to the hydrolysis of PCl3 into HCl, H3PO4 and HPO3. The fog prevented dispersion of the toxic cloud that formed, which began drifting toward the city. Effects were observed 1,500 m from the release point. Nineteen individuals, including 2 employees were intoxicated. The accident occurred when part of the installations were restarted following a 4-month shutdown period. The operator attributed the accident to the untimely restart of the PCl3 transfer pump.

The inquiry revealed numerous installation design problems: excessive max. pump delivery (300 l/min.) in relation to the capacity of the metering unit (500 l) and the actual discharge flow rate (33 l/min.), poor workstation ergonomics (control cabinet not visible from the base of the installations...), the complexity of the control system (numerous timers installed which could present possible interactions), neutralisation of alarms, the disappearance long ago of the diaphragm limiting the metering unit's throughput, the presence of a 2nd diaphragm in the overflow line of this tank unnecessarily reducing its diameter from 80 to 20 mm (an installation error committed during maintenance). These modifications were not indicated on the drawings and the operators were unfamiliar with them. The untimely restart of the PCl3 pump appears to have caused the overfilling.

Manufacturing operation was abandoned.

ARIA 22404 - 04/26/2002 - RHONE (69) - FEYZIN

23.2Z – Manufacture of refined petroleum products

A fire broke out on the vacuum distillation unit in a refinery during its scheduled five-year shutdown. This unit essentially consists of a distillation tower loaded with the heavy fraction from the atmospheric distillation, and a gas-fired furnace on the upstream portion also able to burn incondensable materials from the tower head.

The unit had been restarted the day before following the acceptance of the work, while other job sites were still underway at the site. The reheating operation had begun during the night, and the unit was still in the power build-up phase. At around 9.15 am, thick black smoke was observed coming from the stack (fire in the furnace), with flames shooting from the open explosion vents. This situation was preceded by hammering in the pipes and rising pressure in the tower increase and the opening of valves: hydrocarbons began spilling outside. The accident was surrounded by site crews after performing the following operations: injection of steam into the furnace, injection of nitrogen into the tower, isolation of the units, application of foam around the base of the unit. No one was injured. The effects of the accident was limited to the release of dusts and hydrocarbons around the tower and on in a small portion of the neighbouring installation, the rupture of a steam pipe. The personnel from external companies (1,000) working on the site were evacuated, although activity was resumed rapidly.

Following the inquiry, it appears that erroneous level indicators caused the tower to be overfilled then the backflow of liquid into the furnace via the vacuum system (backflow of incondensable materials). A brief summary of the findings: the local levels were not visible, the chain associated with the control levels in the bottom of the tower had not been completely checked (card), and the configuration of the system and notably the extraction levels were not correct.

An emergency shutdown order was issued requiring the operator to submit a detailed report of the accident's causes prior to the restart of the installation. Following the examination of all elements submitted and an on-site inspection, the Classified Installations Inspectorate was no longer opposed to the resumption of operations (04/30/2002). The measures foreseen by the operator include: an operator dedicated to instrumentation on site on permanent basis, selection of a standard configuration for restart, followed by the material assessment, monitoring by an operator.

ARIA 25247 - 05/23/2003 - ISERE (38) - SAINT-CLAIR-DU-RHONE

24.1G - Manufacture of other basic organic chemicals

In a chemical plant, sulfur began burning from the flare-stack of a carbon sulfide unit (CS2) at 2.45 am. CS2 is obtained through a reaction of natural gas and sulfur at high temperature. The two CS2 production lines had been placed on hot stand-by between 8 pm and 9 pm; one owing to the shut-down of the site's methyl mercaptan workshop (M.S.H.), and the other following an incident a few hours earlier (sulfur fire, see No. 25246). The gas alarm was sounded. The unit's flood network brought the incident under control in just 10 minutes.

The external emergency services, alerted by the guards, remained on site while the internal contingency plan was in force from 3.30 am to 6.30 pm. The flare-stack remains "lit" by 3 methane-fed pilots and is backed up by a propane tank. The flare-stack is designed to burn off various residual gaseous effluents: excess hydrogen sulfide not consumed by the sulfuric unit's furnace, gas released from the line valves due to accidental overpressures and decompression gasses from the CS2 unit when opened, controlled by the line's emergency shut-down or by the general emergency shut-down, on/off safety valves of the reaction section. The accident occurred when the installations were not in operation, and resulted from the progressive and sequential filling of the various tanks of the CS2 unit caused by the opening of valves and the continued supply of new sulfur via the recycled sulfur line (a pump had remained in operation, valves open; the closure of these valves is not required during hot stand-by of the CS2 production lines, and a non-hermetic valve on the sulfur recycling line...). The damaged electric wiring of the heating system and the control circuits controlling the flare-stack's gas flow rate were repaired.

Another incident happened on this same unit just a few hours later (see No. 25248). The operator undertook the following measures: refurbishing of the valve and its systematic overhaul during programmed shut-downs every 24 months, modification of the automatic control systems of certain valves (positions, level slaving) or ensuring the overall shutdown of the installations, protection that is both reinforced and allows for better maintenance of the critical parts of wire troughs around furnaces...

ARIA 25248 - 05/23/2003 - ISERE (38) - SAINT-CLAIR-DU-RHONE

24.1G - Manufacture of other basic organic chemicals

Upon the restart of a carbon sulfide unit (CS2) at 7.50 am, following 2 incidents a few hours earlier (a sulfur (S) fire and burning S projections: see Nos. 25246 & 25247), liquid S spurting from an extinguished flare-torch rained down and slightly burned 3 employees inspecting the instrumentation and the electrical connections. A recurring malfunction was preventing the unit from operating correctly.

The internal firefighters were able to bring an outbreak of fire under control. The external emergency services, alerted by security during the first incident, remained on site while the internal contingency plan was in force from 3.30 am to 6.30 pm. The flare-stack burns the gaseous effluents from the unit that are collected in a specific network: valve exhaust, flare-stack valves... Knowing that the emergency stop had been actuated, the instrument specialists thought that the unit was secured. In compliance with the procedures, although unaware of the 3 contractors present, the operators in the control room injected nitrogen to maintain the unit under pressure and to avoid an influx of air, a potential source of explosion.

The accident resulted from a series of progressive cascade filling operations among the unit's various tanks in order to ensure the continuous supply of 'new' S via a 'recycled' S line; the nitrogen then accidentally pushed out the liquid S present in the flare-stack and its buffer tank following the previous incidents. The supply of S of one of the CS2 production lines had been modified in October 2002, which subsequently caused the reactor to become clogged on several occasions (solidification of the liquid S). An emergency stop requires that the installations be shut down and secured while the causes, consequences and measures to be taken to avoid any subsequent accident are analysed, including the removal of any wastes generated (drainage of a liquid S reservoir that is notably difficult to access in the structure). Several failures were established: stoppage of the recycling pump, valves had remained open as the procedure did not foresee closure in the event both lines shut down, valve not sealed.

Measures were taken: improvement of S injection enabling the temperature to be maintained, the addition of PLC and safety devices, reinforced protection of cable trays, procedures and instructions to limit fouling of CS2 lines (carbon associated with the cracking of natural gas...), and regular follow-up of sensitive equipment and monitoring of subcontractors (maintenance...).

ARIA 29598 - 03/23/2005 - UNITED STATES - TEXAS CITY, TEXAS

23.2Z – Manufacture of refined petroleum products

At 1.20 pm, a violent explosion rocked a gasoline isomerisation unit at the nation's 3rd largest refinery (460,000 barrels/day – 2,000 employees). Having been shut down for maintenance on 02/21, the separator was being restarted 03/22 at 2 am. The operators began filling the raffinate splitter with highly flammable hydrocarbons. During normal operation, the liquid level at the base of the tower is roughly 2 m. The level indicator, with remote reporting in the control room, is designed to measure a maximum level of 3 m. Beyond this, the control room operator has no way of knowing the actual height of the product. The first alarm signalled a high-level threshold, while a second fail-safe alarm was not triggered. The loading operation was stopped at 3.30 am, when the actual level was at 4 m. At around 9.50 am, the operators began circulating the liquid by adding liquid in the already full tower. The furnace burners were ignited at 10 am while the height in the tower was 20 times greater than the normal level (42 m) and the indicator in the control room was displaying a level of 3 m. At 12.40 pm, a high-pressure alarm was triggered and 2 burners were shut down. As the pressure control valve used in the procedure was not operative, an operator opened a manual valve to release the gas into a purge tank. At around 1 pm, the operators opened a valve at the base of the tower and drained the liquids into the storage tanks. These very hot liquids, however, passed via an exchanger heating the load that was supplying the tower, the temperature of which exceeded 150 ℃; the liquid contained was at its boiling temperature, and its expansion increased the level in the tower even more and spilled over into the vertical pipes, exerting a large amount of pressure on the 3 valves located 50 m below. The valves opened at 1.14 pm; the liquid flowed toward the purge tank at the other end of the unit. As the high level alarm was faulty, it was filled up and 28 m^3 of liquid was ejected via the pipe for 2 minutes. A flammable cloud formed and was ignited at 1.20 pm by an idling truck engine located 8 m from the purge tank, igniting several explosions and fires. The blast was felt 8 km away. The flames reached shot up 20 m high and the smoke was visible several kilometres away. The operators installed detectors and the population remained confined indoors for 2 hours. Firefighters were able to bring the fire under control in 2 hours. The blast killed fifteen contractors attending a meeting in trailers located 140 m away and injured 180 others. Property damage was extensive in the unit and storage area where nearby buildings and more than 50 tanks were damaged. The inquiry brought to light the presence of outdated equipment, the malfunction of safety equipment, the lack of or insufficient procedures, errors committed by poorly trained and weary operators on a site where the overall level of safety was tarnished by insufficient investments.

ARIA 29903 - 05/26/2005 - SEINE ET MARNE (77) - GRANDPUITS-BAILLY-CARROIS

23.2Z – Manufacture of refined petroleum products

A fire broke out on an atmospheric distillation unit in a refinery. The fire was started when a leak caught fire on the outlet of a safety valve installed on a gasoline stabiliser (debutaniser). This stabiliser unit is designed to separate gasoline / gases. The internal contingency plan was put into action at 6.56 pm.

The refinery's firefighting resources were mobilised 7.49 pm to combat the fire. The public firefighters called did not have to intervene. The south-easterly wind dissipated the cloud of fumes. The firefighting water was directed to the refinery's internal water treatment facility. The unit was shut down according to the emergency procedures. Property damage was limited; the heat lagging on the atmospheric distillation tower was damaged and electric wiring was burned. Repair work was conducted in compliance with API 579: particularly, the valve on the stabilisation tower was changed, and the valves on the atmospheric distillation tower were removed and inspected.

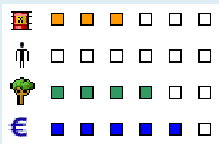
The atmospheric distillation unit had been restarted a few days earlier. Operation had not completely stabilised. A few hours prior to the incident, the console operators and the technicians encountered operating difficulties with the vacuum distillation pump. The stabliser has a reboiler at the base by an exchanger on which the tower's bottom level control is installed. Starting at 3.30 pm, a shift appeared on the corresponding measurement causing the progressive then complete closure of the bottom valve and thus the tower to fill with gasoline. A gasoline and gas mixture then flowed from the main valve, trickled down and ignited on a hot point at the base of the tower. The flames climbed up to the smoke vent, creating a flame above the main atmospheric distillation tower. The pressure sensor was slaved to allow heating to be stopped and avoid a lack of condensation at the installation head, which is a common cause of excess pressure.

The incident shed light on the need for new control of the sensor on the tower by-pass in order to ensure adequate safety regarding the risks associated with overfilling of the tower.

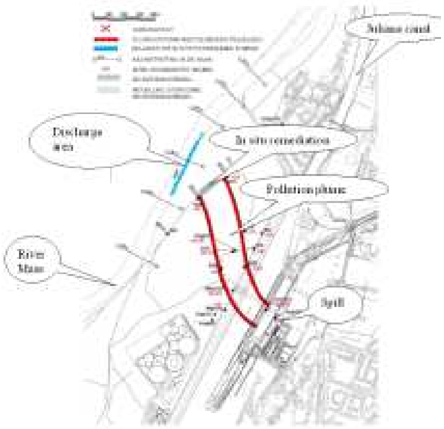
3,000 m³ leak of MTBE in Stein

ARIA 32818 - 05/01/2005 - NETHERLANDS - STEIN

24.1G - Manufacture of other basic organic chemicals



A broken pipe on a harbour-based petrochemical site released 3,000 m³ (2,100 t) of methyl-tertio-butyl-ether (MTBE) causing substantial soil and water pollution. The nearby Meuse River was also concerned; its water is pumped for human consumption and operations had to be shut down. A major clean-up installation was installed following the spillage.



Releases of dangerous liquids

The consequences of a major spillage of liquid chemical or polluting substances may not only be limited to **soil, surface or underground water pollution** as was the case in Baia-Mare (Romania) with the release of 287,500 m^3 of cyanide-charged effluents (No. 17265). According to the type of the substance involved and notably is volatility, **atmospheric pollution** can also occur, sometimes accompanied by a **toxic** (No. 717, *7,000 t of ammoniac released when a cyrogenic storage tank ruptured in Jonova (Lithuania), generating a toxic cloud visible at distances beyond 23 km*), **ignition** (No. 168) or **explosion risk** (No. 2257 *– a leak lasting more than 5 years on an underground hydrocarbon pipe eventually generated flammable vapours in the pipe trenches in the town of Petit-Couronne. The subsequent explosion destroyed a home located more than 2 km from the leak*).
In addition, installations in the immediate vicinity can be damaged by the hydraulic pressure created by the release, or by a weakening of their foundations. Such was the case in Sweden, where the rupture of a large pressurised water pipe caused the soil to subside, destroying an acid storage facility (No. 29133).

Most often, these releases (Nos. 30469, 32113) originate from storage or transfer equipment (loading/unloading pipes or installation), although they can also occur on production units, notably on the wastewater or rainwater networks (No. 27923). The strategy employed to counter this risk has to be intelligently adapted to the installation concerned and its accessibility (storage facilities, piping, both overhead and underground…)

The proper **equipment resources** can effectively prevent this type of accident from occurring. These resources include retention catchpits, provided that they are correctly dimensioned, solidly designed to resists the force of a wave, correctly equipped (level detection, for example) and, of course, hermetic (No. 32113 – *Diesel fuel released in a non-hermetic catchpit leads to pollution of the water table*). **Organisational and human systems** are also key elements in securing these installations:

- Competent, trained personnel must be aware of the risks associated with the products being handled. This is a primary step in **accident prevention**. In 1976, in Pierre-Bénite (Rhone-69), a poorly-informed operator, unaware of proper the maintenance/servicing instructions or the seriousness of what a major release of acrolein would do to the natural environment, drained a full rail car (20 t) into the Rhone River, polluting it over more than 90 km (No. 4999). In Nogaro (Gers-32), in 1996, the unsupervised transfer of wine between 2 storage tanks at a wine cooperative resulted in the spillage of more than 5,000 hl into the natural environment, polluting 4 creaks or rivers and killing more than 7 tons of fish (No. 8695).
- **Early detection** of a leak is essential in limiting the consequences. Even a small leak can lead to a major accident if the proper compensatory measures are not implemented rapidly (No. 2257). In 2002, in Chalampé (Haur Rhin-68), the belated detection of a pipe rupture (40 mm) resulted in the release of more than 850 t of cyclohexane into the soil and water table. The total cost of the accident was estimated at 2 M€ (No. 23839). The case of buried pipelines or installations with difficult access involve specific monitoring and prevention devices (level and pressure sensors, detectors on the unit, in the environment, piezometric monitoring…), and especially the respect of overall **monitoring procedures** (periodic measurements, visual inspections), monitoring of installation protection devices (coating or paint, cathodic protection), **inspection** of the condition of these installations (local corrosion, thickness, endoscopy, periodic testing…) and parameters representative of leaks (flow rate verifications, pressures, transfer compatibilities…) or their environmental consequences in order to ensure timely identification of events that could possibly lead to an accident (No. 30469, 6153) and to efficiently intervene with means that have been carefully studied and adapted to the situation.
- In order to do this effectively, **intervention procedures** must be defined and regularly applied so that the durations of leaks are kept as short as possible. Intervention in an emergency situation, particularly when toxic products are involved – either directly, or through hydrolysis – often takes longer than foreseen in theory (No. 25775, 6135).

Accidents involving the release of dangerous products can have serious consequences on the safety of individuals and property, and especially for the environment. In a certain number of cases, the direct economic consequences or resulting from the implementation of rehabilitation measures are particularly extensive. Also, the required amount of care given the corresponding risk analyses and management measurements, must take the potential dangers in the installations into account and be proportional to the various types of possible consequences.

The detailed report of the Jonova accident (No. 717),
the detailed report of the Baia-Mare pollution (No. 17265),
the detailed report of the Pierre-Bénite accident (No. 4999),
the detailed report of the Chalampé accident (No. 23839),
an analysis of the accidentology associated with retaining catchpits,
and the accidents for which the ARIA No. is not underlined can be consulted at
www.aria.ecologie.gouv.fr

ARIA 4999 - 07/10/1976 – Rhone (69) - PIERRE-BENITE

24.1G - Manufacture of other basic organic chemicals

20 t of acrolein was released into the Rhone River. The manufacturing unit was undergoing its annual shutdown at the time and the neutralisation ponds (2 x 250 m³) were under repair. For the last four months, the tank cleaning water had been directed into a 15 m³ neutralisation channel and released into the Rhone without control. During a rinsing operation, an operator accidentally emptied an full railcar (No. poorly transcribed). The employee noticed the anomaly an hour later, and unsuccessfully attempted to contact his supervisor by telephone. Unaware of the operating instructions and the possible consequences, he allowed the drainage operation to continue. The plant's management was informed only 36 hours after the accident. For a period of 8 days, 367 t of dead fish were collected along the river over 90 km (5 departments). A safety program was set up to prevent swimming along the river, to monitor the reservoirs and wells fed by the Rhone and the drinking water distribution system.

This pollution, as well as other accidents, was one of the 1st safety studies conducted in France.

ARIA 2257 - 08/04/1990 - SEINE MARITIME (76) - PETIT-COURONNE

23.2Z – Manufacture of refined petroleum products

Since at least 1985 there had been leak on a corroded underground pipe conveying unleaded premium gasoline between a storage tank and a petroleum pier. This leak polluted underground water and eventually a DWS (drinking water supply) reservoir had to be abandoned. Gaseous fumes, however, propagated via the cities technical ducts and eventually caused a home to explode 2 km away, most certainly ignited when the hot-water heater tripped on.

Twenty days later, a hole measuring just a few square millimetres was found on the corroded piping. More than 15,000 m³ of hydrocarbons had been lost and more than 13,000 m³ had been pumped into the water table. The operator compensated the homeowners by purchasing their home, and paid compensation to the water distributor and local community. The total cost of the work involved exceeded 50 MF.

ARIA 8695 - 04/22/1996 - GERS (32) - NOGARO

15.9G - Wine-making

Wine was being transferred between two tanks in a wine cooperative. The operation was supposed to be completed the following day. The worker left at 9 pm and left the transfer operation continue unsupervised. On 04/23 at 6 am, a pipe was found uncoupled from the discharge pump; 5,680 hl of white wine (an estimated loss of 2 MF) spilled into the Jurane (Gers-32), Izaute (Gers-32), Midour (Gers-32 & Landes-40) and Midouze (Landes-40) Rivers.

The quality of the water lowered (dissolved O2, pH, NH4+). Dead fish were observed in the Izaute on 04/23 and, on 04/26, a significant quantity of dead fish were also observed there and in the Midour. An estimated 7 to 9 tons of fish of all species were killed along 80 km of river.

ARIA 17265 - 01/30/2000 - ROMANIA - BAIA MARE

13.2Z - Mining of non-ferrous metal ores

A dike of a mine tailings settling pond ruptured after a 25-meter breach had formed. 287,500 m³ of effluent containing cyanides (115 t) and heavy metals (Cu, Zn) were released, contaminating 14 ha and polluting the Sasar River.

A 'wave of cyanide' measuring 40 km long surged along the Lapus, the Szamos, the Tisza and the Danube rivers. The concentration of cyanide reached 50 mg/l in the Lapus, 2 mg/l in the Yugoslavian portion of the Tisza (02/12) and 0.05 mg/l in the Danube Delta, 2,000 km downstream from Baia Mare (02/18). Romania, Hungary, Yugoslavia, Bulgaria and Ukraine were involved. High cyanide contents were measured in wells of private citizens and several individuals were sickened after drinking the water. The consumption of water and fishing activities were prohibited. Fauna and flora were destroyed over hundreds of kilometres: 1,241 tons of dead fish were recovered in Hungary alone and millions of animal corpses were found (swans, wild ducks, otters, foxes…).

As they were rapidly informed, the authorities of the countries located downstream were able to implement efficient counter-measures: release of dams, drinking water reservoir operators were alerted... Environmental rehabilitation measures were estimated at more than 4 MF. Faulty dam design (excessive proportions of fine materials), poor meteorological conditions (high precipitations and melting snow caused the water level to rise in the pond and wetting of dike components which weakened it) and organisational failures (a lack of effluent transfer operations) lead to the accident. The causes of the extensive mortality among fish have not been clearly established; an excessive quantity of javel water may have been used to neutralise the cyanide. Following the accident, the operator built a treatment station for the cyanide-charged effluent and a 250,000 m³ buffer pond designed to receive overflow from the settling pond prior to neutralisation and release into the natural environment. The Baia Mare and Aznalcollar accidents (ARIA No. 12831) resulted in reinforcement of the European legislation relative to the management of mining wastes. Significant leaks had already been observed on the dike in the 2 months prior to the accident. The spilled effluents had killed 5 cows.

ARIA 23839 - 12/17/2002 - HAUT RHIN (68) - CHALAMPE

24.1G - Manufacture of other basic organic chemicals

During efforts the previous day to locate the source of a pressure drop on the cyclohexane supply line of an olone production facility, a leak of this substance was discovered at a chemical site. The substance, used in large quantities, is of relatively low toxicity, although it a pollutant and flammable.

Stored in a 10,000 m³ reservoir, the cyclohexane is supplied to the olone and adipontrile (ADN) facilities by a partly common pipeline. Maintained at the proper temperature by a steam system, the cyclohexane is transferred at 20°C and at 2 to 3 bar through lagged overhead or buried piping. With an output ratio of 266:1, 2 pipes, 100 and 40 mm, provide a continuous supply to the olone shop and a discontinuous supply to the ADN shop.

The leak occurred from the rupture of the ADN shop's 40 mm pipe due, according to the operator, to the dilation of liquid cyclohexane in the overhead part of the pipe between two blockages of crystallized cyclohexane. A malfunction of the pipe heating device ($T < 6.5°C$) led to the formation of blockages, with the cyclohexane then reliquifying primarily in the section the most exposed to the outside heating. As the piping was not yet equipped with a device for rapid leak detection, it took 30 hours to determine the cause of the pressure anomaly. The operator initially estimated the leak at just a few m³ of cyclohexane, then between 850 and 1,200 t in the following weeks, the vast majority had migrated into the ground. A few days later, core samples taken at a depth of 13 m (the depth of the water table) showed the presence of a layer of cyclohexane localized near the site of the leak; lowering of the water table by one of the wells of the site's hydraulic security barrier would have limited the spread of the pollution. Analyses of the water table off site showed no trace of cyclohexene above the drinkability threshold.

On July 2, 2003, 420 t of cyclohexane were pumped from the water table and 16 t extracted from the ground through venting techniques... In July 2004, 590 t of cyclohexane had been recovered, although cleanup operations had slowed considerably since the first of the year, with the quantities of cyclohexane recovered stabilising around ten tonnes per month. Consequently, a Prefectoral order was issued July 28, 2004 to request that risk analysis be conducted within the scope of a remedial plan.

ARIA 25775 - 10/14/2003 - GARD (30) - SALINDRES

24.1G - Manufacture of other basic organic chemicals

A hose broke while a tanker truck containing trichloromethylbenzene (TCMB or phenylchloroforme) under nitrogen pressure (2 to 3 bar) was being unloaded at a chemical plant. The TCMB began producing hydrogen chloride fumes upon contact with the humidity in the air which prevented the operators from intervening rapidly. Of the 24 t of chemical product spilled in the unloading zone in 15 min., 16 tons were recovered in the catchpit and 8 tons impregnated an 200 m² earthen zone in the surrounding area. Part of the product was able to be recovered using absorbent products. The accident, caused by a broken coupling on the container at the flange junction, was aggravated by the excessive reaction time and the disconnection of the nitrogen pressure. The Inspectorate requested the operator to submit a report on the origins and causes of the phenomenon, is consequences and the measures needed to remedy the situation. The polluted excavated soil and the absorbent cleanup products had to be specifically treated.

ARIA 29133 - 02/04/2005 - SWEDEN - HELSINGBORG

24.1E – Manufacture of other basic inorganic chemicals

A sulfuric acid tank with a capacity of 20,000 t exploded in a chemical plant, releasing 11,000 t of H2SO4. The acid spilled into the neighbouring port and formed a toxic cloud upon contact with the water.

A safety perimeter cover the entire city was set up and the 110,000 inhabitants were instructed to stay indoors. The confinement order was maintained for 4 hours. The accident injured 13 people (including 6 employees, 2 rescue workers and 5 members of the public) ranging from slight respiratory difficulties to eye irritation. The wind, blowing towards the sea and not in the direction of the city, was instrumental in quickly dispersing the cloud.

A ruptured water pipe had apparently flooded the ground supporting the acid storage tank involved in the accident. The ground was rendered unstable causing the tank to rupture.

ARIA 30469 - 08/04/2005 - RHONE (69) - COLOMBIER-SAUGNIEU

51.1C – Agents involved in the sale of fuels, ores, metals and industrial chemicals

Since late April, the operator of an aviation fuel storage and distribution company had noticed significant irregularities between his physical stocks and the associated accounting. The employees initially checked the volumetric meters on the trucks, then the gauges of the storage tanks and finally the temperature sensors on the supplier's premises; the sensors were found to be faulty and were repaired.

Following a search, a leak was located in late June on 60 m length of steel pipe, line No.5, covered by a layer of asphalt and buried at a depth of 1.30 m. Further investigations allowed several leaks to be found at the distribution station. An estimated 270 m³ of JET A1 fuel had been lost. Line No. 5 was shut down.

A specialised company performed several core sampling operations at the site, particularly near this pipe. Samples taken at a depth of approximately 2.50 m did not indicate the presence of hydrocarbons. A second company was contacted to take samples at much greater depths. Part of the equipment excavated during the drilling operations exhibited a strong hydrocarbon smell, indicating the presence of fuel starting at depth of around 3 m. Underground water samples taken using a piezometer confirmed that the fuel had reached the water table at roughly 40 m below the ground. A skimming unit was installed near the most polluted zone to pump the supernatant phase of the hydrocarbons from the water table. Ground ventilation equipment was installed to facilitate degradation of the substance, the biodegradability of which has been confirmed.

ARIA 32113 - 08/20/2006 - RHONE (69) - VENISSIEUX

60.1Z - Transport via railways

Between 142 and 340 m³ of diesel fuel were spilled in a railway yard when a flexible coupling ruptured. Part of the hydrocarbons (HC) polluted the wastewater system and a water table, and menaced a treatment facility and a canal of the Rhone River. The coupling had been installed in June during an installation involving the replacement of a section of pipe connecting a 200 m³ buffer tank to the locomotive fuel distribution station. The installation is supplied by a 1,000 m³ tank whose catchpit is interconnected with the buffer tank's catchpit via an older section of piping that had not been dismantled or plugged.

The accident took place on a Sunday. An operator the presence of diesel fuel at around 8 am in the large catchpit and alerted the agent on duty who closed the storage valves at 9.30 am. As the catchpits were not equipped with alarm-type level sensors, the tank continued to automatically supply the buffer tank while it was emptying into the large catchpit. The gravel bottom of the catchpit was not hermetic. The HCs flowed through the trench to the decantation tank associated with the distribution station. The executive on duty noted that the decantation tank had reached saturation at noon and alerted the rescue services at 1.10 pm. An employee plugged the trench connecting the settling tank to the rainwater network at 1.30 pm. At the same time, part of the polluted wastewater system was isolated and the effluents to be treated were deviated to a specific catch tank. Upstream, the firemen set up a preventive dam on the Rhone outlet canal into which the treatment station releases its effluents, requiring river traffic to be stopped until the next day at 10 am; no notable impact was reported on the river. The DRIRE was informed of the accident on Sunday at 3.30 pm and the *Prefecture* initiated the Operational Defence Cell. The spillage also infiltrated below the catchpit and polluted the water table, where 1 m of HC was noted at 7 pm.

The use of industrial well water or private wells for sanitary purposes was strongly discouraged. An emergency shutdown order required the operator to clean up the pollution (pumping of the HC in the networks, cleanup of the water table and piezometric monitoring, soil treatment...) and to secure the site (including the drainage of 2 tanks, expert evaluation of the installations prior to restart, installation of HC alarms in the catchpits, networks and settling tanks...). On October 10, 2006, 61.2 m³ of hydrocarbons were pumped from the water table and 446 t of products were destroyed by the operator.

Dust explosion and fore at Corbenay (Haute Saone - 70)

ARIA 28990 - 01/20/2005 - HAUTE SAONE (70) - CORBENAY

20.2Z - Wood veneers and panels

An explosion occurred at 2.58 am in a wood panel manufacturing plant in a dry wood chip refiner used in the chip sorting and preparation sector. This unit dries, refines and sorts chips (cyclofilter, sifting screen) to supply two 360 m³ silos (A and B). The explosion in the refiner generated a blast that ripped open the cyclofilter, which was protected by vents, and spread to the silos which were also equipped with vents. The explosion was followed by a fire that spread to the associated installations: redler conveyors, vacuum systems, sorters, the refiner silo (28 m³), and silos A and B (about 1/3 full).

Immediately following the accident, the spark detection system began injecting water permanently. The silo sprinkling system was triggered by a manual valve and the drier was secured by the shut down of the burners and chip flow. An alarm indication in the control room allowed the site's firemen to intervene in 10 minutes and also contacted the public fire department. The emergency crews cooled down the silos and the sorters with 5 fire nozzles, checked all of the equipment using a thermal imaging camera and unloaded the silos while being covered with 4 fire nozzles (including 1 on a turnable ladder). As the site's fire supply had run out, equipment was set up to draw water from a natural water supply.

The firefighting water was recovered in a catchpit, then analysed and treated. The chips burned in the fire were disposed of in the plant's boiler but property damage (refiner, cyclofilter, sifting screen, vents, and the refiner's suction system) was estimated at 250K euros and the shutdown of the production line for 36 hours resulted in 750K euros in production losses.

The site's accident procedure manual proved efficient. According to the accident report, a metal part in the refiner had broken, causing sparks which caused the refiner to explode. The operator foresees to uncouple the refiner from the rest of the installations; a third-party expert evaluation of the installations, safety systems and intervention procedures; a thermal imaging camera to check the installations before, during and after an accident and an increase in the surface area of the cyclofilter vents (although already in compliance with current standards). Just five days following this accident, a smouldering fire caused a new fire in silo A.

ARIA 29011 - 25/01/2005 - Haute Saone (70) - CORBENAY

20.2Z - Wood veneers and panels

At 6.10 am, a wood dust explosion rocked a panel manufacturing plant in a 360 m³ silo containing 30 m³ of dry chips (silo A). The accident occurred while the reservoir was being emptied, just 5 days after an earlier fire at the site (ARIA No. 28990). The silo involved in this accident is adjacent to a second dry chip silo (silo B) having a capacity of 360 m³.

The production crew and the site's firemen initiated the manual water injection systems inside and around silos A and B and inside the redler conveyors that supply silo A. The 30 external firemen, called to assist in the firefighting operations, set up a fire nozzle on silo A at 6.24 am. The cooling operation initiated a 2nd explosion (fumes, water gas, dust in suspension?).

The incident opened the silo's vents and projected dust and flames onto the adjacent production building. The fire spread via the electric wires before it was contained by the building's sprinkler system and extinguished by the emergency services. A thermal imaging camera was used to check for residual hot spots in the silo and emptied silo B, which had caught fire 5 days earlier, in order to perform the same tests. A site fireman monitored the installations until noon the following day. The firefighting water was recovered in a catchpit, then analysed and treated. The shutdown of the production line for 14 hours resulted in production losses estimated at 45K euros.

The silos vents had to be replaced and the production building's electrical installations repaired. According to the accident report, smouldering fires had remained after the fire of January 20th under the extraction unit, a 2-ton piece of bell-shaped equipment at the base of the silo. During this fire, the reservoir had been emptied, flushed and cleaned but this piece of equipment had not been raised. The operator initiated a third party expert evaluation of the installations, safety systems and intervention procedures, and the use of a thermal imaging camera to check the installations before, during and after an accident. Further more, the operator also modified the intervention and silo restart procedures; in the event hot spots (embers) are detected, the extraction unit will be raised for cleaning.

Oxidation-reduction, "water gas"…

Two accidents in a wood panel manufacturing facility are a stark reminder of the fire and explosion hazards generated by wood particles present in certain industrial activities and illustrate how explosions can result from smouldering fires and incomplete combustion.

Numerous events included in the ARIA database involve grinders, digesters, driers, dust and chip suction systems, dust control systems… and storage silos. While the consequences most frequently involve property damage, production losses and partial unemployment, certain accidents have resulted in serious consequences for the employees and rescue personnel, notably when explosions occur. In Allouville Bellefosse (No. 27074), an employee was killed an another seriously burned when suspended wood dust exploded when a fire extinguisher was used to put down an outbreak of fire in a chipboard press; in the United States (No. 26575), an employee died in an explosion after a fire started in a drier; in the United Kingdom (No. 22969), an employee was seriously injured when a dust filter exploded.

The installation of adapted pressure reducing vents on equipment has limited property damage in certain accidents (Nos. 928, 15635).

Accident causal analysis has shown that while equipment failures cause heating (Nos. 27911, 14634) and sparks (No. 21552) that eventually lead to accidents, organisational factors play a large part in initiating and aggravating these events. Electrical installations that are not designed for dusty environments (No. 11770), insufficient maintenance of spark detectors (No. 928), inappropriate or insufficient cleaning of installations (Nos. 20368, 25511), internal temperature monitoring fault on a chip storage installation that self-ignited (No. 25978), and no written procedures or personnel training (No. 27074), illustrate this recurring problem.

Construction phases, as in other industrial activities, also induce situations in which accidents are facilitated during the use of equipment that generate heat such as torches (Nos. 15008, 20383), grinding or cutting equipment or caused by defective construction work creating equipment malfunctions (No. 23325).
Construction operations generate specific risks that must be analysed and taken into consideration. A "risk analysis" in keeping with the situation is thus an indispensable preliminary step in all interventions, regardless of its extent (No. 25176). This analysis must be accompanied by written rules to be respected in the form of safety instructions and information for the personnel. The preparation of the work site, particularly including the removal of wood particles from the work zone, is also an important step that must be taken very seriously particularly if hot spots are involved (No. 15008). The monitoring and acceptance of works to ensure proper execution are also indispensable in reducing risks (No. 20383).

During emergency intervention, cases of accidents provoked by initial accidents have been recorded. In Rambervillers (No. 20383) an employee was killed by an explosion CO caused by a smouldering fire; in the United States (No. 20579) the opening of a chip silo created an influx of O_2 which resulted in an explosion which seriously burned a fireman… These events are a reminder that all hazards must be evaluated, including caused by firefighting operations.

Smouldering organic material present special explosion hazards (No. 20383) owing to:

- fine dust particles placed in suspension by the release of gases and smoke,
- the formation of CO through the incomplete combustion of confined materials or by the oxidation-reduction resulting from the humidity in these materials or the possible influx of water.

"Water gas" can also form with mineral materials heated to high temperature as during the combustion of spoil heaps in Alès in 2004 (No. 27877).

Comparable oxidation-reduction phenomena are well-known in the iron industry and can lead to explosions of flammable gases as a result of untimely contact with water / molten metal as is suspected in Dompierre-sur-Besbre (No. 23968) and Florange (No. 15083). Several chemical and physical mechanisms are involved at high temperature:

1) Metal reducing agent + H2O → Oxidised metal + H2
Then H2 + ½ 02 → H2O (Explosion resulting from combustion with the oxygen in the air)

2) C + H2O → CO + H2 (water gas)
The CO + H2 + O2 → CO2 + H2O (explosion resulting from combustion with the oxygen in the air)

3) liquid H2O → steam H2O (volumic expansion caused by the change in physical state).

Operators are not always aware with the oxidation-reduction and incomplete combustion phenomena that are likely to generate explosions. These hazards merit careful evaluation so that appropriate prevention and intervention measures can be implemented.

The accidents for which the ARIA No. is not underlined can be consulted at
www.aria.ecologie.gouv.fr.

ARIA 928 - 11/05/1989 - LOIRET (45) - SULLY-SUR-LOIRE
20.2Z - Wood veneers and panels
A wood dust explosion occurred in the silo located between the chip drier and the vibrating tables. The spark detectors on the transport containers both upstream and downstream from the silo did not operate. These containers were ripped open by the explosion. The injection of water and the reversal of the transporter's direction did not occur. The silo's explosion vents were instrumental in protecting it, although property damage and operating losses were estimated at 10 MF.

ARIA 11770 - 11/20/1994- UNITED STATES - LENOIR, NORTH CAROLINA
20.2Z - Wood veneers and panels
An explosion ripped through the gas heating installation used by the wood particle driers in a particleboard unit of a furniture factory. This explosion was followed by 4 others involving the wood particles put into suspension. A worker changing the blades in the chipper and another employee working with compressed air in the particle silo were killed. The walls of the particle silo were damaged in the blast and the grinding and drying zones were seriously damaged (the structure collapsed). Various fires appeared. The fire in the heating facility was brought under control after several hours. The electrical installations were not adapted to the dusty environment.

ARIA 15008 - 02/23/1999 - LOIRET (45) - VITRY-AUX-LOGES
20.1A – Sawmilling and planing of wood
A nighttime fire destroyed a sawmill housing a batten production line. According to the *gendarmerie*, the fire started in the same location where workers had used a cutting torch to cut metal beams to be used to expand the workshop. Sparks were able to reach the wood chips stored nearby.

ARIA 15083 - 03/15/1999 - MOSELLE (57) - FLORANGE
27.1Y - Manufacture of basic iron and steel and of ferro-alloys
In a refining station of an electric steel plant, an explosion ripped through a dome covering a ladle containing 240 t of molten steel. Seven workers were injured, including one who was seriously injured and had to be evacuated. The station and control room were extensively damaged. Production operations had to be shut down. A rupture of a donut-shaped cooling ring (an elliptical perforation measuring 15 x 7 cm) at the base of the arch of the refining station resulted in an influx of water into the molten steel causing the explosion. Damages were evaluated at 0.6 MF and operating losses at 29.3 MF.

ARIA 15635 - 05/03/1999 - AUBE (10) - VILLE-SOUS-LA-FERTE
20.5A – Manufacture of other wood products
Less than 3 weeks following an identical accident, an explosion followed by a fire occurred in a wood chip and dust storage silo used to feed the boiler of a moulded plywood company. The firemen sprayed and released smoke from the silo (no visible flame). The venting system performed correctly. The silo was completely emptied. The accident was the result of renewed heating of the wood dust caused by the previous fire. The silo had not been totally emptied despite the presence of wood and dusts that were extremely wet from the firefighting water. The operator called upon the various constructions companies that built its equipment in order to find solutions.

ARIA 20368 - 05/16/2001 - LANDES (40) - RION-DES-LANDES
20.2Z - Wood veneers and panels
In a wood panel manufacturing plant, a fire broke out at the exit of a chip drier in the ventilation system's cyclones and ducts. The fire department was alerted as a precaution, who set up 4 small fire nozzles. This incident, apparently known by the operators, was due to the progressive clogging of the ducts and cyclone. Cleaning of these elements was foreseen every 6 weeks during maintenance operations. The operator had reduced this interval to 3 weeks and the next cleaning operation had been scheduled for 2 days later.

ARIA 20383 - 04/06/2001 - VOSGES (88) - RAMBERVILLERS
20.2Z - Wood veneers and panels
In a wood panel manufacturing plant being restarted after 9 days of technical shut-down, a fire alarm on one of the 3 driers stopped the installations after the time threshold was exceeded (10 seconds of continuous alarm) and the detection of sparks (infrared sensors). The operators, assisted by the safety officer on duty, searched the cause of the alarm for 2.5 hours and discovered embers in a duct above the cyclones. A fire nozzle was set up to spray down the inside of the duct via an inspection hatch, accessible using a ladder from an overhead catwalk. The spraying operation had been underway for just 2 minutes when the explosion occurred. The operator holding the fire nozzle lost his balance and fell 9.5 meters to his death. The explosion vents were destroyed. An expert assessment of the accident attributed the explosion to the presence of CO producing a smouldering fire in the final portion of the drier, near the explosion vents. The fire was caused by welding operations that had been undertaken 48 hours earlier.

ARIA 20579 - 05/26/2001 - UNITED STATES – GAYLORD, MICHIGAN
20.2Z - Wood veneers and panels
Following an explosion and fire that rocked a pressed board manufacturing plant the day before, firemen opened a silo to extinguish burning wood chips. When firefighters opened the silo to pour water on the flames, the sudden infusion of oxygen caused the second blast. One firefighter was seriously burned and 5 were treated for smoke inhalation. The plant, whose activity was interrupted after the first accident, remained closed until the investigation of the first blast was complete, idling the 230 workers employed at the plant.

ARIA 23325 - 09/21/2002 - LANDES (40) - RION-DES-LANDES
20.2Z - Wood veneers and panels
An explosion and fire ripped through a wood panel manufacturing unit in a conveyor located at the exit and underneath a 1,000 m³ chip storage silo. The steady fire in the bottom of the fire required that it be completely emptied with the screw conveyor and the door while the silo's internal sprinkling system was in operation in addition to the hoses used by the plant's internal firefighters. Once the fire was extinguished and repairs made, press production operations were able to resume after 44 hours. The fire was initiated by

heating caused by a disc at the end of the screw conveyor that was improperly secured during a maintenance operation conducted a month earlier.

ARIA 23968 - 01/27/2003 - ALLIER (03) - DOMPIERRE-SUR-BESBRE

27.5E - Casting of light metals

An explosion rocked a furnace in a plant manufacturing vehicle cylinder blocks. The fire that followed was brought under control by the firm's internal emergency department; 3 employees were burned, one of who was severely burned on the face and back. Repercussions on the operation of the production line were feared. The operator had an expert assessment of the accident conducted. A cooling failure caused the explosion with a water-metal reduction reaction releasing hydrogen that exploded upon contact with the air.

ARIA 25176 - 06/05/2003 - LANDES (40) - RION-DES-LANDES

20.2Z - Wood veneers and panels

In order to replace cyclones at the exist of a chip drier at a plant manufacturing wood panels, an employee of a subcontracting company began cutting an external element of the drier with a side grinder while it was still in operation. This resulted in a dust explosion and fire; a crack had appeared on the cyclone's access door that had allowed sparks to pass. The firefighters sprayed water on the installation to cool it down. Production was interrupted the time needed to replace a vent destroyed by the explosion and clean and check the installations. The operator modified his work permit to require that the drier be shut down before work involving hot spots.

ARIA 25978 - 10/06/2003 - VOSGES (88) - RAMBERVILLERS

20.2Z - Wood veneers and panels

In a wood panel manufacturing plant, a fire broke out on a stock of 1,200 tons of chips measuring 400 m long, 30 m wide and 15 m high. Wood waste, stored in bulk in a container, was used to supply the boiler. Unable to reach the heart of the fire, roughly twenty firefighters contained the fire using the company's fire system. The employees created a passageway in the mountain of chips using an excavator and, using a steel ram, spread it out to prevent it from collapsing. Five tonnes of waste were partially burned then disposed of in the boiler. The accident was caused by the self-ignition of chips resulting from fermentation. The fire had no repercussions on the production.

ARIA 26575 - 08/18/2003 - UNITED STATES - OCALA, FLORIDA

25.2 - Transformation of plastic materials

An explosion ripped through a plastics manufacturing plant. Dried and pulverulent wood had caught fire. This material was to be mixed with plastic materials to manufacture planks. Wood dust caught fire in a drier creating overpressure which lead to the explosion. A worker was killed by a metal pipe that was projected during the explosion. Numerous irregularities were found: sprinkler system in poor condition, fire hydrant broken and blocked in open position, malfunction of emergency exit lights, no "no smoking" signs and compressed acetylene and oxygen gas cylinders not secured. The plant's operations were suspended, idling the 20 employees.

ARIA 27074 - 05/11/2004 - SEINE MARITIME (76) - ALLOUVILLE-BELLEFOSSE

20.2Z - Wood veneers and panels

One man was killed and another seriously injured in a dust explosion in a particleboard manufacturing facility. In the manufacturing process, wood and flax shives are mixed with a resin, then pressed 210 ℃. The heating medium (mineral oil) is heated to 250 °C and distributed via a system inside various platforms. The upper platform is equipped with 3 heating plates designed to ensure better heat distribution on the structure and brought to a temperature of 140 to 210 ℃. The workshop is sprayed d own except for the top of the press, which is too hot to allow the heads to be installed. Around 5.30 am, the crew in the workshop smelled the outbreak of a fire in the upper part of the press. After an initial search, an electrician and the shop supervisor tired to extinguish the fire with fire extinguisher (50 kg of multipurpose powder). An explosion then killed the first and seriously burned the second. The sprinklers were able to extinguish the supervisor's burning clothes and immediately confine the fire. According to the Classified Installations Inspectorate, the accumulation of wood dust on an excessively hot plate could have initiated the fire, which could have ignited the cloud of dust blown by the extinguisher, thus resulting in its explosion. Two outbreaks of fire had already been reported at the installation due to plate temperature control errors; the incandescent part was thus gathered using a scraper or a brush. The press shop had no written instructions as to the procedures to be followed in case of fire, no written instructions regarding how often the press was to be cleaned and the procedure involved, even though the workshops produce a great deal of dust. The Classified Installations Inspectorate proposed an emergency order making the restart of the press shop subject to the implementation of appropriate corrective measures. The operator implemented the following measures: monitoring of press temperatures, cleaning procedures and a dusting plan, instructions in case of malfunction, thermal insulation at the top of the press, a fixed extinguishing system, a water fog extinguishing installation (to avoid blowing dusts), the drawing up of routine fire procedures and personnel training.

ARIA 27877 - 07/22/2004 - GARD (30) - ALES

10.1Z – Mining and agglomeration of hard coal

A forest fire which spread July 26th to 2 spoil heaps in the Rochebelle (450,000 m³ of washery shale and ashes, order: 1940) and Mont Recato districts (1,750,000 m³ of washery shale, order: 1960), was rapidly brought under control by the emergency services. Between August 2 and 10, rain activated internal combustion which had not been detected up to that time (water-gas formation during the incomplete combustion of carbonaceous wastes). Monitoring operations from August 11 showed indicated that internal combustion was occurring. Solutions were sought with an expert to determine the most appropriate methods, while the fire was menacing the local residents. Seven Canadairs water bombing aircraft and a Convair performed 60 drops without being able to "drown" the combustion as incomplete combustion continued with the formation of CO and H2 (water-gas). The unloading operation, initially planned then postponed, was finally performed by a forest management organisation. Several experts monitored the work as it was feared that the sector may cave in. In late August, the unloaded area had reached 6 m in depth and temperatures had reached 500℃. Operations were predicted to last th roughout the month of September. During operations on the Rochebelle spoil heap, blowing dust led officials to transfer 67 beds from a nearby health clinic to a hospital in town centre. These dusts would contain a fungus, aspergillus, which may be potentially dangerous for fragile individuals.

Hazardous discharge at Saint-Victor and Göteborg

ARIA 31236 – 09/04/2005 - ALLIER (03) - SAINT-VICTOR

28.5A - Metal treatment and coating

In a plant operating 6 metal surface treatment lines (total bath volume: 196 m³), an operator observed around 8:15 pm that 1,000 liters of cyanide alkaline copper had spilled into a concrete retention basin after an output pipe detachment on a regeneration filter for the bath of a multi-treatment line.

Informed of the incident at his home, the plant's safety supervisor requested the operator to close this installation (shutdown of the heating system) and to leave the bath in the retention area. The incident was recorded in the appropriate logbook. At 5 am the next morning, at the start of his shift, an experienced operator (15 years experience in metal surface treatment) noted that the retention basin was filled with a liquid and, after referring to the logbook entry on the anomaly, decided to transfer the product with a mobile pump into the cyanide alkaline discharge tank of the detoxification station. Due to handling error, he accidentally transferred the liquid into a reservoir on the detoxification line of the chrome plating baths, which are not adapted to processing such effluent.

At 9 am, the head of plant security verified, like each morning and by means of colorimetry, the pollutant concentration levels of river discharges and noted excessive cyanide content (> 2 mg/l); the shutoff valve on the sewer outfall was immediately closed. The cyanide concentration of effluent discharged into the Cher River was estimated by the operating company at 3 to 5 g/l. For the rest of the day, the detoxification station was cleaned but not entirely (specifically, the filter press was left as is), and the next day's discharge was once again polluted with cyanide when service was restored. Between 2 and 3 tons of fish were killed by this pollution. The total quantity of released cyanide was assessed at 70 kg. The Classified Installations Inspectorate conducted an investigation, discovered the failure to respect certain guidelines of the prefecture's operating permit (non-declaration of accidents, absence of safety instructions) and proposed that the Prefect issue a default notice.

Photo DRIRE

ARIA 32890 - 21/06/2003 - SUEDE - NC

51.5A - Fuel wholesaler

A spill of 328 metric tons of heavy fuel oil happened in an Oil Terminal during the discharge of the product from a ship vessel to a storage tank.

At 10.30 p.m. the discharge to storage tank No 375 was started by 2 operators. At the same time discharging to tank No 304 was ongoing. When reading the level indicator the operators noticed that the level in T375 didn't continue to increase. They tried to increase the flow by reducing the valve to tank No 304. At 01.52 a.m. they discovered that the manhole of T375 was open and oil was flowing out to the ground outside the tank and to a neighbour company in the harbour. They closed the valve to T375 and the manhole and informed the terminal manager and a local cleaning company. At 03.00 a.m. the cleaning operation started. The harbour service staff inspected the harbour rain water drainage system and closed its outlet. Oil booms were placed in the open port harbour. Cleaning procedures continued during the following day. The authorities were informed about the accident.

On 22/06, a Coast Guard noticed the first indication of the large environmental effects. Approximately 50 t of oil passed the rain water drainage system, reached the open sea and contaminated beaches and seashores.The spill resulted in a contaminated area in the harbour of approximately 2000 – 2500 m². Fishermen tools, hundreds of yachts and many birds were contaminated. The total economic loss was approximately € 2,7 millions.

The major factors which contributed to the accident were a lack of communication between the 2 shifts at the shift take over, absence detailed check lists for tank preparation and start-up process and of the equipment double-check before start-up, and the failure to respect operational procedures. Due to the Midsummer Eve holiday there were less personnel in the Oil Terminal than usual. The shift foreman was on vacation and the terminal manager had taken over the foreman's work. The wide consequences of the accident were caused by the wrong reaction of the employees who assumed there was some problem with the incoming flow but did'nt go out and inspect the tank, the failure to respect the emergency plan which specify that the harbour should be informed immediately and the absence of bund and valves in the rain water drainage system. Moreover, the the water drainage systems and booms were less efficient because of density of the product (higher than 1).

After this accident, the operational procedures, emergency response, organisational related areas, communication and design of the harbour were improved.

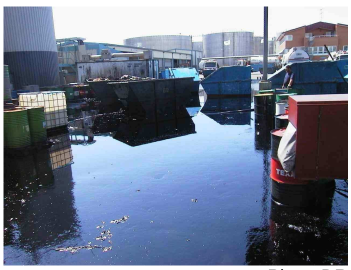


Photo DR

Written instructions…

While risk analysis constitutes a prerequisite for the safety of plant personnel and neighbours, and even for the durability of the means of production associated with many industrial activities, developing well-adapted prevention measures are the ultimate goal. Beyond the eventual technical improvements proposed, the application of procedures and guidelines represents a key component to the risk management process.

Many events recorded in the ARIA database serve to highlight the deficiencies found in this particular area, which serve as the cause of accidents or give rise to one of the causes.

Precise written procedures and instructions must be introduced during actual plant operations in order to control processes and make use of installations under optimal safety conditions. Inadequacies in the content of operating protocols or an absence of protocols: for the transfer or reception of delivered chemical products (Nos. 22217, 28781), machine operations during the set-up phase (No. 27570), drainage of surface treatment baths (No. 27120), or poor transmission of instructions during a shift change (No. 25952) offer some of the examples found in the database. Installation startup and shutdown phases require considerable attention and skill during plant operations and often impose such documentary guidance (Nos. 19261, 29213).

The periods allocated to onsite works, whether preventive or remedial maintenance, modifications and/or reconfiguration of installations, must also be incorporated into the set of written guidelines; these periods allow shutting down the facility under preferable conditions and implementing an action plan during each operational phase. Deficient site preparation (equipment consignment (No. 20656), machinery cleaning (No. 17207), etc.), undertaking actual works without the proper burning permit (No. 12878), equipment acceptance in the absence of requested tests and inspections, and facility reactivation (No. 11845) can also lie at the origin of accidents. Onsite subcontracting necessitates considerable vigilance and oversight as external personnel might very well be less sensitive to risks than in-house staff (No. 31508).

Installation modifications must also be taken into consideration when updating written instructions. Failure to modify a procedure, subsequent to equipping ammonia reservoirs with power valves, resulted in a leak due to operator error during material transfer from a tanker car (No. 27227).

Running facilities under degraded operating conditions, which could be identified via the risk analysis, must wherever necessary rely upon written instructions to ensure heightening safety of plant units and, in doing so, limiting the eventual consequences of malfunctions and accident occurrence.

A well-coordinated organization of emergency services helps limit the impacts of accidents (No. 21823). Written instructions that stipulate how to alert firefighters, which protocol to follow should an accident arise, etc. are provided so as to improve the efficiency of emergency response and avoid secondary accidents.

Accidents, with unfortunately dramatic consequences at times, make up unique events that need to be addressed through feedback in the aim of enhancing in-house risk management. Beyond the technical adjustments introduced, updating written procedures proves critical. Procedural and guideline revisions following a fire on a gas pipeline within a steel mill (No. 6133) or subsequent to a leak on an ammonia installation in Germany (No. 12977) serve as just a couple illustrations. From a similar perspective, an analysis of "near" accidents enables upgrading the measures already adopted (No. 28851).

The availability of a precise set of procedures and instructions is not sufficient in and of itself; these also need to be widely known and perfectly understood by all staff members. Along these lines, a well-adapted communications policy, effective initial training and continuing education of personnel, and easily-accessible instruction displays on all workstations (No. 23010) are some of the prerequisites for staff assimilation of these materials.

Analysing what is supposed to be performed and then writing out the steps and informing personnel and potential subcontractors of the operating procedures to be implemented constitute essential actions in ensuring workplace safety. This approach offers one of the keys to risk management and requires solid commitment at all hierarchical levels of the company.

Accidents whose ARIA number has not been underlined are described on the site:

www.aria.ecologie.gouv.fr

ARIA 11845 – 09/16/1997 - LOIRE ATLANTIQUE (44) - MONTOIR-DE-BRETAGNE
40.2C - Distribution of gaseous fuels
In a methane terminal, at the time of resuming operations following maintenance work, an incident occurred near the flare tower. Two valves connecting the low-pressure gas circuit to the evaporation gas circuit stayed open, causing intake of liquefied gas at the flare tower and producing a flame 50 m high. The POI emergency plan was activated and the situation brought under control 30 min after decompression of these two gas circuits. Procedures for the shutdown and startup phases or for the case of operations under degraded conditions had to be devised or updated.

ARIA 12878 – 05/11/1998 - SAONE ET LOIRE (71) - MONTCHANIN
25.1C - Tire retreading
In a retreading company, a fire broke out at the end of the afternoon inside an 80 m² tire warehouse. The blaze could not be extinguished by the few employees still present onsite and spread, destroying more than half of a 4,400-m² building. A portion of the 30-strong workforce faced being laid off as a result. Some of the fire water supply remained within the site's network, while another fraction entered the zone's stormwater system and was discharged into a pond; no significant pollution was observed. An outside firm had been called in to complete welding work at the warehouse 45 min prior to the accident. No burning permit had been authorized and no special guidelines issued to the crew. Sworn agents were assigned to record these factual details.

ARIA 12977 – 08/03/1994 - GERMANY - FRANKFURT
YY.0Z - Undetermined activity
An ammonia leak occurred in a refrigeration unit equipped with a turbocharger. A subcontractor performing maintenance would have removed non-insulated tubing with a solid plug. The ammonia would up intoxicating the worker as well as two plant employees. The leak was stopped by closing a valve, and a water curtain system dispersed the ammonia cloud. Damage was limited and no environmental consequences were observed. The procedures and instructions intended for subcontractor personnel were duly modified.

ARIA 19261 – 11/20/2000 - BOUCHES DU RHONE (13) - TARASCON
21.1A - Paper pulp production
In a paper mill, chlorine dioxide (ClO_2) used to bleach the paper pulp leaked and 4 explosions were set off during plant downtime. The accident occurred as a dioxide generator reactor was being drained into a polyester tank with a capacity of 18 to 20 m³, while an operator had already begun rinsing the pipes. Methanol forced into the reactor then came into contact with chlorate residue. The ClO_2 formed by this association decomposed exothermically in triggering a considerable and near-instantaneous increase in the gaseous volume, which was responsible for the explosions. The pressure surge was discharged via the open reactor manhole. The chemical reaction propagated into the polyester tank, and one of the explosions caused its destruction. The plant's POI emergency plan was not activated, yet gate staff did notify firefighters subsequent to the erroneous risk assessment. A safety zone was cordoned off around the workshop, which could be confined using a water curtain; all air conditioning units were shut off as a precautionary measure. ClO_2 emissions were contained: 20 ppm over a 1-min period and a peak recorded at 35 ppm shortly after the water curtain was set up. No casualties were reported and property damage estimations amounted to 1 million francs (150,000 euros), consisting of: collapsed tank roof, blown-out cladding, damaged generator valves and heat insulator, and broken pipes. The procedures for shutting down the workshop, and in particular the rinsing step, underwent modification.

ARIA 20656 – 03/29/2001 - SEINE MARITIME (76) - LE HAVRE
40.1E - Electricity distribution and sales
In a power plant, an accidental discharge of 100 to 200 m³ of effluent containing iron oxides flowed into one of the adjoining port's basins and was detected during a routine inspection (brown coloration of the water). During shutdown of the current generating unit, combustion air heaters of the vapor generators, clogged by fly ash deposits, were cleaned; this operation is performed every other year. On this particular occasion, the inspection covers of the heaters were open and the devices were being cleaned using a water jet (yet without any cleaning product). Effluents were conveyed towards a basin located onsite (SNM) as an exceptional measure prior to their evacuation to the wastewater treatment plant at the smoke desulphurisation facility. The basin was equipped with two Archimedes' screws that, when operating normally, discharged the overflow quantity into the wastewater system for eventual evacuation into the port's basin. The screws, according to this set-up, should have been deactivated, and this did not happen. Several organizational malfunctions were noted: consignment requested for the following day, interfacing problem between the two systems involved (shutdown and consignment handling), worksite managed by the maintenance team while effluent monitoring overseen by another unit, continuous round-the-clock site operations whereas inspections were conducted only during daylight (cause for detection delay).

ARIA 21823 – 01/30/2002 - HAUTE SAVOIE (74) - CRAN-GEVRIER
27.4D - First aluminium transformation
Within the rolling workshop of an aluminium and alloy production plant, a fire broke out above a bridge crane, on a double roof frame. The flames crept along the workshop beams where oil vapours had been deposited. Very quickly, around twenty staff members formed an improvised emergency response team and extinguished some of the flames. Firefighters took over once on the scene and brought the fire under control definitively. Thanks to the effective in-house emergency response organization, damage was limited to just the plant's roof.

ARIA 22217 – 01/12/2002 - MEURTHE ET MOSELLE (54) - CHAMPIGNEULLES
15.9N - Brewery
Around 10 am, a brewery received delivery of a mixed load of acids within five 1,000-liter containers: 4 nitric acid (HNO_3) containers, and 1 hydrochloric acid (HCl). The labelling of these containers provides the only distinctive indication of delivery contents. Unloading proceeded normally with the first container of nitric acid being transferred into a 10 m³ stainless steel tank that already contained 3,000 litres of HNO_3; then transfer of the 1,000-liter container of hydrochloric acid was erroneously routed to the same destination. Once aware of his mistake, the delivery truck driver notified onsite staff. In collaboration with the shipper, who sent two of his own agents to the brewery, it was decided to drain the reservoir by pumping the acid mix via the tank emergency valve; this operation started up around 11:30 am. With 2,000 to 3,000 litres of the acid mix already pumped, the operators suspended the transfer for 2½ hours after remarking that the liquid pouring into the containers was coloured red. At the same time, the tank drainage pipes burst and 2,600 litres of acid solution overflowed into the retention basin, with a brownish cloud of nitrous

vapours being emitted into the atmosphere for 10 to 15 min. Local emergency services were alerted, the control room staff of the nearest workshop was evacuated and a safety perimeter laid out inside the brewery. The firefighting team, which included one CMIC chemical emergency specialist, arrived on the scene 5 minutes after being called. The overflow solution was then pumped, placed into a container and removed for treatment at an authorized centre. The burst pipe was no doubt caused by hydrochloric acid attack of the stainless steel, further stimulated by diluted nitric acid that formed an *aqua regia* type of mix, as well as by destruction of the oxide films protecting the steel from deep attack (passivity). The brewing company requested its supplier to ensure the reliability of its in-house procedures relative to both the loading and identification of chemical products delivered in order to avoid all risk of confusion between products; the in-house transfer procedure was also to be updated and strengthened. Moreover, the brewery operator had to consider the risk of mixing acids when redesigning the storage facility.

ARIA 27227 – 06/02/2004 - MOSELLE (57) - FLORANGE

27.1Y - Steelmaking

An ammonia leak (NH_3) occurred during unloading of a tanker car within a steel mill. The stored quantities of NH_3 at this site consist of two 30-m³ tanks (18 tons) supplying the hydrogen production installations. This gas is used as an atmospheric gas for heat treatment ovens within the "finished steel sheet" unit. The reservoirs were coupled, yet could still be isolated by means of manual valves. At the end of 2003, power valves actuated by a palm button were installed as a complement to the sectioning devices designed to reduce reaction time in case of accident. In the hours preceding the leak, the southern tank reached its low point and was isolated form the network by activating the power valve; the emergency intervention report did not make mention of the type of closing device employed. During material transfer, the agents observed that only the northern tank was being supplied and they isolated it using the manual valve in order to fill the two tank capacities evenly. Since the southern tank's motorized sectioning device was closed, the supply pipe rose in pressure and one of the relief valves positioned on the pipes opened. The operator shut off the transfer pump but the leak continued for another hour, and 50 litres of liquid NH_3 were discharged into the atmosphere. The odour nuisance was perceptible at a distance of 500 m from the installation. The POI emergency plan was not enacted, and no casualties were reported. The inspection investigation revealed that subsequent to the works conducted in 2003, material transfer procedures were not updated and did not address the electric sectioning devices. This organizational flaw, which caused the verification of power valve position to be overlooked, is the reason behind the ammonia discharge. The process was then modified: both NH_3 reservoirs were to be replaced at the beginning of 2005 and 2006 respectively by hydrogen storage facilities. A draft prefecture decree, preceding the accident, had been transmitted to the prefect for authorization of this modification and, in the interim, reinforce safety measures for NH_3 installations.

ARIA 27570 – 07/13/2004 - GIRONDE (33) - ARTIGUES-PRES-BORDEAUX

26.1C - Flat glass shaping and transformation

A fire broke out in a factory specialized in decorative screen printing on glass bottles. While a newly-installed glazing machine was being submitted to a pre-production test, the treatment (etching) bath in place was empty. One of the electrical resistances used to maintain the bath at the right treatment temperature was still on during its dewatering. The superheat caused nearby material to ignite, in particular the polypropylene tank that had contained the bath. The fire spread throughout the entire workshop and generated thick, heavy smoke (basically due to tank combustion). Given the suspicion of smoke cloud toxicity, the local gendarmerie officers evacuated the smoke-filled zone, i.e. in all some 300 people (most of whom were employed by neighbouring companies). Fire water was collected from onsite networks, as this water had been contained by lowering gates at the site exit once the incident began. On the next day, the fire water, which constituted more than 18 tons of waste, was discharged by a specialized firm. Property losses were sizable, with the cost of the destroyed machine evaluated in excess of 1 million euros. The operator error, i.e. proceeding with tank draining without shutting off the electrical supply to heating resistances, caused this fire. Since the machine had been scheduled for tuning at the time of the accident, no procedure had yet to be written. A partial startup or suspension of activity is anticipated, depending on the results issued from the follow-up investigation.

ARIA 28851 – 06/27/1977 - ISERE (38) - ROUSSILLON

24.1G - Production of other basic organic chemical compounds

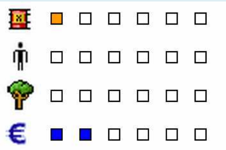
At a chemical site, a tanker car containing vinyl chloride was drained into ammonia spheres. No visible impact on the storage facilities was recorded due to the non-reactivity of both chemical products, yet the production line of a workshop needed to be halted. The incident was caused by a number of procedural errors: non-verification of the numbers and data sheets from the cistern by personnel responsible for material transfer and by the subcontractor assigned to handle the cistern, the absence of verification testing prior to drainage, and the failure to adapt tanker car orifices to the transfer mechanism by use of flanges exterior to the transfer station. The procedures for both vehicle identification and armguard use were reminded to all personnel and a procedure was implemented regarding the identification of products for discharge.

ARIA 31508 – 03/08/2006 - ILLE ET VILAINE (35) - CHATEAUBOURG

15.7A - Production of feed for farm animals

A flameless combustion occurred around 9:00 am within a silo devoted to storing methionine from an animal feed plant, at which time maintenance work was being performed by a subcontractor on the "lid" of this cell. The welding of a pipe onto the inspection cover had begun 10 min prior when the subcontractor's employees noticed the emission of irritating smoke. They immediately closed the cover in order to avoid adding oxygen and then sounded the alarm. Onsite at 9:15, firefighters searched for burning points, using a thermal imaging camera, within the silo and this led to a negative outcome. The storage temperature, which had not exceeded 20℃ according to the site o perator, reached 13℃ around noon and the 13 tons o f methionine were then transferred into big bags. The emergency response team left the site around 1:00 pm. The accident was caused by the spraying of incandescent material during pipe welding. The hazardous facilities inspection team conducted a same-day investigation and reported insufficient guidelines regarding the burning permit (the risk of spattering material was underscored, yet protective measures were left to the choice of work crews), along with a lack of awareness by subcontractor personnel of the risks incurred when working with hot spots. In contrast, the inspector's report did acknowledge that the installations were being cleaned at regular intervals and recorded in a dedicated logbook and that ATEX zones were being delimited. As a follow-up to this work, the site operator anticipates developing a set of specific instructions for the welding and draining tasks on the cells targeted by this process.

Refinery fire in Notre-Dame-de-Gravenchon



ARIA 31681 - 04/21/2006
76 - NOTRE-DAME-DE-GRAVENCHON

23.2Z – Manufacture of refined petroleum products

A fire broke out in a refinery at 10.15 am in the ETX2 oil aromatic extraction unit, using N-Methyl Pyrrolidone (NMP).

After having been shut down for regulator inspection and work, the unit resumed operations on April 19th, then when into production phase on April 20th. A fire developed on April 21st, with flames shooting 15 m high followed by periods of the fire decreasing then starting up again.

The operator used the establishment's fixed and mobile firefighting means, including two emulsifier nozzles (450 l/min.) to cool and protect the structures, then initiated the internal contingency plan at 10.40 am. At 10.46 am, an 8,000-litre foam truck resupplied a pump-and-wagon truck already in action on the scene. The fire was put out at 11 am, and operations to cool down the structure continued.

The operator discovered the cause of the accident at 12.20 pm: a leak on the seal of a temperature sensor mounted on the lower circuit of tower T103 of the solvent (NMP) and raffinate recover section. The break was approximately 10 mm in diameter. The internal contingency plan was lifted at 1.25 pm. The operators continued spraying down the site with a water nozzle to prevent any subsequent re-ignition of the fire.

The flames deformed the scaffolding still present in the zone and numerous electrical cables had melted. The concrete base protecting the two columns of the solvent and raffinate recovery section was damaged superficially. 3 to 4 tonnes of hydrocarbons were released or burned during the fire. Emergency operations were terminated at 3.00 pm.

The unit was shut down, decompressed, emptied and injected with nitrogen. The fire had no significant environmental consequences although its economic impact on the site was evaluated at 1 million euros.

Accident causal analysis highlighted the organisational and human factor during the maintenance operations on the unit. A reducer fitting, not requested by the operator, had been installed on a section of the tower which should have been replaced with an identical piece of equipment during work performed by a sub-contracting company. When the work was finished, the reducer fitting was equipped with a screw-type plug to allow the new circuit to be tested, then removed after the test leaving the pipe open and its contents in direct contact with the temperature sensor, as the operator had not provided a thermowell.

The operator had modified the procedures regarding cooperation with external companies for the various operations on the piping, and particularly for the removal and installation of thermowells and the interface with the site's internal instrumentation department.

Subcontracting of operations

Accidentology highlights the special significance such operations can have with regard to installation maintenance, modification, fit-up and even dismantling. This analysis is undeniably applicable to work performed by site personnel, but more especially for subcontractors which intervene more or less regularly in an environment with which they are not always familiar.

Such operations generate specific risks that must be analysed in order to define prevention methods. This analysis, in keeping with the situation at hand, is the primary initial and indispensable step prior to all subcontracted work, regardless of its scope. It must take the equipment concerned into consideration, as well as nearby or related units and equipment and culminate in the formulation of safety instructions for those potentially exposed.

Numerous accidents recorded in the ARIA database demonstrate that an excessively high number of operations in potentially dangerous sectors that are currently being subcontracted without **prior risk analysis**: for example, cutting operations created an explosion followed by fire in a drier knowingly kept in operation while the operations were underway (No. 25176).

The **preparation of the operation** is as important as the risk analysis stage. The operation must be prepared along the same strict guidelines, both in theory and in practice. The description of the work to be performed, the safety rules to be adhered to in the form of instructions, "fire permit" if required and the action plans must be established by the operator for the benefit of subcontractors and the personnel. As such, in Grand-Quevilly, an incomplete and poorly defined work authorisation issued by the operator resulted in 2 subcontractors being burned by the boiling water following an incorrect manipulation (No. 27564). The workers thought that the installation had been isolated.

The **preparation of the job site** is the first operational phase on which the successful completion of subsequent operations is based: this includes the lock-out of certain equipment or material (No. 18192), securing, identifying and efficient cleaning of the work area (No. 24459), prior reconnaissance of the area by the subcontractor and the operator (No. 26757, No. 26401), and the presence of the appropriate first aid resources and an understanding by the external company of the instructions to follow in the event of an accident (No. 20273, No. 31988).

Monitoring to ensure that the subcontractor actually respects procedures and safety measures during operations is of the utmost importance to ensure the correct execution of operations under satisfactory safety conditions. Many cases of accidents illustrate the immediate or delayed consequences of the operator's insufficient monitoring of the work to completion (No. 26603, No. 8265, No. 25836).

Finally, while the final and formal **acceptance of works** is exceedingly important in limiting the risk of future legal action between the parties, and detecting defective or faulty work likely to create possible accidents in the more or less near future: an error in connecting two pipes led to explosions at a pharmaceutical product manufacturing site in Neuville-sur-Saône (No. 14268) and in Mareuil-sur-Ay, an explosion caused by a natural gas leak which could have been detected by a simple leak test (No. 31337). And finally, a flange cover that had been removed and not replaced by a subcontractor upon completion of work resulted in the accidental spillage of $60m^3$ of orthoxylene in a river (No. 30486).

The use of external companies has developed considerably over the last few decades and has proved to be an essential means of having work performed for which the operator does not have the required skill base.

In all cases, the operator must be particularly attentive in selecting subcontractors, notably ensuring that they possess the skills, training and qualifications required to properly perform the operations.

Beyond these preliminary operations and considering the specific nature of each site in terms of the risks faced by external contractors, risks for which they may have little knowledge or understand the scope, the mutual exchange of information is of utmost importance for the safety of those involved. True risk management necessary for all players in order to limit accidents. It notably involves the operator conducting a prior analysis of the risks for the subcontracted operations, the development and actual implementation of appropriate prevention provisions including first-aid measures, the strict monitoring of operations and serious and formal acceptance of the operations performed.

Each of these steps calls for dialog with the subcontracting entity. Certain conclusions of the risk analysis must be shared (risks incurred, preventive measures, …), the operator's and the subcontractor's actions clearly defined and coordinated, the safety measures explained,… and the difficulties encountered resolved through joint action.

The accidents for which the ARIA No. is not underlined can be consulted at

www.aria.ecologie.gouv.fr

ARIA 14268 - 06/11/1998 - 69 - NEUVILLE-SUR-SAONE

24.4A - Manufacture of basic pharmaceutical products

In a pharmaceutical plant, during an operation intended to remove dimethylsulfide (an odoriferous compound), a violent explosion audible for several kilometres fractured equipment (rupture disc, manifolds...) on a tank containing a cyclohexane-rich flammable distillate, and blew windows out of a 500 m² fine chemical facility. As this treatment was not part of the antibiotic manufacturing cycle, the operation is performed in a 8 m³ reactor, by oxidising dimethylsulfide with hydrogen peroxide in an acidic environment. The establishment's internal contingency plan was initiated.

The site's internal firemen were able to bring an outbreak of fire under control in 15 minutes. An operator was severely injured by a falling electrical cabinet and died a few hours later. Two employees were injured (burns to heels and eardrum trauma), 12 others who were not directly injured were examined as a precautionary measure. The accident occurred while the tank was being rinsed after a blow through valve was opened. The valve had been erroneously connected to a compressed air network and not flushed with nitrogen.

The proposed hypothesis is that the ignition energy was created by the agitation or the transfer of 2 non-miscible liquids (cyclohexane and water, in this case), one of which is flammable and insulating and thus can easily capture a static electrical charge (Klinkenberg experiment). During acceptance inspections following modification operations conducted over the summer to launch new manufacturing operations in the existing workshop, the subcontractor and the operator did not notice the incorrect connection of nitrogen piping on the compressed air network just 10 cm away on the plant's "purge nitrogen" branch connection. The Classified Installations Inspectorate recorded the facts:

Following this accident, the operator decided to abandon the deodorisation treatment, better identify all of the plant's pipework with a colour-coding system, check for oxygen using an oxygen profiler and to form a working group dedicated to finding deficiencies in the qualification procedures and improving them. Two years later, the inquiry conducted following a judicial inquiry implicated 3 companies and lead to the indictment of 14 individuals.

ARIA 18192 - 07/05/2000 - HAUTE GARONNE (31) - TOULOUSE

24.1G - Manufacture of other basic organic chemicals

Operators in a phosgenation workshop at a chemical plant were rinsing a tank with octanoyl chloroformiate, unaware that workers from an external company were working nearby; 40 to 50 kg of chloroformiate poured out of an open line and spilled on to the floor, resulting in splashing and gaseous releases associated with the hydrolysis of the chloroformiate.

One of the subcontractors was sprayed on an arm and leg, and 3 other experienced discomfort. The alarm was sounded and rinsing operations were suspended. The 4 injured individuals were taken to the plant's nursing station, then hospitalised for further examinations as a precaution. They were able to return home the following day.

A pipe had been cut on the circuit undergoing modification in order to install connectors. A prevention plan had been established for the work being conducted, the unit had been drained and a workshop operator had helped to open the circuit, although the equipment had not been properly locked out.

ARIA 20273 - 04/26/2001 - DOUBS (25) - DANNEMARIE-SUR-CRETE

15.7 - Manufacture of prepared animal feeds

A fire was started by a spark while an external company was installing a valve vent in a silo containing 60 t of dehydrated alfalfa (granulate form). A crew of firemen, equipped with self-contained breathing apparatus entered the unit to determine what measures had to be taken to reduce the risk of a possible explosion. A nearby rapeseed container was emptied and the alfalfa was sprayed down then removed.

The fire permit written for the subcontracting company was particularly brief and did not require that a fire extinguisher be kept close at hand.

ARIA 24459 - 03/14/2003 - MARNE (51) - REIMS

71.4A - Renting of linen

A fire broke out during welding operations on the water network of a laundry facility as the hose station network was not in service (outlet valve closed) at the time of the accident. The welding operations were being performed near the plant's ceiling that was covered with hard-to-see textile dust. During the welding, a particle of molten metal was thrown against the ceiling, catching the dust on fire. The resulting flames quickly became uncontrollable. The fire spread to the metal beams nearby. An employee called the fire department while the welder attempted to bring the fire under control with a fire extinguisher from his lift as it started to move along the electrical cable trays. The fire was extinguished before the fire department arrived, but the thick smoke had been generated and an infrared camera had to be used to check for any existing hot spots.

A prevention plan and a fire permit had been established, although no specific measures were asked of the external company performing the work (dust removal or spraying operations prior to welding or grinding work); the foreman had requested that the subcontracting company use manual means to cut the existing extraction chimney would could contain accumulated dust and to supply a water-spray extinguisher. These recommendations were respected.

In its report following the accident, the external company indicated that all future operations at this site would require a fire permit followed by careful dusting of the very wide area surrounding the job site and wetting of the structures by spraying if the absence of electrical installation so allows. The Classified Installations Inspectorate requested that the operator submit a report relative to the origins, causes and consequences of this incident, and the measures taken and those to be implemented to prevent such an accident from happening again in the future.

ARIA 25176 - 06/05/2003 - LANDES (40) - RION-DES-LANDES

20.2Z - Wood veneers and panels

In order to replace cyclones at the exist of a chip drier at a plant manufacturing wood panels, an employee of a subcontracting company began cutting an external element of the drier with a side grinder while it was still in operation. This resulted in a dust explosion and fire; a crack had appeared on the cyclone's access door that had allowed sparks to pass. The firefighters sprayed water on the installation to cool it down.

Production was interrupted the time needed to replace a vent destroyed by the explosion and to clean and check the installations. The operator modified his work permit to require that the drier be shut down before work involving hot spots.

ARIA 25836 - 09/29/2003 - NIEVRE (58) - PREMERY

24.1G - Manufacture of other basic organic chemicals

A fire broke out at the base of a building's wooden structural column, on the job site of a chemical plant undergoing renovation work. The outbreak of fire was detected during a 2nd security round, 4 hours after operations at the job site had stopped. Upon their arrival, the firemen disconnected the site's electrical power supply then were able to bring the blaze under control after 30 minutes. None of the installations in operation were located near the fire; only a 10 m^3 tank of acetic acid was in the immediate vicinity of the wall concerned.

The blaze was apparently caused by pipe welding operations being conducted on the wooden column by a subcontractor 4½ hours earlier. Incandescent particles or burning droplets may have fallen at the base of the column during the welding operations and then smouldered until finally catching fire. The accident only caused property damage: the wooden structure separating the two walls was destroyed, along with 10 m^2 of roof. The firefighting water was recovered in special catchpits designed for this purpose, then treated by the site's treatment station.

Following the accident, the prevention and protection mechanisms were improved: monitoring at the end of the job site is now conducted by the site foreman and the plant's delegated officer in charge; job site wastes are to be removed at the end of each work day. As an internal contingency plan had not yet been developed, the necessary information must be obtained from the fire department (description of stock contents, the site's extinguishing capabilities, location of water sources...). Furthermore, the Inspectorate requested that the electrical installations be inspected by an approved organisation prior before the production equipment be placed back into operation.

ARIA 26757 - 11/25/2003 - SEINE MARITIME (76) - PETIT-COURONNE

23.2Z – Manufacture of refined petroleum products

The accident occurred in a refinery while work was being performed during a production shutdown in a vacuum distillation unit, 3 contractors were sprayed by hot liquid and a product leak was detected.

The workers, working for a subcontracting company, were originally scheduled to work on 2 pieces of equipment: repair of exchanger 602, shutdown since March 2002, on which the rammer had been removed, as well as repair of a water leak on exchanger 581, to rework a seal. On 11/25 at around 2 pm, the team was informed that the sleeve of the 602 had been dismantled. The workers climbed up the scaffolding and dismantled part of the equipment from the exchanger when the hot oil leak occurred: the 3 individuals on the scaffolding were sprayed with the product (200℃), receiving second degree burns.

Loss of containment was detected on the column corresponding to exchanger 581. There was in fact confusion as to the origin of the accident: the individuals had worked on the other exchanger that was still in operation on which a minor operation was to be performed. To them, the equipment did not appear to be abnormally hot.

Following the accident, the operator planned the following action: contractors offered better information prior to operations, improvement of zone preparation (clear indication of the equipment involved, accompaniment on the site, systematically perform risk analysis prior to operations, concretely define required elements in a general manner to avoid confusion). The operator also proposes to explain the operation of the safety showers, the operation of which had not been immediate.

ARIA 27564 - 07/08/2004 - (SEINE MARITIME) 76 - LE GRAND-QUEVILLY

24.1J - Manufacture of fertilizers and nitrogen compounds

In a nitrogen compound manufacturing plant, spraying boiling water burned 2 contractors performing a maintenance operation to replace the motor drive unit on an automatic valve located on the feed line of station dedicated to loading trucks with hot ammonium nitrate solution. The very hot water is used to drain and rinse the piping.

Both employees were hospitalised, one of which was seriously burned. This leak was due to the removal of the valve bonnet due to the non-compliant installation of the motor support on the valve (support directly mounted to the valve's bonnet, while it should have been mounted on a clamp). In addition, the operators thought that the installation had been isolated and emptied of all product, as it was the day before.

The incomplete, imprecise and sometime erroneous work authorisation issued by the operator did not indicate the type of product used, or its pressure and temperature, for example. The operator must conduct an inventory of the entire site, valves/servo-actuators not in compliance with the manufacturers' recommendations and bring them up to standard, draw up a lock-out procedure for equipment conveying dangerous fluids and thus prohibit all intervention by personnel (except in an emergency situation) on installations that have not been drained and isolated.

ARIA 31337 - 12/29/2005 - MARNE (51) - MAREUIL-SUR-AY

15.9A - Manufacture of natural brandies

An explosion rocked the boiler facility in a distillery.

A specialised company was replacing valves, natural gas lines running to the boilers, modifying vents, and installing purge and inerting connections within the scope of preventive maintenance operations. The work began which began on 12/21/2005 was to be completed 01/02/2006 as the distillery was closed from 12/23 to 01/03. The gas line was replaced after the gas was shut off and purged, as planned. On 12/29, the maintenance technician felt that he had completed the work but did not conduct a leak test with compressed air or nitrogen. He opened the gas without closing a flange (dia. 80) on boiler No. 3, releasing a significant amount of gas into the building. Two heat sources may have created enough energy for the explosion: the halogen lighting in the false ceiling was on while the operator was welding on the other side of the wall from where the gas was.

The electricity and the gas were disconnected, and the firefighters and *gendarmerie* arrived at the scene. A security perimeter was set up. The 2 technicians were hospitalised for examination, and were released 2 hours later. The explosion raised the roof of the boiler facility, damaged a gable wall and the room's electrical cables. Operations at the site were shut down considering the extent of the damage. The boiler was reworked, and the building, electrical wiring roof and false ceiling were renovated.

The *gendarmerie* and insurance reports indicated the subcontractor's disregard for recognised trade practices and safety rules were responsible for this accident. The type of cause is not identified in the specific hazard prevention document which does not include human failures. In this respect, the prevention plan reiterates the risks and the protective means to be used without going in to detail with regard to operations that could be considered recognised trade practices.

In the future, the prevention plans for external companies shall be checked by the Industrial Director and the QSE Supervisor. The respect and application of the defined rules shall be followed by the QSE Supervisor who shall have the authority to stop job site operations as required. Delicate phases (reopening of gas lines...) shall be conducted in the presence of an independent organisation or technical representative from the subcontracting company.

Emission of H_2S at Rhadereistedt and Stuttgart waste treatment centres

ARIA 31000 – 11/08/2005 – RHADEREISTEDT - GERMANY

90.0E – Treatment of other solid wastes

During the production of biogas by means of an organic waste reclamation process, a release of hydrogen sulphide (H_2S) killed 3 employees and a truck driver who had come to unload slaughterhouse waste. The high concentration of H_2S in the facility complicated the fire department's rescue operations. Roughly a dozen firemen were intoxicated to varying degrees. Extensive aeration (more than 24 hours) was required before access to the building was authorised. The accident occurred while the truck was being unloaded inside a facility that had been kept closed in order to limit the emanation of foul smells. The load was being dumped into a 100-m³ pit equipped with 2 agitators. The pit's cover could not be closed as the electric actuating motor was out of service. The materials being unloaded were essentially pork entrails, viscera and liquid wastes having high sulphur content, pH near 8.5 and temperature of 60 °C. The waste had been loaded int o the truck 24 hours earlier and was similar to wastes generally delivered by the slaughterhouse once to twice per week. The reaction between these substances and the material already present in the pit (animal and dairy wastes having a relatively low pH as determined by analyses performed after the accident) generated the release of H_2S. The temperature of the environment and the agitation of the mixture promoted the dispersion of toxic gas throughout the unloading facility. To make matters worse, the extraction system at the bottom of the pit, which directs the foul air to the outside via a biofilter, proved to be insufficient.

ARIA 32574 – 12/29/2006 – STUTTGART - GERMANY

90.0E – Treatment of other solid wastes

During the vacuum transfer of liquid waste into steel tanks at a dangerous waste treatment centre, hydrogen sulphide (H_2S) was released from the vent of a receiving tank. As they could not be treated on site, these wastes (received in drums and mixed in the tank) had to be transported to another site. The body of a forklift truck operator was found nearby, and 5 people intoxicated by H_2S were hospitalised. Upon their arrival, the firemen did not detect a high concentration of H_2S and left the scene. The police requested that the suction pipe be emptied into the tank. The vacuum pump was restarted and a second release of H_2S caused the truck driver to pass out. The police ordered that operations be stopped and the fire department and an emergency physician were called to the scene. In all, the accident resulted in: 1 death and 6 intoxications with hospitalisation (2 employees, 2 members of the rescue team and 2 agents from another company). The release of H_2S resulted from a chemical reaction between 2 liquid wastes, an organosulphur compound and an organic acid. This accident demonstrates a faulty organisational structure: inappropriate identification, evaluation and documentation regarding the handling of dangerous products, procedures for vacuum pumping of waste from drums to the tank without a clear indication of the order to be followed, secondary chemical reactions... No safety system was foreseen in the event of a gaseous release from the tank vent. A judicial inquiry was conducted. The mixing of dangerous wastes in the vacuum tanks was stopped and the drums were treated at another site. The administration proposed a series of preventive measures: identification of dangerous wastes alone or in a mixture, safety criteria regarding their treatment (pH...), procedures relative to the storage of products not in compliance with criteria and for mixing with an indication of the order in which they are to be added according to the characteristics of the dangerous materials, connection of the vent to a gas treatment system, and restricted access to the vacuum pumping zone.

Accidental releases of H_2S

Hydrogen sulphide (H2S) is an extremely flammable, heavier than air and colourless gas that forms by anaerobic fermentation. In its native state it is found in coal, petroleum and natural gas. H2S is used in a variety of manufacturing processes : sulphur, inorganic sulphides, organosulphide compounds, and heavy water for the nuclear industry... or in metallurgy to eliminate impurities in certain minerals in the form of sulphides. Numerous industrial activities release H2S during chemical reactions involving sulphur compounds: refining, cracking of rich-rich petroleum products, vulcanisation of rubber, fabrication of viscose, transformation of food products, paper mills, tanneries, and sewers and treatment stations, waste disposal sites, sources of ferruginous water, natural gas extraction... and volcanic eruptions!

The gas is characterised by its irritating properties and by a fetid rotten egg smell detectable even at very small concentrations (0.02 to 0.1 ppm). Olfactory detection does not increase with its concentration in air and its odour can become rapidly undetectable at high concentration owing to the anaesthesia or even degeneration of the olfactory nerve above concentrations of 100 ppm. At 500 ppm, rapid loss of consciousness is often followed by a convulsive coma with respiratory difficulties (shortness of breath, cyanosis), pulmonary oedema, irregular heartbeat (bradycardia or tachycardia, fibrillation) and most often hypotension. Death occurs in just a few minutes at concentrations greater than 1,000 ppm.

The 2 mortal accidents presented illustrate the toxic effect of H2S, generated by the fermentation of wastes or following a reaction between 2 incompatible substances. Hydrogen sulphide can also be released in the following circumstances :

- ***refining or chemical manufacturing processes*** (No. 35, 7023, 18907, 19873, 22971, 23132, 25374, 26103, 26898, 28770, 28938, 29121, 30717, 31154, 32205),
- ***heating installations*** in which coal is used… (No. 8779, 16044)
- ***waste treatment or sewer networks*** (No. 3681, 4537, 6251, 9370, 11275, 15747, 17761, 19967, 21438, 23091, 28200, 29399, 29444, 29906, 31250, 31863, 32189, 32381).

Toxic releases can be caused by equipment or organisational failures. Equipment failures have resulted in leaks (Nos. 18907, 19873, 23132), the rupture of piping, and equipment malfunctions such as an oxidation-reduction sensor at Thann (No. 29339), a gas extractor at Gonfreville-l'Orcher (No. 30717), and pumps at Thenioux (No. 29121) and Romainville (No. 31250).

The organisational and human factor concerns:

- ***general organisation*** : a drilling crew underestimated the quantity of gas in a deposit and an insufficiently prepared drilling operation (No. 26103), presentation of the response plan to subcontractors and working conditions of the intervening parties with safety instructions, confined area work permit, verification of the presence of toxic or anoxiating gases (Nos. 17761, 29444), appropriate equipment (Nos. 9370, 23091), insufficient risk analysis (Nos. 3681, 25374), insufficiently treated effluents and the undetected release of H2S from a hood (No. 28398), and toxic wastes released without an special precautions in Abidjan (No. 32189).
- ***process control*** : new reactions implemented or those rarely used must undergo a risk study (No. 29121). Secondary chemical reactions or incompatibilities can result in the release of H_2S: the mixture of chemical products (No. 35), the addition of cleaning water into a reactor containing aluminium and sodium hydrosulphite (No. 7023), cleaning of a hydraulic testing chamber containing sulphur water with an acid solution in Saint-Martin-d'Hères (No. 9370) and modification of a manufacturing process in Chartres (No. 31554).
  The anaerobic fermentation of vegetal, animal (No. 3681), and household (No. 32381) wastes and sludge can also create accidents. The management of filter cakes is improved and the piping modified to prevent access to the sump, the discharge hose regularly became disconnected: heavy rains had prevented the piles from being property treated and promoted the formation of H_2S (No. 19967).
- ***maintenance*** (No. 16044, 32205) and ***works*** (No. 23091, 28200) : work *in a confined space* during cleaning operations or work enhances the risk of encountering toxic concentrations of H_2S (No. 4537, 9370, 11275, 17761, 19967, 21438, 22971, 29444, 31863).
- ***human error*** : The possible presence of people in the sewers must be insisted upon, whether during verifications, spot inspections or cleaning operations. An employee was seriously intoxicated during a spot inspection in the sewers of an industrial treatment station without the operator's knowledge (No. 15747). A child falls into a degassing outlet and is asphyxiated (No. 10911). Incompatible chemical substances can also be released into urban wastewater networks.

Three hundred two deaths and more than 150,000 people intoxicated by H2S inhalation (most of which were in Abidjan in 2006 – No. 32189) are among the accidents documented in the ARIA database. Human losses are greater when people render assistance without taking the necessary precautions. In China, more than 9,000 people were treated following a major release of natural gas and H_2S, more than 61,000 residents were evacuated and numerous animals were killed (No. 26103). In a similar accident in the USA, 900 people were evacuated (No. 7023). The fetid odour of H2S was detected 10 km from a chemical plant (No. 29121).

Also, employee training and information concerning the dangers of H_2S must not be neglected: toxic atmosphere intervention procedures, working in confined environments, monitoring of the atmosphere, and the wearing of individual protection equipment (No. 9370)…

The accidents for which the ARIA No. is not underlined can be consulted at

www.aria.ecologie.gouv.fr

ARIA 35 - 08/11/2005 - LUDWIGSHAFEN - GERMANY

24.6L - Fabrication of industrial chemical products

An unforeseen release of hydrogen sulphide (H2S) in a chemical plant occurred during a mixing operation. The nature and quality of each of the components was not indicated. The operator was killed; 4 other employees and 1 rescue team member were intoxicated while attempting to intervene.

ARIA 3681 - 06/09/1992 - SARTHE (72) - VIBRAYE

15.1A - Meat production

Animal wastes stored in a pit fermented over a 3-day shutdown of a slaughterhouse. The resulting hydrogen sulphide that formed mortally intoxicated 2 people and seriously intoxicated 2 other employees.

ARIA 9370 - 10/04/1996 - ISERE (38) - SAINT-MARTIN-D'HERES

73.1Z – Research & Development in physical and natural sciences

The SAMU (paramedics) assisted 2 sewermen suffering from cardiac arrest. As part of subcontractor cleaning crew, they were cleaning a laboratory's hydraulic testing chamber using an acid solution. The 3-meter deep chamber contained sulphur water. One of the sewermen died. The second worker was seriously intoxicated while trying to rescue the first worker and dead shortly thereafter. A pronounced hydrogen smell was noted around the pit. A mobile chemical response unit took several samples on the day of the accident between 11.30 am and 4.30 pm. Several samples were taken at the request of the District Attorney. The H2S concentration in some of the samples was greater than 2,000 ppm. The workers were not wearing protective equipment and had not received sufficient training.

ARIA 11275 - 05/16/1997 - NORD (59) - HAUTMONT

37.2Z – Recovery of recyclable non-metallic materials

In a recovery centre for oily food waste, used in the manufacture of fats for animal feed, a release of hydrogen sulphide intoxicated 4 employees who were cleaning a grease pit that had been out of service for many years and which contained oily sludge residues. The victims were hospitalised; 2 employees in serious condition remained under medical supervision for several days. The establishment, which has 13 employees, suspended its activities.

ARIA 15747 - 07/30/1985 - RHONE (69) - SAINT-FONS

90.0A - Wastewater collection and treatment

During a spot inspection, a technician from an external organisation was seriously intoxicated, most likely by hydrogen sulphide, after having entered the sewer system of an industrial treatment station without informing the operator. A 2nd technician was then intoxicated while attempting to rescue his co-worker. Both individuals were saved in the nick of time.

ARIA 19967 - 02/15/2001 - MANCHE (50) - BAUPTE

15.8V - Food industries n.o.c. (not otherwise classified)

Gases rich in hydrogen sulphide (H2S) killed 2 employees at a natural algae-based food additive factory. The insoluble fractions derived from the gelling agent extraction process, not directly usable in the finished product, are recovered on a filtering soil (perlite) then pressed. The filter cakes are then lixiviated (a salt removal process) on 0.5 ha of land prior to composting. The drippings flow into 2 sumps, one of which is equipped with an effluent lifting pump for treatment at a processing station. The discharge hose sometimes disconnects requiring the sump to be drained and intervention on the pump. The 2 employees were performing this operation when the accident occurred. The alert was sounded 3 hours later when it was noticed that the employees had not returned. They were found at the bottom of the sump. H2S concentrations in excess of 500 ppm were measured. The *gendarmerie* conducted an inquiry and an expert evaluation was performed. This type of accident, often underestimated, is associated with all types of anaerobic fermentation of sludge or compost in cavities in which gases can be confined. High concentration levels (6,000 ppm and above) can catch the personnel unawares insofar as the sense of smell shuts down and the onset of sickness practically instantaneous. In this case, heavy rains prevented the piles from being handled and promoted the formation of H2S; the proportion of soluble gas in the effluent represented an additional danger. The piping was modified to prevent access to the sump. Cake management was optimised.

ARIA 26103 - 12/23/2003 - CHUANDONGBEI - CHINA

11.1Z - Extraction of hydrocarbons

An explosion occurred on well No. 16 of a natural gas deposit (having an estimated capacity of 50 to 60 billion tons), while a drilling and exploration crew was working on a well at a depth of 400 m. A leak of consisting of a mixture of natural gas + hydrogen sulphide followed, erupting into a violent jet roughly thirty meters high.

More than 61,000 people living in communities located several km away were evacuated and sent to stay with friends and family or to one of the 15 sites set up by the authorities. At the site, 300 technicians were mobilised and the situation was brought under control two days following the accident: The leak had caught fire. The well in which the explosion occurred was plugged 5 days later with 480 m^3 of sludge. More than 2,100 people (including rescue personnel, firemen, soldiers and police,...) combed through 80 km^2 of territory and removed numerous animal carcasses that had been poisoned by the toxic gases.

In addition, the rescue personnel feared a possible risk of soil pollution due to the rainy weather forecast. Twelve days after the accident, the accident resulted in 243 deaths and 396 people still hospitalised, including 27 in critical condition. More than 9,000 people had to undergo medical treatment after having inhaled hydrogen sulphide. According to the initial information available, the majority of the victims had by intoxicated through gas inhalation. Many of the victims were children and elderly people.

According to the information relayed by the Chinese national television and after having had reported technical difficulties, the explosion was the result of negligence on the part of the drilling crew: numerous procedural errors, notably including underestimating the quantity of gas contained in the deposit, drilling without sufficient preparation, and failure in managing the gas leak properly (omitting to set it ablaze). The industrial safety administration conducted an inquiry on behalf of the Chinese authorities.

ARIA 29121 - 12/13/2004 - CHER (18) - THENIOUX

24.1E - Fabrication of other basic inorganic chemical products

A chemical plant released hydrogen sulphide (H2S) into the atmosphere for 3 hours. Foul smells were noted east of the establishment up to 10 km away, leading many residents in the neighbouring cities to contact the fire department. This pollution was caused by a malfunctioning soda distribution pump on the gaseous effluent scrubbing installation of the strontium sulphide-manufacturing unit (SrS). On the day of the accident, batch production was underway for the first time in several years at the site as the older installations (reactors) had been coupled to a temporary system designed to convey gaseous effluents to the gas scrubbing installations. When production was launched, as the soda-scrubbing pump disconnected twice, the operator stopped the fabrication process without neutralising the chemical reaction. The process thus continued until the reagent (ammonium sulphide) was totally consumed, and resulting in the release of hydrogen sulphide. The Classified Installations Inspectorate acknowledged the facts and proposed that the Prefect require that all resumption of the installation's activity be subject to a risk analysis. The operator considered doubling the pumps on the gaseous effluent treatment installations and re-evaluation of the site's dimensioning.

ARIA 31154 - 12/09/2005 - EURE ET LOIRE (28) - CHARTRES

24.5A - Fabrication of soaps, detergents and cleaning products

In a cleaning and toilet product manufacturing plant, a handling error occurred while a truck transporting a 50% liquid potash was being unloading, resulting in the substance being introduced into a tank of thioglycolic acid. An exothermic reaction between the two chemical substances resulted in the release of hydrogen sulphide. This mixture is generally implemented, in the presence of water, in the production of a hair removal product. In this case, the temperature of the reaction mixture without water is 60℃. The activation of an emergency stop button by an agent in acid/antigas gear and PBA stopped potash from entering the tank. As a precaution, the plant was evacuated, traffic stopped and the neighbouring school was informed of the situation. The truck driver was taken to the hospital. Measurements showed the presence of 130 ppm of H2S in the company's basement level. A forced ventilation system was set up to eliminate the smell of H2S throughout the establishment. The operation took several hours. The potash unloading operation was then completed. Of the 37 production lines, 27 resumed operations the same day.

ARIA 31863 - 06/12/2006 - YVELINES (78) - VIBRAYE

90.0G - Other drainage and road construction work

During a flushing operation on a settling tank of the Poissy sewer system, 3 sewermen died, ranging from 22 to 44 years of age, and another was severely injured, following a release of hydrogen sulphide (H2S). Two times per year, 4 employees of a drainage and road construction company clean the settling tank of the located in the "La collégiale" district. The operation consists in sludge and other waste from the 5-meter deep, 30 m³ settling tank into trucks. The company has worked under contract for the city more than twenty years. According to the company, this preventive maintenance operation, which had begun at 9.30 am, was designed to ensure the proper flow of wastewater in the sewer. Around 10 am, 3 of the workers were immediately intoxicated (according to a member of the rescue team) as the probably reached a pocket of H2S, a highly toxic gas formed from the decomposition of organic materials. The fourth worker, the 48-year old father of one of the dead employees, was located a slight distance from the others and was seriously injured and transported to the hospital. Alerted by a passer-by, roughly fifty firemen and twenty vehicles came to the scene, and were joined by 4 paramedic teams (SAMU). A judicial inquiry and an inquiry by the labour inspectorate were conducted to determine if all the protocols for this type of intervention had been respected. The company's management indicated that wastewater systems operators receive training regarding interventions in confined atmospheres, that they have atmosphere testers and gas masks. An autopsy was ordered by the court to know the exact cause of death of the three workers.

ARIA 32189 - 08/20/2006 - IVORY COAST - ABIDJAN

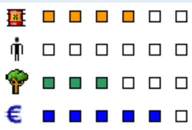
90.0G - Other drainage and road construction work

During the night of August 19 to 20, a Panamanian flagged ship with Russian crew began unloading its cargo holds of wastes onto the docks of the Autonomous Port of Abidjan. According to Dutch authorities, the ship had cancelled the unloading of its oily black sludge in July due to complaints about their toxicity and then set sail for Estonia. With the authorisation of the competent authorities, a specialised Ivory Coast company unloaded the 528 tons of toxic waste at 17 sites, with the majority being unloaded in Abidjan. According to the affreighter, the wastes were a mixture of fuel oil, water and caustic soda used to clean the holds. According to other sources, the waste contained H2S, mercaptans, phenols and organochlorine compounds or petroleum refining sludge. The presence of petroleum derivatives was confirmed by the detection of methyl mercaptan and phenols, both of which are derived from the refining process. Subsequent analyses showed that the drinking waster was not polluted, although extensive measures were taken to protect drinking water supply sites and safety perimeters were set up around waste disposal sites. The hospitals recorded more than 100,000 consultations, roughly ten thousand intoxications, 69 hospitalisations and 10 deaths including 4 children. Patients suffered from headaches, nosebleeds, vomiting and cutaneous eruptions… The population expressed its dissatisfaction for several days. The government spokesperson announced that intoxicated individuals would be cared for free of charge in the capital's 32 heath centres and requested technical assistance from other countries. A French civil defence team was dispatched with 500 kg of analysis equipment to assist the authorities with the short and long term action to be taken to protect the populations. As the waste disposal sites were closed, piles of nauseating refuse accumulated throughout the city. The government decided to close the market gardens located near polluted sites and the fishponds in which numerous fish had died. According to the Dutch press, between May and June, 70,000 tons of crude oil had been transformed into gasoline on the ship: 72 t of sulphur-containing wastes were thus produced. 18 people were charged with poisoning and violation of toxic waste legislation. A French group was designated to treat the polluted sites: it was estimated that 2 months would be required for soil excavation and the pumping of leachates into special tanker trucks. The wastes collected and stored in a secured warehouse were then transported to specialised installations in France. The cost of decontamination was 30 M euros.

Accidental rupture of a crude oil tank in Kallo and Italy

ARIA 30934 - 10/25/2005 - BELGIUM - KALLO

23.2Z - Oil refining



In the refinery's depot area, about 6:35 pm, a tank buckled causing 37,000 m³ of crude oil to pour out like a wave. The site's 4-hectare retention basin was covered 1 m deep in oil and 3 m^3 of petroleum spilled over the several meter-high dike walls. Based on computer records, the tank emptied its entire contents within 15 min after the burst. Following the accident, the reservoir drifted to one side and its foundations partially shifted.

Local authorities implemented Phase 3 of the disaster plan, under the Governor's supervision; emergency response measures were lifted the following day. Both internal and external response teams sought to cover the retention basin with foam (214 tons of foam liquid supplied by the refinery, with the contribution of local firefighting crews, civil protection agencies and contracted firms). The vast extent of the area to be covered, coupled with high winds (which fortunately helped limit the risk of explosion), rendered the operation fruitless. Local residents were asked to close their doors and windows due to the pungent odours. The oil present in the depot's other tanks was channelled to the refinery and basin contents were transferred into 3 onsite reservoirs using the wastewater pumping station. The basin was nearly fully emptied by the afternoon of October 27. Beginning the next day, a layer of sand was deposited by trucks and bulldozers operating in the freed zones as well as by blowers between tanks, which served to attenuate the odours. The damaged foundation could be stabilized by supporting the tank using 4 cranes. Phase 1 of the disaster relief plan, coordinated by firefighters, was maintained until the depot was just about entirely cleaned on November 18.

A ditch had formed at the tank bottom 1.5 meters from the sidewall, locally preventing water from circulating through the drains and thereby creating considerable internal corrosion over a portion of the bottom metal plates (35 cm x 20 cm), thinning the plates down at their extremities. On October 25, a small leak, which first remained confined in rough areas of the stone foundation ring, had apparently saturated the compacted sand below the tank with oil. Since the foundations had been locally weakened by this fluidised bed under the oil pressure, the bottom of the tank split open along the ditch width.

The inspection revealed that all depot tanks contained the ditch and internal corrosion. The ruptured reservoir was dismantled, while the others were repaired where required and their stability verified prior to being placed back in service. The depot operator then covered all tank bottoms with a layer of protective lining to prevent against corrosion and analysed the aggressive composition of decanted water in the crude oil tanks. Measurements have been conducted since by means of acoustic emissions between two internal inspections of the reservoirs; when the slightest doubt arises, a scan is taken of the tank bottom thickness over the entire surface area.

Accidental failure of a hot bitumen tank in Italy

ARIA 32829 - 09/08/2004 - ITALY – NC

23.2Z - Oil refining

.In the bitumen storage and loading/unloading unit at a refinery, a 12-m high tank installed on the site for 30 years featuring a floating roof, a capacity of 1,200 m3 and a heating coil, suddenly ruptured at the level of the shell-foundation joint. The casing was projected a distance of 15 m, breaking in its path the piping braces placed 5 m aboveground; it then fell onto another bitumen tank. Some 550 tons of bitumen and 120 tons of hot-oil at 170℃ used in the heating coil, spilled over a zone of about 13,000 m2.

Fire subsequently broke out in the tank basin and spread by domino effect to nearby installations, other storage areas and the tanker trucks being loaded. Internal and external emergency plans were immediately activated. The fire is estinguished after about 3 hours of internal fire team's intervention and external fire brigades.

It was determined that this tank failed due to internal overpressure caused by the presence of light flammable hydrocarbons overheated by the heating coil and wrongly introduced into the tank during unloading from tank-trucks to the tank of bitumen in excess present in the trucks. This accident killed 1 and injured 3 truck drivers due to the ensuing fire. The smoke plume was seen by the near city population, but its effects were juged at low impact by the regional environmental protection agency. Bitumen also spilled into the adjacent sea through wastewater discharge pipes and polluted the seaside beach for 8 km far away.

The explosion and fire damaged a number of facilities and structures on site. The coasts were estimated at 25 M€ for production losses and 3 M€ for the property damage and environmental restoration/cleanup.The investigation bring out deficiencies in management factor and human factor (SMS) and the operator decided to remove the loading platform from the storage area and modify operative procedures to load tank-trucks.

Photo: Corriere della serra

Sudden failure of large-capacity tanks

While sudden tank ruptures occur quite infrequently, their consequences are often spectacular: powerful wave-like effects that submerge retention basins, environmental pollution, domino effects, etc. People and equipment located in the vicinity are highly exposed to injury due to the amount of energy released, compounded by the kinetics of the phenomenon.

Design flaws inherent in both the tank and its auxiliary facilities give rise to plenty of the potential triggers leading to sudden rupture, particularly in the event of added stresses. The tank manufacturer must pay special attention to the quality of materials employed as well as to the assemblies created. Defective welds were the source of failure for a residuary liquor tank within a Provins distillery east of Paris (No. 2201), a 15,000-ton cryogenic storage facility for ammonia at a Geismar fertilizer production plant (No. 5421), a crude oil reservoir at a Pittsburgh refinery (No. 223), and a 13,800-m³ tank at the time of filling with water at a refinery in Notre-Dame-de-Gravenchon (No. 23275). A poorly-built ammonia tank broke upon completion of hydraulic testing, killing 18 in South Africa (No. 5348). In Rotterdam (No. 23866), insufficient wall thickness of the tube used for a heating coil led to a vapour leak that generated a pressure wave and eventually the rupture of a tank containing 1,600 m^3 of ortho-cresol.

Accident analyses have shown that large-volume tanks, even if adequately designed, can still break **during operations** when subjected to excessive stresses. In several cases, pressure surges followed by tank explosions have been recorded: beet molasses fermentation while tank vents were obstructed (No. 4138), the accidental introduction of a product with a low boiling point into a heated tank (Italy, No. 32829), or "hot" ammonia added into a cryogenic tank (No. 717). In France's Roussillon region (No. 22987), a tank ruptured after it had been inadvertently placed in a vacuum then returned to atmospheric pressure. Another accident occurred in Guingamp (No. 6887), where a poorly-fastened tank collapsed emptying its 150 m^3 of milk. Lastly, in the town of Berre l'Etang (No. 163), a 15,000-m^3 hydrocarbon tank tore apart while being filled, after being subjected to a hydraulic overload. An analysis of the initial causes of such accidents has revealed the lack of organizational procedure, handling errors, flawed planning or poor judgment of the situation all play a part.

Ensuring high levels of structural resistance over time necessitates regular **maintenance** in accordance with a set of normalized, applied and well-controlled operating procedures, which may be accompanied by professional guides[1] (for inspection, maintenance, etc.) focusing on reservoirs. Detection of corrosion phenomena proves essential and, in some instances, relies upon enhanced methods. An assessment of tank shell or floor thickness reductions is indeed crucial since such reductions are capable of leading to a loss of sealant, thereby lowering tank strength and bringing about sudden rupture. This phenomenon has been illustrated by depot accidents occurring in both Antwerp (No. 30934) and Ambes (No. 32675), containing 37,000 m^3 and 12,000 m^3 of crude oil respectively and generating wave effects. In Rouen (No. 15725), failure to respect works program sequencing procedures caused a tank of phosphoric acid to collapse.

Despite occurring less frequently, **external aggressions** constitute another known cause of failure in large-capacity tanks. In Japan, a powerful earthquake destroyed three *Top Crude* tanks with a capacity of 23,000 m³ each (No. 6307). The accident might also have been triggered by equipment or utility infrastructure separate from the site's main activity: a leak in a water main caused flooding in the foundations of a tank that abruptly collapsed, releasing 11,000 tons of H_2SO_4 (No. 29133). It is thus pivotal for risk analyses conducted on large-capacity tanks to incorporate not only those risks intrinsic to the activity itself but also a number of contextual elements specific to each organizational set-up (natural phenomena, neighbouring facilities, topography, etc.).

Beyond the risk prevention means available, it is imperative for mitigation measures to be evaluated by considering the effects of a potential tank rupture. More specifically, accident analysis has shown that retaining walls rarely fulfil their confinement role when subjected to wave effects: either their strength proves insufficient and they break (Nos. 2201, 15725) or they lack the necessary height and the wave passes over (Nos. 163, 6307, 30934, 32675).

The rupture of these large-capacity tanks brings about physical injuries (fatal in some cases), serious environmental pollution and domino effects for adjacent installations. The property damage and economic impacts consequently tend to be considerable. Guided by feedback from experience, tank failures now lie beyond the realm of mere theoretical scenarios. Though these large-scale facilities seem to be rather "passive" in their application, they must at every stage of their life cycle undergo a thorough risk analysis and receive attention commensurate with the potential losses they can generate.

Accidents whose ARIA number has not been underlined are described on the site:
www.aria.ecologie.gouv.fr

[1] As an example, see "Guide for the inspection and maintenance of aboveground, cylindrical and vertical metal reservoirs containing liquid hydrocarbons in a refinery setting", UFIP, August 2000.

ARIA 163 - 12/25/1988 - BOUCHES (13) - BERRE-L'ETANG

23.2Z - Oil refining

Within a refinery storage zone, the shell of a fragile 15,000-m³ tank (at the end of its filling cycle) containing 13,500 m³ of HTS residue (at 130℃) split open. The flow of HC then destroyed two other tanks (15,000 m³ each) located in the same retention basin. The wave submerged the dike walls and flooded a 8-ha area of the site. During this incident, pipes burst (including a GO pipe) or got repositioned. The absence of an ignition source prevented the outbreak of fire. Rerouting the flow into a stormwater basin and installing a floating boom avoided pollution from spreading into a nearby pond. Submitted to a hydraulic overload (at the highest filling level heretofore ever reached), cracking initiated on a door weld in the lower part of the tank and then propagated by means of ductile fracture.

ARIA 717 - 03/20/1989 - LITHUANIA - JONOVA

24.1J - Production of fertilizer and nitrogen compounds

In a fertilizer plant located 12 km from a city with 40,000 population, a cryogenic ammonia (NH_3) tank weighing 10,000 tons and filled to 70% capacity suddenly experienced a pressure rise and burst at its base. Under the impact of the wave gushing through the gaping opening, the tank separated from its platform, was pushed in the opposite direction and destroyed the reinforced concrete protection wall before coming to a stop 40 m from its foundations. A 70-cm high pool of liquid NH_3 spread over the site and took 12 hours to fully evaporate. A flare stack ignited the vapours emitted and the fire reached the 55-kt NPK storage area; the thermal decomposition of these stocks lasted 3 days. The toxic cloud (NH_3, NO_x) contaminated a an area extending over 400 km². The official casualty reports indicated 7 dead and 57 injured among the plant's operating personnel and construction crews working in the area. Local authorities evacuated the high-risk zones once the ammonia concentration of the air had exceeded 10 mg/m³; in all, 32,000 people were displaced.

The single-sided ammonia tank, insulated using perlite, was fed by a production unit (at a rate of 1,400 tons/day) located 600 m away. A few hours prior to the accident, one of the two liquefaction turbochargers was shut down for some lengthy repair work. One hour before, the second turbocharger was stopped for a short repair job. Operators were not easily able to activate the backup piston compressor and rerouted the NH_3 flow to a pressurized storage area. Fourteen tons of hot NH_3 (+ 10℃) were nonetheless introduced into the lower part of the cryogenic tank, whose gaseous atmosphere rose quickly in pressure. Despite the presence of relief valves, the tank bottom deformed and then burst. The rollover phenomenon anticipated by some was not confirmed by expert assessment.

The subsequent investigations showed:

- that greater strength of the tank lid, in comparison with the bonds in place between the internal chamber sidewall and the tank bottom or with anchoring brackets, caused tank failure at its base, as the tank bottom remained fastened to the foundations;
- the liquid ammonia wave caused the protection wall to break, before spreading over a much wider surface area; and
- since protection wall strength was not in compliance with the specifications stipulated during plant design as a result of modifications made at the time of construction in order to reduce material and labour costs. During construction, other modifications were supposedly introduced for the same reasons at the storage foundations and its anchorage device.

ARIA 4138 - 11/20/1992 - MARNE (51) - CHALONS-EN-CHAMPAGNE

51.2A - Cereal and livestock feed wholesaler

Following a tank explosion, 1,200 tons of beet molasses spread over the ground and then into the Le Mau river. One week later, the pollution became concentrated near a lock on the Marne Canal. Thousands of fish were found dead, yet 3 to 5 tons could be saved by transfer into the Marne River. A neighbouring and similar tank was drained as a precautionary measure. A metallurgical examination revealed a poor-quality tank (cracked welds, lack of a chamfer). The low concrete walls of the retention basin were not able to resist the flow pressure. The eventual tank rupture was likely due to a pressure surge subsequent to molasses fermentation coupled with vent obstruction. Storage was removed from the site.

ARIA 5348 - 07/13/1973 - SOUTH AFRICA - POTCHEFSTROOM

24.1J - Production of fertilizer and nitrogen compounds

Within a fertilizer plant, a cylindrical horizontal tank containing 50 tons of ammonia under pressure (6.2 bar) failed during unloading, releasing 30 tons of NH_3, with 8 tons escaping from the tanker truck. A cloud measuring 150 m in diameter and 20 m high immediately formed and extended a total of 450 m. An employee standing 45 m from the tank at the time of the explosion was killed instantly. In all, 18 people died, 6 of whom were located outside the plant and 65 intoxicated to a point of requiring hospitalisation. The burst tank bottom was composed of two metal panels (one wide and one narrow) assembled by welding before the forming operation undertaken for the tank bottom. The rupture occurred transversally to this bottom weld, with a quarter of the bottom surface separating, practically without any deformation, and being projected. The point of failure surrounded a zone where 2 years prior metal rolling flaws had been detected during an ultrasound inspection; these flaws were subsequently repaired with welds. The investigation performed indicated various causes of rupture, including: failure to release tension on the device following construction, a tank bottom metal plate warped and deteriorated due to the cold forming operation applied to the large tank radius, and the introduction of additional stresses from hydraulic testing performed a few days prior.

ARIA 5421 - 10/02/1984 - UNITED STATES - GEISMAR

24.1J - Production of fertilizer and nitrogen compounds

Inside a fertilizer plant, the splitting of a 15,000-ton cryogenic ammonia storage tank at the joint between the tank skirt and roof placed 9,200 tons of NH_3 into contact with the atmosphere, with the rupture extending 2/3 of the way around the storage circumference. Concentrations of 150 to 400 ppm of NH_3 were measured, under windy conditions, during the 6-hour period following the accident. No environmental impact was noted. The accident was caused by a defective weld between the tank shell and dome. A metallurgical expert assessment indicated that the weld displayed major penetration flaws, and these flaws would have worsened by exposure to metal fatigue effects due to pressure cycles. The analogue pressure recording at the time of the accident revealed the presence of a pressure surge (not quantified since the measurement scale had been surpassed) when rupture occurred, yet computations still showed that the pressure increase speed before the accident had a normal value. Furthermore, the weld break over 2/3 of the tank circumference induced deformation of the vertical sidewall, which could have led to tank failure below the liquid level.

ARIA 6307 - 06/21/1978 - JAPAN - SENDAI

23.2Z - Oil refining

A Japanese refinery experienced damage from the Miyagi-Ken-Oki earthquake whose epicentre was 100 km away (magnitude = 7.4, local horizontal acceleration of between 1/5 and 1/3 g). The most serious property damage, concentrated east of the refinery's 160-ha site, primarily concerned three tanks with fixed roofs containing 23,000 m^3 of Top Crude, produced as black crude from a topping unit. Subsequent to the breaks caused on the shell/bottom welds, 68,100 m^3 of product were spilled into the retention basin common to the three tanks, having a total capacity of only 23,000 m^3. The excess quantity then spread over the entire site and flowed outside the installation until reaching the port. The site's spherical LPG tanks fitted with 10 legs reinforced by thick cross-braces remained intact. All of the refining units were fully inspected prior to restarting operations.

ARIA 15725 - 04/23/1999 - SEINE MARITIME (76) - ROUEN

24.1J - Production of fertilizer and nitrogen compounds

An older lead-lined steel tank (diameter: 8 m, height: 9 m, bottom thickness: 8 mm, shell thickness: 5-7 mm) containing 450 m^3 of phosphoric acid burst at a chemical facility. The acid wave destroyed the reinforced concrete retention basin (with a combined core and wall thickness of between 10 and 15 cm). An in-house inspection had detected considerable corrosion on a generator and led to requesting a thickness verification. The maintenance team proceeded by locally reinforcing the tank (6-mm polyester layer, etc.) without actually performing the requested controls. The proper works sequencing procedure was not respected and consideration was not given to the fact that this site had been programmed to shut down over the near term. The strength loss subsequently detected, related to a localized leak in the lead lining, affected 4/5th of total tank height. No serious environmental impact was observed. An emergency order was issued, and all site personnel were reminded of applicable procedures and informed of the inspectors' guidelines.

ARIA 22987 - 08/02/2002 - ISERE (38) - ROUSSILLON

24.1E - Production of other inorganic basic chemical compounds

Within a chemical plant, an operator noticed the day before around 8 pm a deformation caused by the accidental pressure drawdown of a 100 m^3 storage tank shortly following filling with hot para-nitrophenol. This pressure drop resulted from the intake of a cold substance into the gas cover of the reservoir, due to introduction of a carousel. The accident occurred the next day, with the metallic reservoir roof breaking apart subsequent to a pneumatic rupture during tank pressurization by means of heating and evaporation of water content. The rupture surface extended along the roof/shell weld. Several tens of kg of a yellowish-orange chemical substance projected into the air fell as a spray both into and outside the facility; some 10 kg of the substance surprised motorists travelling in the area, whose vehicles became spotted with colour in very little time. The plant's medical unit treated 6 individuals suffering from a stinging sensation after washing their cars. The 50 m of pavement contaminated by the falling substance were flushed with large quantities of water. Once collected and treated initially in an external water treatment facility, the washing water was discharged into the site's sewer system and treated onsite. Total cost of the incident was estimated at € 100,000. The accident had two apparent causes: the rise in tank pressure introduced without any suitable preliminary analysis (i.e. conducted by the assigned operator alone, an informal unwritten operating procedure), and the presence on the liquid seal of a 3-channel valve that one of the broken thrust bearings could position in such a way to isolate the tank from all vents. This position was subsequently eliminated and all valves checked in order to prohibit such a position; moreover, operating procedures were modified to include shutdown of the nitrogen supply network and definition of exceptional operations requiring constitution of a preliminary working group, with a written formalization of conclusions.

ARIA 23866 - 01/16/2003 - THE NETHERLANDS - ROTTERDAM

51.5A - Fuel wholesaler

In a dockside warehouse of oil and petroleum products, a reservoir containing 1,600 m^3 of ortho-cresol broke and a vapour cloud rose in the direction of the nearby Rotterdam metropolitan area. The reservoir collapsed on one of its sides and the roof came loose and slid into the basin. The ortho-cresol, a corrosive, toxic and highly-pungent product, then spread over more than 3 ha of site land area. The accident caused no casualties. Local authorities took control of the terminal during the crisis period. Neighbouring industrial activities were shut down. In addition, sirens were sounded in the adjacent city, public transit service was halted and authorities requested the local population to remain indoors with windows and doors closed. River traffic on the Nieuwe Maas watercourse was also interrupted as was rail traffic on the Rotterdam-Hoek van Holland line. Following the accident, the top priority was site cleanup (consisting of clearing reservoir peripheries and cleaning the retention basin), mitigation of strong odours in the immediate area, and public communications. In all, 17,000 tons of earth were polluted. This accident resulted from failure of the vapour coils, which were composed of a material assembly that lacked sufficient thickness over a 10-cm long segment and that displayed corrosion on the internal surface.

Vapour had penetrated into the reservoir, causing turbulence as well as pressure waves. The vapour pressure reached 7 bar inside the tank, which was full at 96% capacity. With the presence of a weaker zone on the shell caused by a poor-quality weld, the reservoir broke, due not to the vapour expansion-induced pressure surge but rather to the pressure waves.

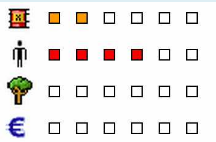
ARIA 29133 - 02/04/2005 - SWEDEN - HELSINGBORG

24.1E - Production of other inorganic basic chemical compounds

In a chemical plant, a 20,000-ton capacity tank containing sulfuric acid exploded, releasing 11,000 tons of H_2SO_4. Upon spreading into the neighbouring port, the acid mixed with water and formed an expansive toxic cloud. A safety zone was cordoned off covering the entire city and the 110,000 residents were requested to remain indoors; this advisory remained in effect for 4 hours. The casualty count stood at 13 injured (6 employees, 2 rescue workers and 5 members of the public) suffering from slight respiratory problems and eye irritations. The wind, which was blowing out to sea and not towards the city, helped disperse the cloud. The accident was found to be due to a burst water pipe that inundated the ground supporting the acid storage facility, destabilizing the soil to a point of causing the tank to break.

Ammonia leak in Nemours (Seine-et-Marne)

ARIA 29687 - 04/23/2005 - Seine-et-Marne (77) - NEMOURS
63.1D - Cold storage

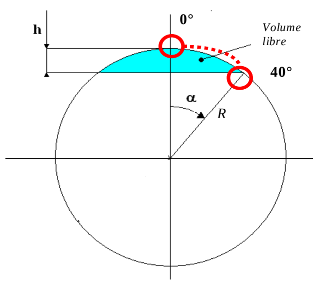


An ammonia container or pressurised drum (NH_3) was leaking within a frozen foods warehouse located in an industrial estate. The accident occurred at the time a refrigerating unit condenser was being replaced after being partially emptied of its NH_3 contents the previous day; 1,500 kg of NH_3 at -18℃ were transferred into four 930-litre (450-kg) drums rented to a chemicals distributor by the refrigerationist in charge of the works. Three full drums and a fourth, half-full drum were stored outside the warehouse under night-time supervision.

The following day at 11:50 am and with these containers not having been handled in the meantime, one of drums built in 1998 and then recertified in 2003 (49-bar water pressure, 32.5-bar static pressure, -20 ℃ < T < +50 ℃ tempe rature) abruptly burst. The internal contingency plan was activated at 12:15 am and significant human and material resources were deployed: a hundred firefighters, around forty vehicles and 2 helicopters. A toxic cloud was responsible for causing physical irritations to about 100 individuals at the industrial site (including 21 warehouse employees) and, 200 m from the drums, at a motorway rest stop where several cars were parked. 52 injuries were reported, of which 28 required hospitalisation for analyses into the evening, 5 of these individuals suffered from more serious cases: 2 gendarmes, 1 warehouse forklift driver, and 2 asthmatics.

A 150-m safety zone was cordoned off and a street closed to traffic; highway message signs informed motorists that the rest stop was not open and that vehicle windows should be closed and ventilation systems turned off. Firefighters wearing masks dispersed the NH_3 fumes using peacock tail spray nozzles. In order to maintain sufficient retention capacity, the dilution water collected in a 300-m³ catchpit was discharged into the network following a pH reading (8 to 9), 550 m³ were thus used. The intact NH_3 barrels were then transferred into the refrigeration unit. The motorway rest area was reopened at 9:26 pm, and the incident was completely over around 10:00 pm.

An expert evaluation noted that the pressure equipment ruptured as a result of overfilling attributable "inappropriate" operating procedures and recommended that drums be systematically weighed. According to the CII (Classified Installations Inspectorate), the procedure is particularly difficult to perform: careful positioning of the "multi-purpose" drum on its side at an angle of 40° so that the 85 or 100% top-up limiting tube can serve its purpose. In addition, these drums are liable to contain liquefied gases or liquids according to 2 marks painted on its side... This setting is nevertheless imprecise as the end of the tube, based on its design, can vary in distance from the wall of the cylinder. The mixing of products (water / NH3...) can also not be disregarded due to the multipurpose nature of the arrangement. Finally, systematic weighing may also be difficult: cramped machine rooms... A room adjoining the machine room and connected to the latter's stack, capable of resisting a heat flux and equipped with an appropriate detection system, shall be built to store the containers. The internal contingency plan has been reinforced. A more formal approach has been taken in developing the mobile tank filling/draining procedures.



Photos : DRIRE Ile-de-France

Ammonia and ammonia water tank failures

The accident presented above focuses on the rupture of an overfilled liquid NH_3 container caused by an inappropriate operating procedure or at least one that is difficult to implement. Some forty cases of failure or serious damage to tanks and other fixed or mobile capacity devices containing NH_3, in liquefied cryogenic form, pressurised, gaseous, or in solution (NH_3, H_20), have also been identified in the ARIA database. The corresponding events were responsible for 15 fatal accidents resulting in 201 deaths.

One historic accident, in which the base of a cryogenic tank containing 10,000 tons of NH_3 burst in Lithuania (No. 717), was caused by several factors, extending back to an initial installation design that sought to cut costs, especially during storage operations (run in downgraded mode). The addition of 14 tons of hot NH_3 into the lower part of the tank, in bypassing the defective cooling unit and undersized valves, was enough to explain the pressurisation of the tank's entire capacity. Another tank failure, this time on the upper part, was also recorded in 1984 in the United States (No. 5421) due to weld penetration flaws in association with metal fatigue, directly correlated with pressure cycles. More recently (2005) in Germany (No. 29517), a double-walled steel cryogenic tank that had just been placed back into operation burst following the introduction, as specified in the procedure - yet at a slower rate, of cold NH_3 into an ammonia water solution.

The rupture of several fixed or mobile capacity devices for pressurised liquefied NH_3 has been loaded into the database. The most serious accident pertained to the abrupt opening in Dakar (1992) of a tanker truck awaiting to be unloaded in a plant treating oilseeds (No. 3485); 129 were either killed instantly or contracted the highly-fatal wet lung disease and a total of 1,150 injuries were reported. The accident was due to a regular pattern of overfilling the tank, with the rupture occurring at the level of a repair weld performed after a leak had been discovered 2 years earlier. Another accident involving a faulty weld and stress corrosion also occurred on a tank in Lievin (Pas-de-Calais, 62) in 1968 (No. 4988). A fixed cylindrical tank broke during filling in South Africa in 1973 (No. 5348) subsequent to flawed construction techniques (the tank failed to be relieved of its internal stresses following construction, the bottom metal plate was degraded by the same type of cold forming process...) and additional stresses after a hydraulic test conducted a few days earlier. Metal fatigue, defective welds, corrosion activated by humidity or pH, and the use of recycled equipment have been cited in other accidents (Nos. 5274, 5384, 15585, 24126 and 24897).

As a result of a domino effect during a fire, several Boiling Liquid Expanding Vapour Explosions (BLEVE) on tanks used to store NH_3 have occurred at refrigeration installations (Nos. 5272, 5275, 11547 and 15585) or other facilities (Nos. 5390 and 5412). A 20% ammonia water tank rupture due to exposure to a straw fire is also included in the database (No. 5826).

While being stored on docks or in industrial zones, a few cylinder and container ruptures, whether caused by exposure to the sun or not, have also been recorded (Nos. 5442, 6959, 14298, 24897 and 31699); even before an eventual overheating of the tanks, overfilling undoubtedly constitutes the primary cause of such accidents. The errors committed in this area show up regularly: inadequate or inaccurate preliminary inspection of the tank when taking level measurements, or poor calibration readings (Nos. 3485, 6959), failure to monitor tank filling (Nos. 24897(?) and 31699), associated or not with deficient equipment (No. 14880). Even more insidious, a simple physical phenomenon related to differential pressures can lead to overfilling a storage capacity or siphoning interconnected tanks (Nos. 14880 and 31699). Another case worth mentioning involved an unloading error, fortunately without any serious consequences, whereby a vinyl chloride tanker car was drained into an ammonia sphere (No. 28851). Luckily, the two substances were not reactive with one another and must have been at equivalent pressures.

NH_3 is considered not easily ignitable. Ignition of an NH_3 cloud in an unconfined environment (outside a building) has only been cited on one occasion (No. 717); the presence of hydrogen however cannot be fully excluded. Several ignitions of the gaseous atmosphere, with possible explosion or implosion of the tank, were nonetheless inventoried (Nos. 120, 15585, 14880 and 16078(?)); such incidents typically arise while conducting works and often result from a lack of communication between onsite personnel. In some cases that entail a refrigeration installation, the presence of powdered oil (for compressor use) might also have triggered cloud ignition.

Furthermore, some explosions were accompanied by missile projections ranging between several tens to several hundreds of meters (Nos. 120, 3485, 4988, 5384, 14298 and 15585).

Given the progress accomplished in the field of metallurgy, along with the current state-of-the-art and rules, both the "resiliency" and "fatigue" factors that could have caused accidents in the more distant past are only rarely cited nowadays. In contrast, organisational flaws and human error remain very much present, as the overview provided below can attest.

Accidents whose ARIA number has not been underlined are described on the site:

www.aria.ecologie.gouv.fr

ARIA 717 - 03/20/1989 - LITHUANIA - JONOVA

24.1J - Production of fertiliser and nitrogen compounds

In a fertiliser plant that has been operating since 1969 and located 12 km from a city having a population of 40,000, a 10,000-ton cryogenic ammonia (NH_3) tank filled to 70% capacity rose in pressure and burst at its base. The wave that escaped from the gaping opening loosened the tank from its base. Thrust in the opposite direction, it destroyed the protective reinforced concrete wall and shifted 40 m from its foundations. The NH_3 liquid jet stream created a pool 70 cm deep, spreading over the site and requiring 12 hours to fully evaporate. The vapours emitted were strong enough be ignited by a flare stack, and the fire reached the 55-kt of NPK stored on site; the thermal decomposition of these stocks lasted 3 days. The toxic cloud (NH_3, NO_x) contaminated a zone spreading over 400 km². The official accident report included 7 dead and 57 injured among the plant's operating personnel and construction crews working in the area. Local authorities ordered the evacuation of all high-risk zones once the NH_3 concentration in the air had exceeded 10 mg/m³. In all, 32,000 people were displaced.

With a Japanese design, the single-sided perlite insulated tank was fed by a production unit, at a rate of 1,400 tons/day, located 600 m away. A few hours prior to the accident, one of the two liquefaction turbochargers was shut down for some lengthy repair work. The second turbocharger was stopped for a short repair job one hour before. Operators were not easily able to activate the backup piston compressor and rerouted the NH_3 flow to a pressurised storage area. 14 tons of hot NH_3 (+ 10℃) were nonetheless introduced into the lower part of the cryogenic tank, whose gas cover rose quickly in pressure. Despite the presence of relief valves, the tank bottom deformed and burst. The rollover phenomenon anticipated by some was not confirmed by expert assessment.

The subsequent investigations showed:

- that greater strength of the lid, in comparison with the bonds in place between the internal chamber sidewall and the tank bottom or with anchoring brackets, caused tank failure at its base, as the tank bottom remained fastened to the foundations;
- the liquid NH_3 wave caused the protection wall to break and spread over a much wider surface area, thereby exacerbating the impact of this accident; and
- a protection wall strength noncompliant with specifications stipulated during plant design as a result of modifications made at the time of construction in order to reduce material and labour costs. Other modifications were also introduced for this same reason at the storage foundations and anchorage systems.

ARIA 3485 - 03/24/1992 - SENEGAL - DAKAR

15.4C - Production of oils and refined fats

A unconnected tanker truck carrying liquid ammonia (NH_3) burst open at an industrial facility. Propelled by chemical reaction, with the front part "of the tanker clipped some of the installations then smashed into the wall of an electrical service building, while the back part angled at 45° upward violently smashed against the reinforced concrete lintel of a neighbouring building, then ricocheted in the direction of the unit, seriously damaging its upper level. An axle was found 200 m away on a nearby site. A portion of the 22 tons of NH_3 contained in the tank spread through the installation, while another portion was projected with the back of the tank beyond the site boundary. According to eyewitness accounts, the whitish toxic cloud moved about 250 m and dissipated within 10 to 15 min. Liquid NH_3 projection lengths reached some 30 meters. The noxious atmosphere hindered the emergency intervention team, which was not equipped with adequate protection, including masks and oxygen cylinders. Both the time (1:30 pm, as a new shift was taking over) and the place of the accident, near the port's industrial rehabilitation zone, would explain in part the tremendous number of casualties: 129 dead and 1,150 injured, with some victims being burned directly by NH_3 or intoxicated by NH_3 vapours. Other victims with outbreaks of lesions were diagnosed as not serious at first, but went on to develop a fatal pulmonary oedema just a few days later. According to the press, onlookers heard the sound of the explosion and flocked towards the contaminated zone, only to fall victim to the accident as well.

This accident was due to overfilling of the tank (22.2 tons for a 17.7-ton capacity), which seems to reflect frequent practice. The tank broke at the level of a repair weld performed 2 years prior upon detection of a leak during a hydraulic test.

ARIA 4988 - 08/21/1968 - PAS DE CALAIS (62) - LIEVIN

24.1J - Production of fertiliser and nitrogen compounds

A tanker truck containing 19 tons of ammonia (NH_3) burst open during an unloading operation. A toxic cloud (1.5 km long, 150 to 400 m across, with wind blowing at 1 m/s and fog observed over the first 300 to 400 meters) surprised employees exiting the cafeteria. The front of the tank and the tractor-trailer were propelled 26 m by the gas pressure release and crashed through a 22-cm wall of a disused workshop before being stopped by a second wall. The back of the tank was held in place by piping running through the plant. The driver and two plant workers were killed instantly, and 7 other employees (3 of whom died in the days following) and 20 local residents were hospitalised. The tank's baffle plates were found some 25 to 30 m from the site of the explosion. The rupture, which caused the accident, was tangent to an weld bead of an internal iron support on which one of the tanker's baffle plates was mounted. Another internal weld bead showed signs of a weld executed after a rather primitive assembly, subsequent to a repair performed on the tank that had been deformed by an impact which occurred 2 or 3 years earlier. The accident was due to corrosion under stress exposure (high-resistance T1 steel + NH_3 + stresses).

ARIA 5348 - 7/13/1973 - SOUTH AFRICA - POTCHEFSTROOM

24.1J - Production of fertiliser and nitrogen compounds

A cylindrical tank containing 50 tons of ammonia (NH_3) under pressure (6.2 bar) failed during an unloading operation in a fertiliser plant, releasing 30 tons of NH_3, with 8 tons also escaping from the tanker truck. A cloud 150 m in diameter and 20 m high formed and spread over 450 m. The explosion immediately killed an employee located 45 m from the tank. In all, 18 people died, 6 of whom were off site, and another 65 intoxicated to a point of requiring hospitalisation. The tank bottom was composed of wide and narrow metal panels welded together before the forming operation on the tank bottom. The rupture occurred transversally to this bottom weld, with a quarter of the bottom surface separating, practically without any deformation, and then being projected. The point of failure surrounded a zone where 2 years prior metal rolling flaws had been detected during an ultrasound inspection; these flaws were subsequently repaired with welds. The investigation performed indicated various causes of rupture: failure to release tension on the device following construction, a tank bottom metal plate warped and deteriorated due to the cold forming operation applied to the large tank radius, and the introduction of additional stresses from hydraulic testing undertaken a few days prior.

ARIA 5421 - 10/2/1984 - UNITED STATES - GEISMAR

24.1J - Production of fertiliser and nitrogen compounds

Inside a fertiliser plant, a 15,000-ton cryogenic ammonia (NH_3) storage tank split open at the joint between the tank skirt and the roof, placing 9,200 tons of NH_3 into contact with the atmosphere. Concentrations of 150 to 400 ppm of NH_3 were measured, under windy conditions, during a 6-hour period thereafter. The accident was caused by a defective weld between the tank shell and dome. A metallurgical expert assessment indicated that the weld displayed major penetration flaws, and these flaws would have worsened by exposure to metal fatigue effects due to pressure cycles. The analogue pressure recording revealed the presence of a pressure surge (not quantified since the measurement scale had been surpassed) when rupture occurred, yet computations still showed that the pressure increase speed before the accident had a normal value. Furthermore, the weld break over 2/3 of the tank circumference induced deformation of the vertical sidewall, which could have led to tank failure below the liquid level.

ARIA 6959 - 05/02/1995 - PYRÉNÉES-ATLANTIQUE (64) - PARDIES

63.1E - Non-refrigerated warehousing

A 50-kg cylinder of liquefied ammonia exploded on a storage site; 9 other cylinders were also damaged. The tank had been filled on April 18 with a 64-kg load of ammonia subsequent to a calibration reading error. The toxic cloud dispersed quickly and no impact on human health was reported. The tank was submitted to an expert evaluation.

ARIA 11547 - 08/19/1997 - SEINE MARITIME (76) - LE HAVRE

63.1D - Refrigerated warehousing

An arsonist struck at 4:20 in a warehouse of 30,000 m² in floor area and built on two levels, housing an archives room and an empty refrigerated hangar (on the ground floor) that included a shutdown refrigeration unit containing 5 tons of ammonia (NH_3). The flame front was measured at 350 meters 15 min after the warning. A safety perimeter was established and major resources deployed: around 100 fire-fighters, and 2 ocean-going tugs. Evapo-condensers exploded during the fire, releasing 2 tons of gaseous NH_3 into the atmosphere. A CMIC imaging centre performed sample extraction (4 ppm of NH_3 in onsite fumes, negative at 300 and 1,200 m). Under control by the end of the day, the accident caused no casualties. The heavy property damage estimates came in at 115 million francs. The refrigeration unit was drained in the following days and the NH_3 was stored in containers.

ARIA 15585 - 12/08/1969 - NORD (59) - DOUAI

15.9N - Brewery

An explosion and ammonia leak (NH_3) occurred 30 minutes following start-up of a brewery refrigeration unit. An employee sustained eye burns. A second explosion with flames then occurred. A liquid NH_3 tank (475 litres, 12 bar), at the condenser output, was connected to an overheating cylinder by a pipe fitted with a lens and a manually-adjusted valve to pulverise the NH_3 into droplets and lower pressure to that of the cylinder. The leak occurred on this recycled, modified tank adapted to the unit, which displayed penetration-free welds. The NH_3 that filled the premises ignited with a spark from the electrical cabinet (destroyed by the explosion), or on the bare light bulbs used to illuminate the room, or the glass level (broken by the cold NH_3 vapours); the tank then exploded from the heat. A 2-m^2 hole was ripped through a 25-cm wall, a staircase was moved 10 cm, and the tank bottom was projected a full 15 m. The site was closed the following year.

ARIA 28851 - 06/27/1977 - ISÈRE (38) - ROUSSILLON

24.1G - Production of other basic organic chemical compounds

At a chemical site, a tanker car containing vinyl chloride was drained into ammonia spheres. No visible impact on the storage facilities was recorded due to the non-reactivity of both chemical products, yet the production line of a workshop had to be shut down. The numbers and data sheets from the tank had not been verified by the personnel responsible for conducting material transfer operations and by the subcontractor assigned to handle the tank. The incident was due to the absence of verification testing prior to drainage and to the adaptation of tanker car orifices to the transfer mechanism by use of flanges exterior to the transfer station. The procedures for both vehicle identification and armguard use were reminded to all personnel and a procedure was implemented regarding the identification of products for discharge.

ARIA 29517 - 01/04/2005 - GERMANY - ROSTOCK

24.1J - Production of fertiliser and nitrogen compounds

At a chemical site, a double-walled steel cryogenic tank of anhydrous ammonia (NH_3) with a capacity of 11,800 tons burst during filling after a down period for maintenance; 105 tons of NH_3 were released into the atmosphere (30 tons from the pressure surge). One employee was seriously injured. The tank had been turned off and drained, yet not inerted, 5 months prior in order to change the two bottom valves which had been leaking slightly. Restart operations then proceeded according to a well-defined process: introduction of 20% cold ammonia water (NH_4OH) to protect the tank bottom (over 25 cm), followed by spraying by the tank lid with cold anhydrous NH_3 to gradually return the storage chamber to its temperature. After around ten days, the anhydrous NH_3 introduced by spraying (30 additional cm at the tank bottom) enabled the temperature to be lowered to -20℃. The dec ision was thus made to fill the tank normally via the bottom valves. When the valves were opened, the pipes began to shake and a considerable pressure rise in the storage chamber was noticed until the shell of the tank bottom opened and lifted nearly a meter and a half off the ground, causing partial drainage of the contents. Despite the precautions taken, the anhydrous NH_3 and the 20% solution of NH_4OH mixed too rapidly, and the presence of oil in the tank would have been responsible for the accident. The oil would have formed a separating layer between the ammonia water and the anhydrous NH_3, and this separation would have broken upon opening the bottom valves, placing the NH_4OH and NH_3 in contact with one another too quickly.

ARIA 31699 - 12/26/2005 - HAUTE SAVOIE (74) - CLUSES

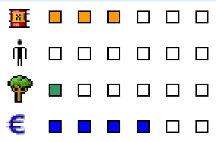
28.5A - Metal treatment and coating

Around 8:30 am, two cylinders of ammonia (NH_3) exploded in a metal surface treatment plant that had been shutdown for the Christmas holidays, with the personnel onsite solely performing maintenance tasks. A smell of NH_3 in the vacuum oven workshop drew the Maintenance Supervisor's attention. The two cylinders were connected to one of the two booms containing 5 cylinders each as part of the distribution system. The employees quickly brought over a tank filled with water to immerse the damaged cylinders and dissolve the remaining gas. A similar accident had already occurred during a summer downtime period on 08/18/2002 (ARIA 24897). An analysis was conducted in conjunction with the supplier. A new cylinder contains 85% liquid NH_3 and 15% gaseous phase. If several cylinders are in service on the same boom and one or more are at a slightly higher temperature than the others, a liquid NH_3 transfer may take place from the hottest cylinders towards the coldest: it is thus possible for one or more cylinders to fill during use. After a cylinder containing 100% liquid NH_3 is closed, a slight temperature rise could suffice to exceed its allowable pressure and cause an explosion. Following these two incidents, user instructions concerning the NH_3 installation were revised in order to specify the service start-up/shutdown steps, operating rules and cylinder changing procedure.

Oil spill in Nanterre

ARIA 30007 – 12/13/2004 - HAUTS DE SEINE (92) - NANTERRE

51.5A - Fuel wholesaler



As part of the ongoing dismantling taking place in a lubricant depot, a subcontractor disassembled aerial pipes connected to the depot network as well as their concrete foundations. During these operations, the removal of one of the blocks led to extracting a segment of underground pipe that neither the depot nor the subcontractor knew about and whose purpose was unclear. In reality, this pipe was one of the three supplying oil products to a neighbouring depot directly from the fuel transit terminal. On the morning of December 15, a fuel oil delivery intended for this depot was ordered. The delivery conveyed through the pipe that had been partially extracted 2 days earlier caused an oil spill. The depot operator, warned by the lubricant depot subcontractor, activated the emergency shutdown of the fuel transfer process in order to stop the leak, yet could not avoid the spillage of 370 m³ contained in the abandoned site. A shutdown order was served to the site operator on December 21 imposing remedial measures to be taken (site monitoring conditions, pollution assessment, pollution cleanup of the soil and subsoil, treatment of polluted ground, etc.).

The oil reached the underground water at 4 m deep but no immediate and mid-term contamination of neighbouring basin and of the SEINE was detected. Pumping capacities were settled on the site and on the neighbouring drainage system on December 16th : 3 months later, approximately 70% of the hydrocarbons were recovered. 2500 m² of soil needed decontamination : 1800 t of soil were excavated. The supplying of hydrocarbons by pipeline was suspended during 1 month, till the rehabilitation of the 3 pipelines. Total costs involved by this incidents, including decontamination, loss of production and material damages were assessed at 1,5 M€ including 550 000 €.for the rehabilitation of the 3 pipelines.

Measures shall be taken on both technical (hydrocarbon detectors at the carrier terminal manifold, tightness of bunds at the transfer and reception zones, installation of sound and/or visual alarm systems in the operational area of the oil terminal that indicates the start of tank filling) and organisational levels (revision of procedures on monitoring of reception by the pipeline during and outside working hours, drawing-up of a formal protocol stating the responsibility of pipeline and oil terminal operators). The document resources must be properly managed (plans of facilities at risk) and the site-related information and its background must be communicated to the sub-contractors for the successful completion of such types of projects.

Photo DR

Installation dismantling

The dismantling of an industrial facility or installations must be performed with care and close attention to detail. In many instances, this process actually entails fairly heavy work on a wide array of equipment, whose components are sometimes poorly understood or even completely unknown. Moreover, these operations are often carried out by specialized subcontractors that do not possess all the information on company history or on the installations they are being requested to dismantle. Against this backdrop, such operations necessitate an effective preparatory period that includes a comprehensive risk analysis and appropriate precautions to minimize the risk of hazardous substance discharge, fires, explosions, etc.

The **discharge of hazardous substances** represents the most frequent type of accidents recorded in the ARIA database. Given that dismantling operations cover all sectors of activity, the liquids capable of overflowing may be of any type: refrigerants (ammonia, sulfur dioxide), solvents (alcohol), gaseous, liquid or liquefied hydrocarbons (LPG, inflammable vapours, oil), PCB, acid baths and other liquid wastes. These accidents result, often, from an inadequately-prepared action conducted on an abandoned installation either as is or having undergone incomplete safety updates prior to the dismantling works: cut-off pipes or storage areas without having first been drained or degassed (Nos. 5292, 14711), parts connected to equipment still being operated and not yet recorded (No. 5905). Human errors and negligence also often lie at the origin of leaks: erroneous choice of pipe segment to be cut (Nos. 13023, 20284), inappropriate equipment handling (No. 14654) or use of valves (No. 6844), direct discharges into the natural environment or lack of precaution taken during draining or degassing steps (Nos. 5292, 5955, 10068, 20888, 31880), mix of chemical substances (No. 27101). Some equipment cannot be fully drained and the chemical products they contain continue to flow even after shutoff (No. 27463). Cases have been reported of shocks caused by construction vehicles inadvertently breaking pipes (No. 6025) or installations being dropped during dismantling and content disposal (No. 14605). These accidents often give rise to serious pollution of soils and natural environments (Nos. 10068, 14605, 20888, 27463, 31880) and, in some instances, even lead to disturbances or the temporary evacuation of neighbouring residents (Nos. 5955, 6025, 14605, 14654, 14711, 27101).

Fires frequently break out during dismantling operations that entail hot spots (e.g. a welding torch). Fires start at the level of the combustible materials that compose the structural frame of installation premises, are stored in the vicinity of the site (Nos. 16475, 19919, 31340), or that constitute the equipment undergoing dismantling (No. 20385). Accident statistics also point to fires involving residual inflammable gases (No. 14225), vapours and liquids (No. 15487), dust, residue and various chemical deposits contained in the machinery, or installations insufficiently cleaned prior to the dismantling works (Nos. 11784, 18224, 20212, 29547, 32118). Sparks caused by equipment dropped during dismantling (No. 17228), friction created as parts are disassembled (No. 25590), and error in the choice of element to be cut using the weld torch (No. 30107) may all serve to ignite a fire. Reinforced vigilance is also needed in determining how best to store the dismantled elements, especially should such elements have contained chemical substances capable of decomposing, depending on climatic conditions (rainfall, sunshine, cold, etc.) (No. 27576).

Potentially-fatal explosions sometimes occur on dismantling worksites; these often result from uncontrolled reactions that arise in order to neutralize residual chemical substances (Nos. 5135, 22170), or from the presence of inflammable gases and vapours within enclosed settings not fully degassed and inerted prior to the dismantling works, e.g.: reservoirs (No. 22998), chimneys (No. 22967) or pipes (No. 20109). The dismantling of explosives factories and pyrotechnics facilities necessitates reliance upon well-experienced crews (Nos. 25389, 28342).

Other accident typologies have also been identified, with effects that prove equally as lethal: intoxications of two plant workers not wearing any respiratory protection during decontamination of an electric transformer tank (No. 8143), heavy machinery falling on operations personnel (No. 31351).

The dismantling process requires considerable preparation, faultless task organization, and must be performed by operators adequately informed of the risks involved. Each of the following aspects must be thoroughly analysed with respect to the exposed risks: layout of work program and knowledge of the installation and machinery to be dismantled, implementation of durable site safety measures, protection of onsite contractors, use of well-adapted equipment (explosion-proof, etc.), work task coordination, adoption of operating procedures and management of wastes and recycled materials.

Accidents whose ARIA number has not been underlined are described on the site:

www.aria.ecologie.gouv.fr.

ARIA 5135 – 03/31/1994 - BOUCHES DU RHONE (13) - SAINT-PAUL-LES-DURANCE

73.1Z - Research & development in the physical and natural sciences

An explosion occurred inside a nuclear research centre at 5:45 pm, in the side gallery of a former experimental reactor that had been shut down for 10 years and was undergoing dismantling. The shockwave caused a 300-m² concrete slab to fall, devastating the nearby circular gallery. The body of a reactor staff member was found underneath the slab around 10:30 pm; four other individuals sustained multiple fractures and required hospitalisation. The explosion was caused by a pressure surge in a tank following the introduction of an alcohol intended to destroy 100 kg of sodium. No contamination was detected either on those injured or within the environment. The (alcohol-related) fire was quickly extinguished by the centre's emergency response team.

ARIA 5292 – 06/02/1994 - LANDES (40) - DAX

15.1E - Industrial preparation of meat-based products

Within a former cannery, little used over the previous 5 or 6 years, empty and undergoing renovation, a few litres of ammonia leaked out during the dismantling of a refrigeration installation while in a non-drained, non-operating state. Three workers cut through an ammonia transfer pipe and noticed, but did not report, a leak; they then left the area for lunch. Passers-by concerned over the odours being emitted notified firefighting services, which set up a water screen and spread a resinous acid dust to absorb and neutralize the ammonia (the pH of this resin was not modified). Upon their return, the three workers had to be hospitalised a few hours for observation. The accident had no impact on the environment.

ARIA 5905 – 04/11/1994 - UNITED KINGDOM - PURFLEET

51.5L - Chemical product wholesaler

In an oil and chemical product warehouse, a series of valves were disassembled on the supply line of a drum-filling station that was being demolished; certain components of this station were also used to supply the adjacent truck-loading station. At the time a vehicle was being loaded, 7,144 litres of ethanol escaped from the drum-filling station and flowed into the facility's sewer system. Onsite operators decided to let the product evaporate, and the emergency plan was not activated: the accident was of no consequence.

ARIA 5955 – 08/11/1994 - MARNE (51) - REIMS

15.9F - Champagne production

A champagne producer proceeded with the dismantling of a refrigeration installation shut down since 1990 and containing 280 kg of ammonia (45 kW rating). Two technicians from two subcontractors first recovered 250 kg of liquid NH_3 in 8 bottles specially intended for this operation. The installation was then degassed by immersing all pipes connected to the unit's various tapping points in a bucket filled with water. The saturated ammonia solution was then poured, undoubtedly in several sequences, into the manhole of the site's storm drains. Informed by a neighbour of the presence of ammonia odors in the city's sewer system, local firefighters solicited the Water Department to notify all personnel potentially working in the area.

ARIA 13023 – 06/15/1998 - MANCHE (50) - CONDE-SUR-VIRE

15.9J - Apple cider production

In a cider production facility, an ammonia leak occurred while dismantling a refrigeration set being replaced by a direct freon expansion device. A subcontractor disassembled the surrounding ice water pipes as of 10:30 am. At 2:50 pm, an NH_3 riser was mistakenly cut; the toxic gas released, between 600 and 700 kg out of the 1,200 kg of NH_3 contained in the unit; this quantity was spread into the disused room and a portion of the adjacent premises by means of pipe connections through the walls. The leak was contained by closing valves and the site was evacuated; a 100-m safety zone was cordoned off. One asthmatic employee was hospitalised as a precautionary measure. Firefighters removed the gas with nozzles, and the polluted water was treated onsite.

ARIA 14225 – 11/03/1998 - HERAULT (34) - LODEVE

23.3Z - Production and transformation of nuclear materials

During degassing of a 107-m^3 propane tank on an industrial site undergoing dismantling, some gas escaped from the reservoir and ignited, while at the same time operators were replacing flange bolts on the manhole. The three subcontractor employees experienced shock and were treated in hospital for relatively minor burns. The POI emergency plan was enacted, 100 employees evacuated and a safety zone cordoned off. Firefighters cooled the tank (the reservoir had not been operated since March 1998). The accident in fact had multiple causes: a defective manometer, which incorrectly indicated the absence of gas inside the tank; subcontractor procedural error by removing the manhole cover before filling the reservoir with water in order to speed reservoir draining; and subcontractor misjudgement - despite their experience with this type of operation - as evidenced by the failure to use explosion-proof equipment within a zone where their activity necessarily created an inflammable atmosphere.

ARIA 14605 – 12/17/1998 - LOIRE ATLANTIQUE (44) - NANTES

75.1A - General public administration

Within a municipal electrical control room, the failure of a sling caused the transformer to fall while being removed for eventual destruction; 400 litres of pyralene spread over the concrete floor forming a pool in the control room. PCB splashes hit the skin of two people and firefighters were called on the scene. The local prefecture ordered that the site be cleaned of pollution, with all liquid and solid waste being eliminated at an appropriate facility and with access to the installations being restricted during decontamination operations. The external environment was not adversely affected.

ARIA 14654 – 04/24/1996 - GERMANY - DRESDEN

YY.0Z - Undetermined activity

Prior to draining a refrigeration installation scheduled for dismantling and containing 6 tons of ammonia, a 5-kg NH_3 leak occurred while employees were attempting to extract a sample at the level of the liquid separator, for purposes of performing a qualitative analysis. The leak occurred when a protective shell was removed. This pressurized shell had been installed to enable connecting a relief valve to a test flange. Firefighters closed the valve with a pipe clamp. Twelve people were evacuated from adjacent offices and no casualties reported. A specialized company was contracted to extract the samples and then drain the installation.

ARIA 15487 – 03/02/1999 - PAS DE CALAIS (62) - VENDIN-LE-VIEIL

24.1G - Production of other basic organic chemical compounds

At a site that had remained derelict since 1997 and was undergoing dismantling, fire broke out when a subcontractor cut into a naphthalene tank using a weld torch. A thick cloud of non-toxic, yet highly-irritating, black smoke spread in the direction of two neighbouring towns. Firefighters used foam and were able to quickly contain the blaze without any casualties. Though it had been cleaned and inspected prior to the works, this tank design featured a double envelope where naphthalene could accumulate.

ARIA 17228 – 01/12/2000 - RHONE (69) - LYON

51.5A - Fuel wholesaler

In an oil depot closing its business, fire broke out in a tank undergoing dismantling. The internal floating screen of the reservoir fell during shearing, causing the metal panels of the screen to crack open and the component foams to ignite. This ignition could have been triggered by a spark generated as a roof panel fell; the tank was holding fuel and the fire was contained by the installation's in-house intervention teams.

ARIA 19919 – 02/01/2001 - AUDE (11) - PORT-LA-NOUVELLE

24.2Z - Production of agrochemical substances

Within an agro-pharmaceutical industry, phytosanitary products packaged in small quantities and palletised (1-ton loads) ignited underneath an awning positioned against an empty building that had previously contained sulfur in bulk storage. The first alarm sounded at 7:30 pm; for 3 hours, emergency teams tried in vain to extinguish the fire by spraying water, before control could be achieved in a matter of a few minutes once they resorted to using foam: 24 of the 83 tons of phytosanitary products (fungicides and growth substances) warehoused at the facility were destroyed. A subcontractor had removed the roof during the day and cut the building's wooden frame with a crosscut saw. The property loss was due to the heating and slow combustion of the wood, which would have been imperceptible at the time the work shift ended (the site was evacuated around 5:45 pm). The ignited beam that crossed through the partition wall extended beyond the awning. The fire grew due to the presence of sulfur residue on the walls and building structural frame and then spread to the packaged solid and liquid phytosanitary products, with combustion particles falling on the plastic covers. The loss of phytosanitary goods was estimated at 38,000 euros and the evacuation / incineration of the waste and contaminated soil at 185,000 euros. Piezometric monitoring allowed eliminating any soil pollution. An inspection of the regulated facilities incited the local prefect to request the operator to extend fire/work permitting procedures to the entire business, even outside zones with inflammable atmospheres, as the floors and walls would be better cleaned. Any subsequent action on this site will give rise to an inspection.

ARIA 20109 – 02/02/2001 - UNITED STATES - BURNS HARBOR

27.5C - Steel foundry

In a steel mill, explosion occurred while a disused blast furnace was being dismantled. According to the expert evaluation firm, initial elements indicated that maintenance crew were working in a room 6 meters below ground level, seriously limiting evacuation possibilities. They were disassembling a 25-cm diameter valve located on a blast-furnace coke gas supply pipe. Fuel still present in the pipe exploded and fire broke out. Among the 10 workers in the zone at the time, a mill employee and a member of the subcontractor's staff died and another 4 were injured (from smoke intoxication), one of whom in serious condition. According to the procedure employed, coke gas (mix of methane, hydrogen and carbon monoxide) was produced from coal, by means of a chemical combustion process, similar to that producing charcoal from wood. The gas was used as fuel, and the coke (solid) introduced into the steelmaking operation. The Chemical Safety Board, an independent American federal agency assigned to carry out technical evaluations of the accident, sent a team to the site to determine the precise causes of the accident.

ARIA 20212 – 04/03/2001 - LOT (46) - CAHORS

28.6F - Manufacturing of locks and fittings

During dismantling of a disused facility, which had formerly been devoted to collecting and filtering polishing dust and set up in an unoccupied room, some polishing residue (composed of tallow + aluminium dust + abrasives) contained in a concrete pipe ignited. A welding torch used to cut the bolts of piping fastened to the ground, a task typically contracted out, would have caused the fire. The personnel were not able to extinguish the blaze, but firefighting crew called onto the scene subsequently controlled the incident, which at no time threatened to spread beyond 4 meters of pipe length.

ARIA 22967 – 05/27/2002 - UNITED KINGDOM - WESTHOUGHTON

28.7C - Production of lightweight metal packaging

A violent explosion ripped through a chemical site during destruction of the installation's chimney. Two employees from the demolition company were positioned on a platform inside the chimney, some 35 m high, when the explosion reached the chimney, causing both to fall to their deaths. A spark might have suddenly triggered the ignition of chemical products impregnated into the chimney (perhaps on the lining). The HSE Office conducted an investigation to determine the exact causes of the accident.

ARIA 25389 – 08/19/2003 - VAL D'OISE (95) - SURVILLIERS

24.6A - Explosives factory

Around mid-afternoon, an explosion occurred in a cartridge workshop following demolition of a derelict building. Two people were seriously injured and 3 others in a state of shock. The plant operator was dismantling a shop area used between 1932 and 1983 to produce mercury fulminate, employed to produce the igniters installed to activate car airbags; the site was known for this specialized manufacturing. The dismantling operation consisted of destroying the smoke processing facility, composed of 44 refractory "bowls", by use of a power shovel. Two employees then sorted through the debris, with materials potentially contaminated by mercury separated from the others and placed in bags for eventual discharge via a special waste dump. The accident happened during this second phase of the operation, and the site was closed and secured. A judicial investigation was launched and the court appointed an expert. According to the initial technical assessments, pyrotechnic residues made more volatile by the various handling steps would have caused the explosion.

European scale of industrial accidents

Graphic presentation used in France

This severity scale was made official in 1994 by the Committee of Competent Authorities of the member States which oversees the application of the Seveso directive. It is based on 18 technical parameters designed to objectively characterise the effects or consequences of accidents: each of these 18 parameters include 6 levels. The highest level determines the accident's severity index.

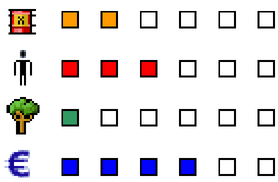
Further to difficulties which stemmed from the attribution of an overall index covering the consequences that are completely different according to the accidents, a new presentation of the European industrial accident scale with four indices was proposed. After having completed a large consultation of the various parties concerned in 2003, this proposal was retained by the Higher Council for Registered Installations. It includes the 18 parameters of the Europe scale in four uniform groups of effects or consequences:

- 2 parameters concern the quantities of dangerous materials involved,
- 7 parameters bear on the human and social aspects,
- 5 concern the environmental consequences,
- 4 refer to the financial aspects.

This presentation modifies neither the parameters nor the rating rules of the European scale.

The graphic charter adopted for the presentation of the 4 indices is as follows:

When the indices are yet explained elsewhere in the text, a simplified presentation, without the wordings, can be used:



Dangerous material released		1	2	3	4	5	6
Q1	Quantity Q of substance actually lost or released in relation to the « Seveso » threshold *	Q < 0,1 %	0,1 % ≤ Q < 1 %	1 % ≤ Q < 10 %	10 % ≤ Q < 100 %	De 1 à 10 fois le seuil	≥ 10 fois le seuil
Q2	Quantity Q of explosive substance having actually participated in the explosion (equivalent in TNT)	Q < 0,1 t	0,1 t ≤ Q < 1 t	1 t ≤ Q < 5 t	5 t ≤ Q < 50 t	50 t ≤ Q < 500 t	Q ≥ 500 t

* Use the higher "Seveso" thresholds. If more than one substance are involved, the higher level should be adopted.

Human and social consequences		1	2	3	4	5	6
H3	Total number of death: including - employees - external rescue personnel - persons from the public	- - - -	1 1 - -	2 – 5 2 – 5 1 -	6 – 19 6 – 19 2 – 5 1	20 – 49 20 – 49 6 – 19 2 – 5	≥ 50 ≥ 50 ≥ 20 ≥ 6
H4	Total number of injured with hospitalisation ≥ 24 h : including - employees - external rescue personnel - persons from the public	1 1 1 -	2 – 5 2 – 5 2 – 5 -	6 – 19 6 – 19 6 – 19 1 – 5	20 – 49 20 – 49 20 – 49 6 – 19	50 – 199 50 – 199 50 – 199 20 – 49	≥ 200 ≥ 200 ≥ 200 ≥ 50
H5	Total number of slightly injured cared for on site with hospitalisation < 24 h : including - employees - external rescue personnel - persons from the public	1 – 5 1 – 5 1 – 5 -	6 – 19 6 – 19 6 – 19 1 – 5	20 – 49 20 – 49 20 – 49 6 – 19	50 – 199 50 – 199 50 – 199 20 – 49	200 – 999 200 – 999 200 – 999 50 – 199	≥ 1000 ≥ 1000 ≥ 1000 ≥ 200
H6	Total number of homeless or unable to work (outbuildings and work tools damaged)	-	1 – 5	6 – 19	20 – 99	100 – 499	≥ 500
H7	Number N of residents evacuated or confined in their home > 2 hours x nbr of hours (persons x hours)	-	N < 500	500 ≤ N < 5 000	5 000 ≤ N < 50 000	50 000 ≤ N < 500 000	N ≥ 500 000
H8	Number N of persons without drinking water, electricity, gas, telephone, public transports > 2 hours x nbr of hours (persons x hours)	-	N < 1 000	1 000 ≤ N < 10 000	10 000 ≤ N < 100 000	100 000 ≤ N < 1 million	N ≥ 1 million
H9	Number N of persons having undergone extended medical supervision (≥ 3 months after the accident)	-	N < 10	10 ≤ N < 50	50 ≤ N < 200	200 ≤ N < 1 000	N ≥ 1 000

Environmental consequences		1	2	3	4	5	6
Env10	Quantity of wild animals killed, injured or rendered unfit for human consumption (t)	Q < 0,1	0,1 ≤ Q < 1	1 ≤ Q < 10	10 ≤ Q < 50	50 ≤ Q < 200	Q ≥ 200
Env11	Proportion P of rare or protected animal or vegetal species destroyed (or eliminated by biotope damage) in the zone of the accident	P < 0,1 %	0,1% ≤ P < 0,5%	0,5 % ≤ P < 2 %	2 % ≤ P < 10 %	10 % ≤ P < 50 %	P ≥ 50 %
Env12	Volume V of water polluted (in m^3) *	V < 1000	1000 ≤ V < 10 000	10 000 ≤ V < 0.1	0.1 Million ≤ V< 1 Million	1 Million ≤ V< 10 Million	V ≥ 10 Million
Env13	Surface area S of soil or underground water surface requiring cleaning or specific decontamination (in ha)	0,1 ≤ S < 0,5	0,5 ≤ S < 2	2 ≤ S < 10	10 ≤ S < 50	50 ≤ S < 200	S ≥ 200
Env14	Length L of water channel requiring cleaning or specific decontamination (in km)	0,1≤ L < 0,5	0,5 ≤ L< 2	2 ≤ L< 10	10 ≤ L < 50	50 ≤ L< 200	L ≥ 200

* The volume is determined with the expression Q/C_{lim} where :

- ✓ Q is the quantity of substance released,
- ✓ C_{lim} is the maximal admissible concentration in the milieu concerned fixed by the European directives in effect.

Economic consequences		1	2	3	4	5	6
€15	Property damage in the establishment (C expressed in millions of € - Reference 93)	0,1 ≤ C < 0,5	0,5 ≤ C < 2	2 ≤ C< 10	10 ≤ C< 50	50 ≤ C < 200	C ≥ 200
€16	The establishment 's production losses (C expressed in millions of € - Reference 93)	0,1 ≤ C < 0,5	0,5 ≤ C < 2	2 ≤ C< 10	10 ≤ C< 50	50 ≤ C < 200	C ≥ 200
€17	Property damage or production losses outside the establishment (C expressed in millions of € - Reference 93)	-	0,05 < C < 0,1	0,1 ≤ C < 0,5	0,5 ≤ C < 2	2 ≤ C < 10	C ≥ 10
€18	Cost of cleaning, decontamination, rehabilitation of the environment (C expressed in millions of € - Reference 93)	0,01 ≤ C < 0,05	0,05 ≤ C < 0,2	0,2 ≤ C < 1	1 ≤ C < 5	5 ≤ C < 20	C ≥ 20