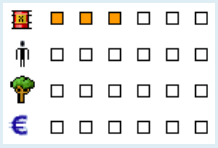
Explosion of a chlorine pipe in Champagnier

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 m³/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 (NH3) 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 (O2, N2), a valve opened on a vaporised O2 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 O2 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 O2 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 m^3 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 ℃ 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 ℃ for several hours and 200 ℃ 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 ℃ 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.

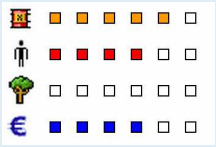
Within the scope of maintenance on the installations since October 28th, the reactor had been placed under a nitrogen atmosphere with a 60 cm hose connecting it to the site's N2 network. Before restarting the unit, a round was conducted the day before to disconnect all hoses from the "N2 injection points". 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 (H2S, CS2, SO2) and HCN. Although the concentrations of CS2 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 m³/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 m³ 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-m² 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 m³ 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 m³ catchpit built on the site was unable to contain the 10,000 to 15,000 m³ 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

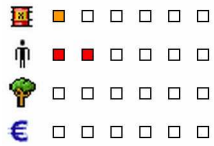
24.6L - Fabrication of industrial chemical products

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

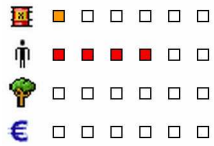
A chemical plant that had stopped its production for the weekend released a toxic cloud containing 2,3,7,8-tetrachlorodibenzodioxin into the atmosphere: 6½ hours earlier, at the end of the shift, the production cycle of 1,2,4,5-trichlorophenol had been stopped while only 15% (instead of 50%) of the solvent (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 ($C > 50$ µg/m²) covers 110 ha, its 736 inhabitants were evacuated; zone B ($5 < C < 50$ µg/m²) covers 270 ha, children and pregnant women were evacuated during the day, agriculture and animal husbandry were prohibited; zone R ($C < 5$ µg/m²) 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

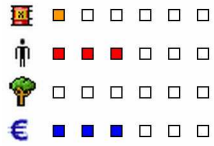
A major fire started in a phytosanitary product warehouse. The fire destroyed 50 to 60 tons of products including profenofos, cypermethrine and monocortophos (insecticides), triasulfuron and turbutryn (herbicides), and metalaxyl and mancozebe (fungicides). The fumes spread into the surrounding environment 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

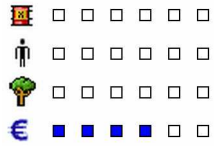
A fire broke out in a parathion and methyl-parathion storage facility. Fifteen people were intoxicated and 10,000 others evacuated due to the formation of a toxic cloud. The cloud passed over the area, then was pushed by the wind over the Canadian border and totally dispersed approximately 100 km from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



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

24.1J - Fabrication of nitrogen products and fertilisers

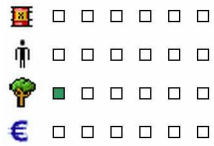
In a factory packaging agro-pharmaceutical products, an insecticide (LANNATE) fell from a hopper on a packaging line while employees were changing the valve at the base of the machine. The building was evacuated owing to the presence of toxic dusts. A slight explosion occurred slightly thereafter (electrical 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

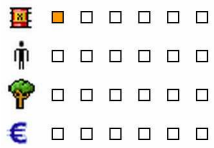
In an agro-chemical plant, a mono-product workshop, dedicated to formulating a liquid herbicide, was being used for the salt formation process of another acid. Three days after production had started, market gardeners noted that 40 ha of crops began to wilt. The plant's management was informed 10 days 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 Cl2/H2 mixture then entered the Cl2 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 H2 pressure or chlorine gas polluted by flammable gas. Corrective measures were implemented: Elimination of the causes of pressure build-up in the H2 manifold, reinforcement of hydrogen overpressure detection systems and the presence of hydrogen in the chlorine, adaptation of the initiator operating procedures (H2 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 ℃ 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 ℃ maximum. The procedure proved to be ineffici ent, each load lowering the temperature only 0.7 ℃ . 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 be low 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℃, pressure of 5.2 bar). The the rmal 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 (SCl2) 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 SCl2 supply valve and the steam control valve of the distiller's heating system. Before replacing the sensor, the distiller containing 50 kg of SCl2 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°C in 30 minutes, resulting in the release of SCl2.

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…)

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 m^3) was collected in a 150 m^3 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 m^3 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 m^3) 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 (PCl3) 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 PCl3 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 m³ of liquefied ammonia. Considering the outside temperature (- 17 °C), 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 (NH3) was being unloaded. Twenty-seven tonnes of NH3 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°C. 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 m³ each), 2 spheres (500 m³ each), 2 gasometers (10,000 m³ and 4,000 m³), 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 2nd 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 (PCl3) 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 PCl3 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.

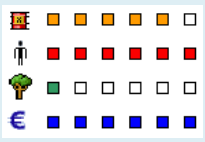
Analysis of the accident showed thread wear on both parts of the threaded union: on the arm, the threaded union of the brass bushing (ACME, 3¼"; female) was particularly worn (the initially trapezoidal section of the threads had become triangular). The threads on the tank's connector were also extremely 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.

Tank overflowing

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 m³, a 2,500-m³ 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 m³/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 m², 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 m³ of PCl3 had been transferred (container capacity = 14.6 m³). 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 m³ 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 m³ of diesel fuel (3 m³ inside the walls and 2 m³ 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 m³; 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 m³) 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.

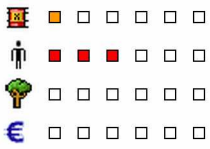
Other activities are also concerned by the equipment overfilling problem involving risks created by the potential hazards of the products involved or the configuration of the installations. Inappropriate equipment, insufficient instrumentation, restart operations and particularly the poor management 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.

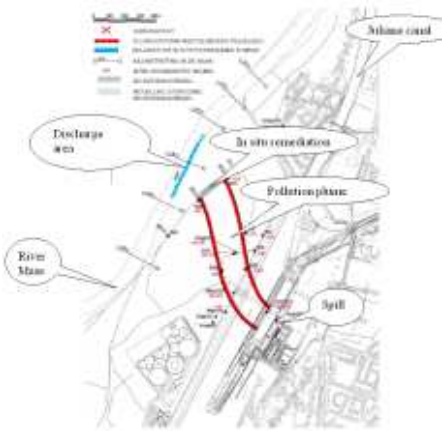
The incident shed light on the need for new control of the sensor on the tower by-pass in order to ensure adequate safety regarding the risks associated with overfilling of the tower.

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

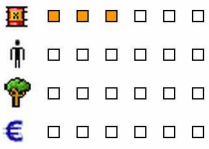
24.1G - Manufacture of other basic organic chemicals

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℃ 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℃) 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

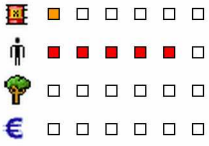
the pollution. Analyses of the water table off site showed no trace of cyclohexene above the drinkability threshold.
On July 2, 2003, 420 t of cyclohexane were pumped from the water table and 16 t extracted from the ground through venting techniques... In July 2004, 590 t of cyclohexane had been recovered, 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

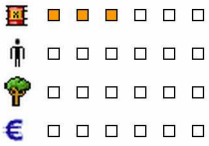
A hose broke while a tanker truck containing trichloromethylbenzene (TCMB or phenylchloroforme) under nitrogen pressure (2 to 3 bar) was being unloaded at a chemical plant. The TCMB began producing hydrogen chloride fumes upon contact with the humidity in the air which prevented the operators from intervening 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

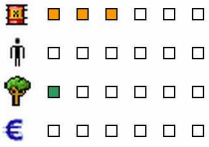
A sulfuric acid tank with a capacity of 20,000 t exploded in a chemical plant, releasing 11,000 t of H2SO4. The acid spilled into the neighbouring port and formed a toxic cloud upon contact with the water.
A safety perimeter cover the entire city was set up and the 110,000 inhabitants were instructed 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 °C. 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 °C. 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

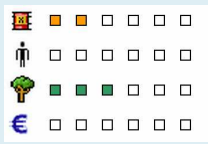
10.1Z – Mining and agglomeration of hard coal

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°C. 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.

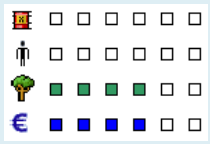
Informed of the incident at his home, the plant's safety supervisor requested the operator to close this installation (shutdown of the heating system) and to leave the bath in the retention area. The incident was recorded in the appropriate logbook. At 5 am the next morning, at the start of his shift, 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.

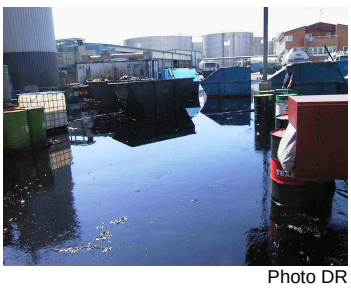


Photo DR

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

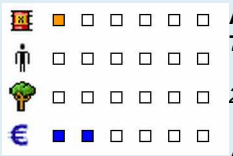
At a chemical site, a tanker car containing vinyl chloride was drained into ammonia spheres. No visible impact on the storage facilities was recorded due to the non-reactivity of both chemical products, yet the production line of a workshop needed to be halted. The incident was caused by a number of 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 operator, reached 13℃ around noon and the 13 tons of 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 m³ 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 m² 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°C), 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.

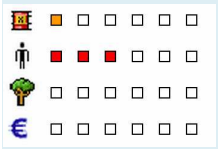
In the future, the prevention plans for external companies shall be checked by the Industrial Director and the QSE Supervisor. The respect and application of the defined rules shall be followed by the QSE Supervisor who shall have the authority to stop job site operations as required. Delicate phases (reopening of gas lines...) shall be conducted in the presence of an independent organisation or technical representative from the subcontracting company.

Deadly gas

Emission of H_2S at Rhadereistedt and Stuttgart waste treatment centres

ARIA 31000 – 11/08/2005 – RHADEREISTEDT - GERMANY

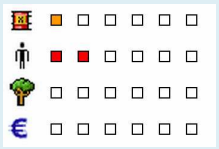
90.0E – Treatment of other solid wastes



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 into 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 m³ of sludge. More than 2,100 people (including rescue personnel, firemen, soldiers and police,...) combed through 80 km² 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°C. 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.

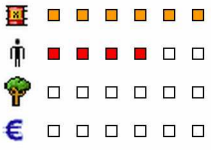
Accidents whose ARIA number has not been underlined are described on the site:
www.aria.ecologie.gouv.fr

[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°C) 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

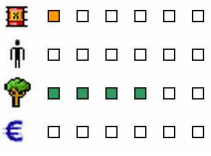
24.1J - Production of fertilizer and nitrogen compounds

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°C) 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:

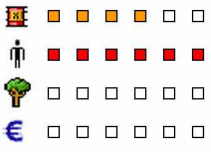
- that greater strength of the tank lid, in comparison with the bonds in place between the internal chamber sidewall and the tank bottom or with anchoring brackets, caused tank failure at its base, as the tank bottom remained fastened to the foundations;
- the liquid ammonia wave caused the protection 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

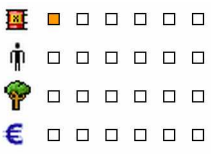
Following a tank explosion, 1,200 tons of beet molasses spread over the ground and then into the Le Mau river. One week later, the pollution became concentrated near a lock on the Marne Canal. Thousands of fish were found dead, yet 3 to 5 tons could be saved by transfer into the Marne River. A neighbouring 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 m³ of Top Crude, produced as black crude from a topping unit. Subsequent to the breaks caused on the shell/bottom welds, 68,100 m³ of product were spilled into the retention basin common to the three tanks, having a total capacity of only 23,000 m³. 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 m³ 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 m³ 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 m³ 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.

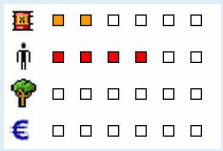
ARIA 29133 - 02/04/2005 - SWEDEN - HELSINGBORG

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

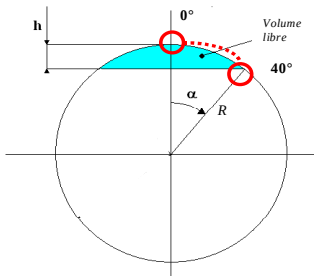


An ammonia container or pressurised drum (NH_3) was leaking within a frozen foods warehouse located in an industrial estate. The accident occurred at the time a refrigerating unit condenser was being replaced after being partially emptied of its NH_3 contents the previous day; 1,500 kg of NH_3 at -18℃ 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°C) 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

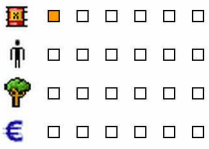
A cylindrical tank containing 50 tons of ammonia (NH_3) under pressure (6.2 bar) failed during an unloading operation in a fertiliser plant, releasing 30 tons of NH_3, with 8 tons also escaping from the tanker truck. A cloud 150 m in diameter and 20 m high formed and spread over 450 m. The explosion 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

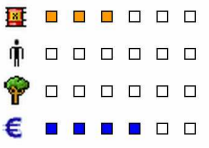
thereafter. The accident was caused by a defective weld between the tank shell and dome. A metallurgical expert assessment indicated that the weld displayed major penetration flaws, and these flaws would have worsened by exposure to metal fatigue effects due to pressure cycles. The analogue pressure 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

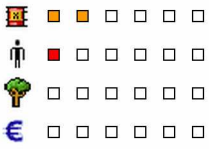
A 50-kg cylinder of liquefied ammonia exploded on a storage site; 9 other cylinders were also damaged. The tank had been filled on April 18 with a 64-kg load of ammonia subsequent to a calibration reading error. The toxic cloud dispersed quickly and no impact on human health was reported. The tank was submitted to an expert evaluation.



ARIA 11547 - 08/19/1997 - SEINE MARITIME (76) - LE HAVRE

63.1D - Refrigerated warehousing

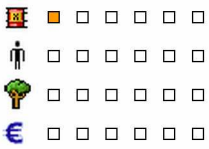
An arsonist struck at 4:20 in a warehouse of 30,000 m² in floor area and built on two levels, housing an archives room and an empty refrigerated hangar (on the ground floor) that included a shutdown refrigeration unit containing 5 tons of ammonia (NH_3). The flame front was measured at 350 meters 15 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

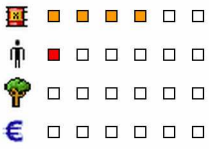
An explosion and ammonia leak (NH_3) occurred 30 minutes following start-up of a brewery refrigeration unit. An employee sustained eye burns. A second explosion with flames then occurred. A liquid NH_3 tank (475 litres, 12 bar), at the condenser output, was connected to an overheating cylinder by a pipe 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

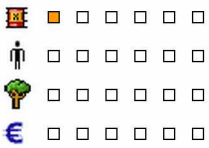
At a chemical site, a tanker car containing vinyl chloride was drained into ammonia spheres. No visible impact on the storage facilities was recorded due to the non-reactivity of both chemical products, yet the production line of a workshop had to be shut down. The numbers and data sheets from the tank 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°C. 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.).

Photo TOTAL

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.

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.

Graphic presentation:

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:

Technical parameters of the European scale:

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

Environnemental 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.

Conséquences économiques		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

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

TECHNOLOGICAL ACCIDENTS ONLINE

Safety and transparency are two justifiable requirements of our society. Therefore, since June 2001 the website www.aria.ecologie.gouv.fr of the Ministry for ecology and sustainable planning and development has been giving lessons learnt from the analysis of technological accidents to professionals and general public. The main sections of the website are presented in French and in English.

Under the general sections, the Internet user can, for example : inquire for the state's action, access to wide extracts of the ARIA database, discover the presentation of the European scale of industrial accidents, inquire for the parameter concerning the dangerous substances used to complete the "on the spot communication" in case of accident or incident.

Accidents description, which is the raw material of any method of experience feedback, constitutes an important part of the event, consequences, origin, circumstances, established or presumed causes, actions taken and lessons leamt.

Hundred detailed and illustrated technical report present accidents selected for their particular interest. Numerous analysis grouped by technical subjects or by activities are also available. The section dedicated to the technical recommendations develops various topics : chemical, pyrotechnics, surface treatment, silos, type storage, fire license, waste treatment, handling...). A multicriteria research engine enables to reach information about accidents arisen in France or abroad.

The website www.aria.ecologie.gouv.fr grows richer constantly. Currently, more than 32 000 accidents are on-line and new topics will be regularly added.

www.aria.ecologie.gouv.fr