



Operations in a degraded mode



Thermal decomposition of fertilisers inside a dryer

ARIA 37825 - 08/02/2010 - 60 - Ribecourt-Dreslincourt

20.15 - Manufacturing of nitrogenous products and fertilisers

 When observing yellow smoke emanating from the chimney of a drying unit located downstream of the fertiliser plant granulator, an employee notified a control room technician; the workshop extraction fan was turned off at 10:30 am in order to limit discharges of both nitrous and chlorine gases, which were beginning to fill the workshop. A technician was overcome by the gas and required hospitalisation for a few hours as a precautionary measure. The internal emergency plan was activated at 10:58 am, and fire-fighters arrived on the scene at 11:10. The dryer was started and then flooded; the incident was brought under control at 12:34 pm. The device was drained, with all fire extinction water collected in a retention basin; recovered sludge was recycled over the following week. A few hundred kg of aggregates were decomposed ; the 20 tonnes of system load were recycled that very night.

Thermal decomposition had occurred inside a dryer, of the rotating tube variety, fed with hot air by a 7 MW natural gas generator containing 20 tonnes of aggregates, over which an ammonium phosphate slurry had been sprayed. This ammonium phosphate supply was obtained by means of a chemical reaction between phosphoric acid (H_3PO_4) and ammonia (NH_3). The site operator considered the possibility of accidental overheating, since the NPK 11-11-32 fertiliser had not been prone to self-sustaining decomposition. The unit had been shut down for the maintenance of a chain conveyor. The pertinent operating instructions would have been followed for this mission, given that the granulation loop contained dry matter, with the burner operating at the minimum setting (35%) and the drying drum no longer rotating.

Subsequent to an excessive production temperature ($> 300^\circ C$), the "dryer input" temperature, which was also abnormally high, surpassed the temperature at the onset of dry fertiliser decomposition (i.e. $> 170^\circ C$). This thermal disequilibrium was caused by use of an H_3PO_4 at 38% concentration, which was more diluted than the normal level (53%). With a slurry containing a large quantity of water to be evaporated, gas temperature at the reactor output (set at $110^\circ C$) decreased, while the drying air temperature was automatically increased as a compensation to $300^\circ C$, by exceeding the typical threshold of $240^\circ C$. No alarm was triggered, with the $300^\circ C$ value remaining below the $370^\circ C$ threshold recorded on the "hot air intake" temperature probes. Afterwards, the dryer required more time to cool.

The acidic dilution stemmed from an incident that had occurred 10 days prior, involving the unit's three H_3PO_4 tanks, two containing a 53% acid and the other a diluted corroded acid ($< 30\%$). With its shell leaking at a height of 1.5 m above the bottom, tank contents had been transferred into the other two tanks, thus diluting the acid used for manufacturing purposes.

The operator modified production standards, by introducing a "hot air intake temperature" alarm threshold adapted to each production run ($260^\circ C$ for ammonium nitrate fertilisers), along with the relevant maintenance shutdown procedure by indicating temperature controls and thresholds correlated with the steps required for installation shutdown, plus an internal emergency plan reminder to avoid stopping the fan in the event of toxic gas emissions.

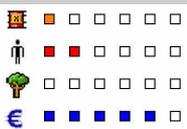


Crédit photo : Do Visser / De Gelderlander / R.R.

Explosion of ethanol vapours inside a vacuum belt filter

ARIA 40097 – 11/07/2010 – The Netherlands – Nijmegen

20.15 – Manufacture of other chemical products



In a chemical plant producing mainly cellulose derivatives, an explosion and fire occurred at about 4 pm during the restart of a production line stopped for 9 h after a breakdown.

The commissioning of the vacuum belt filter by the team leader caused the explosion and several fires started in several points of the line. An employee of 52 years was seriously injured. Despite being rapidly cared of by firefighters, he died from his injuries later in the evening.

The fire lasted 38 hours, causing thick black smoke; public spaces were enclosed within a radius of 3 km and residents were asked to confine themselves at home. The navigation on the WAAL is interrupted for several hours. A fireboat protects acid and hydrogen tanks. In the evening, the mayor announced that smoke analysis eliminated any health-related risk.

The procedure governing the operation of the filter dated back to 2005, it stated that the filter had to be purged with nitrogen for maximum 2 hours before being restarted. However, technicians indicated that in practice, the purge was carried out only if the doors of the filter had been opened. Otherwise, even in case of long-lasting stopping of the filter, no purge was launched. It was "assumed" that the air was saturated with ethanol and thus above the upper explosive limit (UEL).

The day of the accident, the temperature in the confined space of the belt filter vacuum was between 24 and 35°C, leading to a volume percentage of ethanol vapours between 5 and 15 %. The stoichiometric ratio of reaction of ethanol with oxygen is 5.6% by volume. An explosive atmosphere was thus created and inflamed with a low activation energy, causing the loud explosion. The amount of ethanol vapour in the filter is estimated at 100 m³ (with about 300 kg of liquid ethanol).

An explosion scenario in the filter had been studied, and its theoretical effects did not overpass the enclosure. This accident shows that the power of solvent vapour explosion is often undervalued and possible sources of ignition of explosive atmospheres (ATEX) poorly studied. It stresses the importance of identifying and managing situations of degraded mode of operation, as well as ATEX prevention measures, including inerting.

The insurance estimated internal damage up to 50 million euros. The company fired its 65 employees and transferred its production in China. The Labour inspectorate requested another factory producing CMC 25 km away to revise its explosion prevention plan and related protective measures.

Operations in a degraded mode

The expression "degraded mode of operations" refers to the situation of a system whose operations are sustained or kept on course without possessing all of the functional resources necessary or normally allocated upon completion of the corresponding risk analysis, whether such resources are organisational or technical in nature, i.e. : competent personnel in appropriate numbers; availability of a machine, a utility or a function; lack of raw materials or consumables.

The pursuit, even temporary, of operations under these conditions, without any study of the implications through a risk analysis (ARIA [5611](#) / Continued operations despite cyclohexane leaks) or without specification and implementation of targeted compensatory measures (ARIA [7022](#) / Operations without a cooling circuit, without nitrogen or a backup tank) within the scope of a unique organisation that requires at the least information regarding the full set of individuals involved, i.e. supervisors, technicians, subcontractors (ARIA [37440](#) / Information on technicians assigned to use a mechanical gauge onsite and on control room technicians, due to malfunction in the level measurement system), exposes actors to "encounters" whose consequences may be unfamiliar to them. Any deviation in operating conditions could in fact prove hazardous, since the safety of individuals, property and the environment merely depends on a set of improvised responses of moderate relevance, which in turn rely upon information and resources available in real time to those capable of recognising the importance and acting expeditiously (ARIA [3536](#) / Improvised action on the unit's control system, [7022](#) / Lack of an operable siren, unavailability of an emergency plan).

The system operator may be aware of this degraded mode of operations and of the need to implement compensatory measures that correspond to a level of risk comparable to the reference level. Given the magnitude of other constraints, which may be technical (ARIA [5611](#) / Need to halt production for a long period in order to conduct reactor repairs) or economic (ARIA [7022](#) / Risk of commercial loss), the operator might also underestimate risks subsequent to a summary analysis and then introduce insufficient measures (ARIA [717](#) / Malfunction of a cold air unit, lowering output to a minimum and injecting hot ammonia into a cryogenic tank).

Moreover, the operator may lack the time required to perform such an analysis and adopt appropriate measures once the source of degraded operations has been identified ; rapid dynamic events such as runaway reactions receive special attention here (ARIA [7135](#) / Generic accident involving a runaway phenol-formaldehyde reaction subsequent to insufficient reactor cooling). These types of situations often reveal inadequacies in the initial risk analysis, or a failure to incorporate feedback (ARIA [7135](#) / Reaction ongoing for tens of years), or the onset of undetected deviations with respect to the adopted benchmark (ARIA [37902](#) / Technicians failing to employ the protocol specified in safety manuals).

In the absence of an appropriate reaction that allows bringing the situation back to normal or "restoring" the situation, the degraded mode of operations, or partial operations, whether in an overloaded or slowdown mode, could result in a "loss of process control" (ARIA [20382](#) / Excessive inflow of residual gas in order to increase boiler output rate, [19295](#) / Unit operating in slowdown mode to prepare for upcoming repairs).

The ARIA database has catalogued many incidents involving a degraded mode of operations known to the site operator and originating from not only physical defects, but sometimes and more importantly organisational and human breakdowns :

- An emphasis on "ensuring safety on paper" while overlooking in situ controls : ARIA [34990](#) / Heavy corrosion of gasoline pipelines that had been poorly monitored as the result of being considered acceptable by a specialised inspection body, with the lack of appropriate diagnostics leading to delayed and inadequate maintenance of installations:
- Standardisation of allowable service deviations : ARIA [25900](#) / Basins used as storage facilities / degraded operations becoming routine, [30304](#), [37902](#) / Non-use of a safety feature that was interfering with handling.
- Deliberate installation safety lapses: ARIA [25900](#) & [32484](#) / Manual mode of operations, alarm override.
- Phenomenon of "ageing" and insufficient maintenance (ARIA [24923](#)...).
- Installation of a "temporary" nature or inappropriate modifications / deferred, incomplete repairs (ARIA [37597](#) / Delayed repairs subsequent to an erroneous assessment) or repairs completed "in haste" (ARIA [595](#), [608](#), [5118](#), [5611](#) / Supervision with a short-handed staff, stopgap and improvised installation modification, absence of testing, [6958](#) / Sulphitation tower temporarily supplied by an SO₂ tanker truck for the time required to repair a sulphur oven burner [19122](#), [37476](#), [37597](#) / Erroneous assessment of installation conditions, exaggerated optimism over the service life cycle prior to upcoming repairs, [21460](#) / Service reactivation of an installation before repair work has been fully completed).
- Installation overuse or application of excessive loads: ARIA [5791](#), [7043](#), [7879](#), [20382](#), [30304](#), [36349](#), [36387](#), [37825](#) Excessive thermal load correlated with the quantity of water to be evaporated.
- Design flaws with partial automated mechanisms, insufficient redundancy inherent in safety devices, non-positive safety design, inappropriate materials: ARIA [608](#), [3536](#) / Partial automation of the unit's emergency shutoff switch, non-independent control and safety devices, [31691](#) / Non-independence of regulation/safety functions, non-positive safety, [32814](#), [34990](#) / Pipe lining poorly adapted to marine corrosion, [37088](#), [37720](#) / Alarm system in need of repairs, inadequate pipe material.
- Poor design (ARIA [19119](#)) or premature wear (ARIA [5611](#) / Rupture due to shear of the bellows).
- Equipment defect or malfunction (ARIA [636](#), [3536](#) / Defective automation card, [4687](#), [24020](#) / Gradual deviation in process parameters, malfunctioning and unrepaired equipment, [24923](#), [36877](#), [37440](#) / Malfunctioning of automated level controls, [37720](#) / Permeable retention basin undergoing repairs), instrumentation with late or inadequate information relay and lack of positive safety features: ARIA [25900](#) / Placing alarms offline, [31691](#) / Defective pressure sensor, [32016](#) / Malfunctioning remote communications lasting several days.
- Breached seal, obstruction, clogging : ARIA [3536](#) / Regulation valves without an impermeable seal, [25900](#) / Retention basin connected to the stormwater drainage network.
- External physical causes (ARIA [32679](#) / Downed electrical supply line on the German network interfering with French network supply).
- Naturally-occurring aggressions : ARIA [17321](#) / Storm and site flooding, [32240](#), [34990](#) / Corrosive saline fog, [37720](#).

- Intentional malicious acts : ARIA 32016.

The available accident records also indicate a number of cases in which compensatory measures were missing or insufficient due in particular to :

- Overly broad or inadequate risk analysis : ARIA 174, 608, 5118, 6958 / Introduction of connection components without any real analysis of the risks for an SO₂ leak on a flange, 7879, 19145, 21315, 24020 / Unidentified risk of thermal decomposition, poorly-defined scope of process safety and "foam plug" preventing rupture of a safety disc, 25900 / Retention basin connected to the stormwater drainage network, 31691 / Glass debris clogging a tap, 36387, 37476 ; the transient phases of a process and one-time or exceptional operations are especially singled out herein : ARIA 636, 13099, 19117, 19119, 32440, 36368, 36490, 36797, 36877, 37087, 37088, 37476.
- Design / ergonomics of equipment or workstations : ARIA 174, 608, 636, 19117, 19119, 20507, 21315, 37087, 37088, 37440 / Local mechanical gauge; inconvenient repair protocol.
- Absence of instructions and procedures (ARIA 24020), incomplete, inappropriate or noncompliant: ARIA / 636, 753, 3536 / Lack of clarity in available procedures and instructions, 4687, 5118, 7879, 17152, 19117, 20507, 25900 / Absence of work guidelines, measurement devices rendered inoperable, 36368, 36490, 36877, 36881.
- Poor internal management: ARIA 32016 / Depletion of spare parts inventory.
- Insufficient monitoring and controls : ARIA 753, 4687, 15725 / Hasty repairs for final permeability testing campaign, despite the tank storing higher-density phosphoric acid 24020 / Gradual and undetected deviation in process parameters, 34990 / Inadequately monitored corrosion.
- Improper diagnostics, maintenance delay (ARIA 34990 / Corroded gasoline pipelines not receiving adequate monitoring as the consequence of being considered acceptable by a specialised inspection body, lack of appropriate diagnostics leading to delayed and missed maintenance of installations. For the site's other pipelines, this accident led to adopting new compensatory measures).
- Diagnostic error, poorly analysed precursor events, insufficient feedback : ARIA 21315, 24923, 31691 / Drain tap clogged for 3 weeks goes unnoticed, sulphur dichloride leak during maintenance work, 37440 / malfunctioning automated level control replaced by human observation with local recordings ; tank overflow and UVCE, unaware control room technicians failing to recognise the initial signs of tank overflow, 37597 / Poor evaluation of installation conditions.
- Ill-prepared, hasty or inappropriate human intervention, due to a lack of training or (more seriously) performed by personnel either poorly equipped, uncertified or unskilled : ARIA 636, 3536 / Centralised control system left accessible to all personnel, whether certified or not, 4687, 5118, 7879, 13099, 17152, 19117, 19145, 21304, 21315, 36797.
- Lack of an emergency intervention plan: ARIA 25900.

The starting point consists of a preliminary definition, within the initial risk analysis, of special operating conditions ; these entail taking into account the various hazardous situations and identifying both the stable phases of a process and the protocol for returning to initial states. Such an analysis is critical for accidental mechanisms with rapid kinetics, which leave little room for reaction should the degraded situation not be diagnosed from the outset : ARIA 3536 / Thermal decomposition, 7135 / Runaway reaction.

Though all life cycle phases of an installation may be concerned, chief among them are daily production operations, continued service provision during maintenance phases or when conducting works often constitutes an exacerbating circumstance : ARIA 5611 / Installation modified by means of circumventing a reactor undergoing repairs, 6958 / Temporary lorry supply due to a furnace undergoing repairs, 13099, 21315, 21460 / Equipment placed back into service without first being completely repaired, 24020 / Mechanical stirrer shut down 48 hours for maintenance, 25900 / Retention basins used as storage capacities during the works period, 31691 / Ongoing sensor maintenance, 37476, 37720 / Retention basin undergoing renovation with momentary removal of its antacid liner.

The multiple causes sometimes cited as part of accident evolution are very often on display here, as reflected in featured events that have often been listed several times in previous paragraphs. Operators can thus decide to continue activities at any cost by whatever means available or scale activities back to just the "vital functions", while maintaining installation safety, despite the functions themselves being capable of deteriorating or degrading over time, subsequent to potential deficiencies in the backup resources either implemented or available: electric generating set, power inverter, cooling unit, etc.

Without being able to avoid degraded operations by introducing appropriate measures such as preventive maintenance or via organisational steps like early detection of weak signals, a specific protocol beyond mere economic constraints needs to be adopted in order to continue operations at a level of safety comparable to the reference guideline. Such a protocol, which is best designed to match the stakes involved, typically features reinforced monitoring of the state of degradation for the targeted function, in addition to introducing remedial measures and close performance tracking. This response presumes supplemental controls on sensitive installations and machinery, which normally implies deploying additional human and equipment resources (ARIA 34990 / Reinforced monitoring procedures, 37597/Daily monitoring). The implementation of compensatory measures could aid in preventing worst-case scenarios, as well as in mitigating and intervening when an incident or accident arises, more specifically in cases where prevention efforts have been thwarted (ARIA 37597 / Sand dams in the retention basin, regular pumping of hydrocarbons, gutter for channelling flow, replacement of the surface layer on polluted gravel).

Beyond some of these purely technical measures and in order to avoid improvised decision-making as much as possible, customised training intended for response teams (including management) during "crisis situations" will effectively complement the existing physical resources at industrial sites.

Additional references :

- Detailed accident reports ARIA 717, 3536, 5611, 5620, 7022 and 24020.

Accidents whose ARIA number has not been underlined are described on the Website :

www.aria.developpement-durable.gouv.fr

  **ARIA 717 - 20/03/1989 - 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 (NH₃) 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 NH₃ 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 (NH₃, 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 NH₃ flow to a pressurized storage area. Fourteen tons of hot NH₃ (+ 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, thus aggravating the consequences of the accident ;
- this 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 3536 – 22/04/1992 - 38 - JARRIE**

20.13 - Manufacturing of other basic inorganic chemical products

  An explosion perceived tens of km around and an ensuing fire destroyed 1,000 of the 4,000 m² of a hydrogen peroxide unit (H₂O₂) located near a series of hydrogen and chlorine tanks. The fire spread into the adjoining sewers, and a nauseating odour permeated the air. A safety perimeter was set up. One employee was killed and 2 others injured ; property damage was valued at 483 million francs and 1,000 m³ of fire extinction water containing a solvent polluted the DRAC river after having overflowed from a retention basin that had an insufficient volume.

  This accident was due to a defect in the electrical supply card in one of the unit's control system (digital command control) cabinets. The situation was exacerbated by : difficulties encountered when analysing the situation, an unfortunate attempt of human intervention on the automated system, partial automation of the unit's emergency shutdown function, non-independent control / security features, insufficient controls over the proper sequencing of installation security combined with several manual steps failing to be carried out by technicians to assist with the night-time shutdown, absence of specific guidelines for ensuring installation safety, and lastly a lack of clarity in the available instructions and procedures.

  Due to a breach in the seal of the *in situ* safety shutoff device (pump discharge check valves, automatic regulation valves), oxygenated water backflow from the extraction column to the oxidiser allowed for the reactive mass to gradually build its concentration of powerful metal agents capable of destabilising H₂O₂, whose exothermic decomposition was triggered and then accelerated. The resulting oxygen caused a rise in installation pressure and the bursting of a connecting pipe that had not been equipped with a shutoff valve or equivalent protective device. The reactive mass, which was partially emptying from the production machinery, ignited on a hot spot. An organisational deficiency in the area of safety training would lead 3 years after to filing a suit against several plant managers.

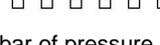
Several technical and organisational improvements were introduced at the site: installation of impermeable shutoff devices, protection of pipeline sections capable of undergoing a pressure rise during H₂O₂ decomposition, enhancement of the command/control system (safety system designed for an emergency shutdown independent of the operating control device, new control room, improved workstation comfort/ergonomics), increased installation retention capacities and sewer protection, redefined scope of site intervention, more efficient information dissemination / training, publication of adapted safety instructions, and completion of safety reports dedicated to the manufacturing, transfer and storage of H₂O₂.

  **ARIA 5611 – 01/06/1974 - UNITED KINGDOM - FLIXBOROUGH**

20.60 - Manufacturing of artificial or synthetic fibres

  A cyclohexane cloud violently exploded at a caprolactam plant; 28 employees were killed, and a total of 89 individuals were seriously hurt, 53 of them among the general public. Property loss was considerable : buildings destroyed within a 600-m radius, 1,820 dwellings and 167 businesses sustained damage.

  Caprolactam was being synthesised by means of catalytic oxidation of cyclohexane at 155°C and under 8.8 bar of pressure inside 6 reactors placed in series ; some 250 to 300 m³/hr of liquid was being conveyed by straight pipes 28" (711 mm) in diameter connected to the reactors via stainless steel expansion bellows.

  A cyclohexane leak had been detected in March of the same year on Reactor No. 5, which revealed a slight vertical crack due to stress corrosion in the presence of nitrates. To avoid shutting down production, a bypass pipe with an elbow joint was planned to connect Reactors 4 and 6. The plant was undergoing a complete reorganisation. Lacking the requisite engineering capacities and managerial oversight, a 20" diameter pipe was installed without any preliminary design, then the unit was restarted without appropriate initial controls or testing. Production resumed on April 1st and until May 29th, no problems had been reported. On Saturday, June 1st, the unit was shut down and then restarted several times, with small cyclohexane leaks apparently plugging themselves. The blast, which occurred at 4:53 pm and could be noticed as far away as 50 km, completely levelled the site and was followed by several fires producing flames rising 70 to 100 m into the air.

The investigation concluded the occurrence of a shear rupture of both attachment bellows on the temporary 20" pipe, combined with a massive leak of 40 to 60 tonnes of hot pressurised cyclohexane. The cloud formed ignited at a distance of 100 m from the leak some 25 to 35 seconds later on the hydrogen unit's reforming tower. These conclusions, delivered in April 1975, would not however meet with unanimous approval, and various theories regarding the causes of this accident would be aired in publications for decades.

The overall context of site operations contributed heavily to this disaster, with an understaffed management team (the Maintenance Manager's post had gone unfilled for 6 months), a situation not in compliance with current regulations (i.e. an inventory of hazardous products 50 times higher than the authorised limit), and a business facing serious economic difficulties. This accident would lead to a major revision in both English and European regulations.

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

 **24.4 - Pharmaceutical industry**

 A chemical plant that had stopped its production for the weekend released a toxic cloud containing 2,3,7,8-tetrachlorodibenzodioxin into the atmosphere : 6½ hours earlier, at the end of the shift, the production cycle of 1,2,4,5-trichlorophenol had been stopped while only 15% (instead of 50%) of the solvent (ethylene glycol) had been distilled. Agitation was stopped and the vacuum broken. No water was added to the mixture. The unit was left unsupervised for the weekend. At 12.37 pm, the safety valve, calibrated at 3.8 bar, ruptured due to the increase in temperature and pressure in the reactor.

The heating of the reaction mixture's surface at rest initiated the secondary exothermic reaction forming the dioxin. It was only the next day that the company informed the authorities that a release of herbicide had occurred. Two days later, crops were declared unfit for consumption. The company reported the dioxin release only 10 days later. In all, 11 communities were effected, including 2,000 ha contaminated. 3 zones were defined : zone A ($C > 50 \mu\text{g}/\text{m}^2$) covers 110 ha, its 736 inhabitants were evacuated ; zone B ($5 < C < 50 \mu\text{g}/\text{m}^2$) covers 270 ha, children and pregnant women were evacuated during the day, agriculture and animal husbandry were prohibited; zone R ($C < 5 \mu\text{g}/\text{m}^2$) measuring 1,430 ha.

More than 250 case of chloracne were diagnosed, and 220,000 people were exposed to the pollution. In all, 81,000 animals were killed 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 6143 – 19/12/1994 - 38 - LE PONT-DE-CLAIX**

 **20.14 - Manufacturing of other basic organic chemical products**

 At a chemical facility producing a hormone for herbicides, an explosion accompanied by the splashing of viscous material occurred at 8:45 pm on a column used to distil dichloroethane (DCE) / methyl nitrochlorobenzene (NBE). A temperature increase at the base of the column, which had ceased 25 min earlier following difficulties encountered during drainage operations, attracted the attention of technicians at 9:10 pm. The explosion took place at the time this crew was working on the column ; 5 technicians were injured, 2 seriously (one of whom would succumb as a direct result of injuries sustained). The column equipment was completely destroyed. The surrounding environment was not contaminated. The return of an acidic solution between 2 tanks by the siphon effect and its concentration in the column caused the NBE to decompose. The unit was subsequently modified.

 **ARIA 6958 – 06/05/1995 - 02 - VENIZEL**

 **17.21 - Manufacturing of paper and cardboard, paper / cardboard packaging**

 A 200-litre leak of liquefied sulphur dioxide occurred on the flange joint of a tanker truck whose contents were being unloaded into a sulphitation tower typically supplied by a sulphur oven (undergoing maintenance). The technician cut the tanker supply line (pushbutton control). A leak remained unplugged on the stuffing box of one of the tanker valves. The bypass valve was turned on and the alarm was tripped. The emergency response team proceeded by closing the valves and spraying the tanker. The French "red plan" for serious emergencies was activated. A plant employee, who had sustained local skin burns, remained hospitalised for 5 days ; the protective suit he wore had been stored in non-airtight premises, where it was in contact with SO₂. Within a 50-m radius, a total of 32 employees became slightly intoxicated, as did 11 fire-fighters, 4 of whom had more serious consequences. Use of an inadequate hose (for connection with the tanker flange) was the cause of this accident.

 **ARIA 7022 - 02/12/1984 - INDE - BHOPAL**

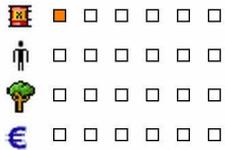
 **20.20 – Manufacture of pesticides and other agrochemicals**

 In 1969, an American company set up a production unit manufacturing a powerful pesticide called Sevin in Bhopal. The unit included three 60 m³ tanks (50 tonnes) of liquid methyl isocyanate (MIC) (E610, E611 and E619), each connected to various safety systems : cooling facility, wet scrubber, flare and water spray system. The Indian government had granted approval for the production of 5,000 tonnes of Sevin per year.

 To keep pace with competition in the insecticide market and overcome a budgetary deficit of 4 million \$/year, the parent company decided to stop the local production of Sevin, lay off numerous supervisory-level staff members (especially maintenance) and run the site at low cost... The accident took place on the night of 2-3 December 1984. After cleaning the pipes, water entered the tank E610 and triggered several chain reactions causing an increase in temperature (200°C) and pressure (13.79 bar). In 2 hours, the safety valve let out 23 to 42 tonnes of MIC and other toxic gases according to sources. Several safety systems failed: cooling facility stopped (06/84), wet scrubber out of order (23/10/84), flare out of service (a few days before the accident), temperature, pressure and liquid level indicators in the tank faulty, water curtain not powerful enough. The toxic emission took a heavy toll on the population. According to sources, 1,754 to 2,500 people lost their lives and 170,000 to 600,000 were poisoned. More than 4,000 animals (cattle, dogs, cats, birds) died as well. The chronic pollution caused by the toxic release had long term consequences on the population. The list of victims had grown in numbers by end of 1998. 16,000 people were reported dead and 15 to 20 people died each month following the accident.

Initiated in 1987, these legal proceedings were somewhat chaotic. Charged at first with homicide, the 8 detainees (7 Indians and the American company President) then benefitted from a 1996 Indian Supreme Court injunction. The highest tribunal of the nation ruled that the case should be tried as homicide by negligence, a misdemeanour punishable by at most two years of prison. In 1989, the operator signed an agreement with the Indian government: the industrialist would pay compensation in the amount of \$470 million in exchange for dropping all charges.

On June 7, 2010, the Bhopal Court of First Instance sentenced to two years of prison and 100,000 rupees (€1.751) in fines 7 individuals deemed liable for the disaster. A \$10,000 (€8,354) fine was imposed on the operator's Indian subsidiary for negligence. The company's CEO at the time, declared by the court as a "fugitive", was not specifically named when the verdict was announced.



ARIA 7135 – 26/07/1995 - 60 - RIBECOURT-DRESLINCOURT

20.52 - Glue manufacturing

At a 40-ha chemical facility located on the outskirts of an urban area, the safety disc set at 1.5 bar on a 15.2-m³ reactor burst in a plant working with formo-phenolic resins used for glues applied to agglomerated material. The operator informed the Classified Facilities inspector, who promptly made a site visit.

The batch production of a formo-phenolic resin lasted 10 hours. Both formaldehyde and phenol were loaded into the warmed reactor, then the soda used as a catalyst was gradually introduced into the device, which was maintained in a vacuum. The reactor's cooling system (consisting of two double shells) and the return of emitted vapour condensates served to control this highly exothermic chemical reaction.

At the time of this event, all 3 reagents were inside the reactor when the reaction started to run away, with a rise in both the temperature and pressure of the enclosure, followed by bursting of the adjusted safety disc protecting the installation ; 6 tonnes of reactive media (formaldehyde at 11.5%, phenol at 0.6%, soda and resin) released from the roof fell both inside and outside plant premises, at distances as far as 400 m. Vegetable gardens and several vehicles received residue on their surface.

The Classified Facilities Inspectorate proposed shutting down operations of the malfunctioning reactor, given that its service start-up was contingent on filing a report indicating the exact accident causes and suggesting a framework to avoid repetition of the incident. The operator was also required to submit within 24 hours a precise and readable map of the zones affected by this chemical fallout, so as to notify local elected officials and set the stage for implementing appropriate measures. This submission was to include all documentation and information (e.g. on toxicology) required to ensure an effective assessment of the risks potentially posed to residents and occupants of the identified zones. The operator was moreover asked to propose remedial measures for treating the polluted zones, e.g. disposal of affected plantations, soil treatment.

The operator performed site cleanup work : 1,000 m³ of washing water were stored in an onsite basin. Soils and plant life were analysed, yielding: 0.02-0.87 mg/kg of phenol in the soil samples, and 0.17-4.08 mg/kg in plants. A selection of vegetables grown in neighbouring gardens was retrieved, and a wheat field in the line of chemical substance fallout was mowed ; all damages incurred were reimbursed.

After an overly rapid injection of soda, exacerbated by a high reactor loading level, reactor cooling was initiated too late (12 min after the temperature increase according to equipment recordings). The quantities of products introduced were considerable, although the plant operator insisted that the operating protocol had not been violated (15,190 kg measured by a mass flow meter, i.e. 15,792 kg per load cell for a 15.2-m³ reactor). The reaction ran away while reactor cooling devices (which had reached 127°C) were malfunctioning. The reactor loading level, combined with insufficient available cooling capacity and inappropriate temperature settings, impeded control over the reaction process. Also, the loading of all primary reagents at the beginning of the cycle, noncompliant with good professional practices, facilitated this runaway reaction. The plant had not been granted the necessary regulatory authorisations to produce this new type of resin, and no safety report for either the process or installation had been previously conducted.

The operator modified the relevant process in favour of a continuous injection of formaldehyde, leading to improved control over reaction exothermicity and runaway protection by stopping formaldehyde injection. Reagent quantities were reduced, and the monitoring of both reactor operating parameters and chemical reaction stages was improved.

ARIA 15725 - 23/04/1999 - 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 17321 – 27/12/1999 - 33 - AMBES

20.15 - Manufacturing of nitrogenous products and fertilisers

A storm flooded a "Seveso"-rated fertiliser plant employing 97 staff and producing ammonium nitrate pellets.

The installation experienced a 20-hour current outage. During cleanup of a small stream running near the site 48 hours later, the 63-kV line supplying the site was affected by the outage and the plant would ultimately go without electricity for a full 7 days ; the production unit however remained operable on backup power throughout this period thanks to its cogeneration equipment.

Damages were estimated at 4.5 million francs : a loading arm was down, unusable rail track, a number of roofs and fences damaged, and an empty railcar derailed subsequent to an SNCF Railway Company switching error that routed to the site a set of 25 railcars, though the line's capacity was only designed to accommodate 22...

Several areas on the GARONNE River side of the embankment were opened and then completely submerged by the height of floodwaters (2.6 m). An 80-cm wave swept over the Ambès peninsula. The main difficulty encountered was the slow speed at which water was flowing from the ground towards the DORDOGNE and GARONNE Rivers, given that the existing discharge system (consisting of local streams, gates and valves) had not performed adequately as a result of improper maintenance. The damaged rail track throughout the zone was still unusable 2 weeks after the storm had passed, as the teams assigned to clean up and restore service required a long time to access the track due to flooded conditions.

These floods affected some 10 companies (ARIA 17316 through 17324) and underscored the vulnerability of some Seveso sites. An update of the relevant safety reports and internal emergency plans would be requested of the various site operators so as to specifically incorporate flood risks. The creation of a Permanent Secretariat for Industrial Pollution Prevention (S3PI) overseeing the 4 concerned municipalities was viewed as the appropriate entity to coordinate these problems with all actors involved.

      **ARIA 19295 – 31/05/1993 - GERMANY - LUDWIGSHAFEN AM RHEIN**

      *20.14 - Manufacturing of other basic organic chemical products*

      At an organic chemical plant, an ammonia (NH₃) discharge occurred inside a urea unit operating in slowdown mode in preparation for a repair job. A regulation valve was activated to limit the quantity of NH₃ fed to the reactor by re-injecting a portion of the flow to supply the pump; however, the valve was vibrating strongly while in this operating mode. Sensing difficulties in adjusting the quantity of NH₃ intake, the technicians partially closed a manual valve positioned downstream of the regulation valve. A short time thereafter, 500 kg of NH₃ escaped from the unit, which underwent an emergency shutdown. A water curtain prevented the NH₃ vapours from becoming airborne. This accident was due to the partial opening of a safety valve discharging NH₃ into the absorption device, causing an overload and evacuation into the open air via the washing column. In order to avoid repetition of these conditions, the operator installed orifices on the expansion pipes to evacuate liquid ammonia towards the absorption device. In short, this accident was due to human error.

      **ARIA 21460 – 23/11/2001 - 25 - EXINCOURT**

      *29.1 - Automobile construction*

      At an automobile plant, an employee working on the subcontracted dumpsite was snared in a compactor mechanism while using a pole to free boxes that had become stuck. According to initial investigation findings, the press that had malfunctioned earlier the same day was restarted before being totally repaired.

      **ARIA 24020 – 28/11/2002 - ITALY - MESTRE**

      *20.14 - Manufacturing of other basic organic chemical products*

      At a chemical plant, a tank containing a mix of toluene-2,6-diisocyanate (TDI) / tars with a high boiling point increased in pressure and exploded around 7:40 pm. The cloud ignited 5 min later ; afterwards, the fire was fed by 20 tonnes of oil and 1 tonne of toluene flowing from the burst pipes. An identical tank burst 40 min later due to a domino effect, causing a 2nd explosion whose blast extinguished the main fire.

      In-house first responders and some 60 external fire-fighters were mobilised. The external emergency plan was lifted at 9:30 pm, and the internal plan at 10:45. Projected by the blast and sprayed by viscous fallout, 4 subcontracted workers received medical treatment and would be off the job between 3 and 53 days. External property damage was assessed at €2.8 million; internal damage resulting from pressure waves and flying metal fragments was extensive and affected: supporting frames, pipes, electrical connections, and installation utility lines. Some 15 tonnes of TDI/tar mix were released. The authorities conducted pollution measurements in the industrial park sewer system, revealing TDI concentrations of 5,280 mg/l. A temporary, yet intense, pollution of the water treatment lagoon was observed over more than 1 km. The atmospheric measurements recorded indicated a major presence of No_x / carbon, along with traces of hydrocarbons (toluene, ethylbenzene).

Following the maintenance shutdown of the reactor stirrer upstream of the damaged tank 48 hours prior, temperature rose from 150° to 230°C in the TDI/tar tanks. This temperature, coupled with extensive residence time (13 hr) in the tank, prompted the initiation of TDI exothermic dimerisation, with CO₂ production as the source of this pressure build-up. A foam plug formed in the connecting pipe at the purge manifold prevented the tank's safety disc from bursting. Inspection authorities also found no evidence of written procedures relative to a degraded mode of operations (such as the presence of high temperature). Moreover, none of the associated risks or tank pressure measurements, pressure increases in the TDI/tar tanks or eventual exothermic reactions had ever been specifically identified during the process risk assessment. The tanks were designed for a max. temperature of 95°C, while the measurement scale and calibrated instrumentation were set to tolerate temperatures of less than 120°C ; moreover, temperature indicators were broken and tank pressure measurements were either missing or unusable. Prior to resuming plant activity, the operator performed a detailed safety evaluation of the entire site and undertook the technical/organisational modifications necessary to achieve and then maintain a high level of safety.

ARIA 25900 – 18/08/2003 - 21 - MONTBARD

24.20 – Production of pipes, including hollow profiled pipes and corresponding steel accessories

Within a surface treatment plant that had been closed for the summer holiday period, a leak of a basic degreasing agent (pH = 10) seeped into the stormwater drainage network and then polluted a river subsequent to a thunderstorm event. The spill stemmed from a retention basin connected to this network (yet the operator was unaware of any such connection) ; this oily liquid substance was deliberately stored in the basin at the time of maintenance work in the plant. In order to contain the pollution, emergency service personnel used an inflatable plug to block the discharge pipes leading from a stormwater retention basin. Notified at the end of the day by the Departmental Fire and Safety Centre (CODIS), the Hazardous Installations Inspectorate requested the operator to pump and dispose of 2 m³ of polluted water. On the next day, a site manager informed the inspectorate of a rise in basin water level and of the difficulties encountered in identifying a disposal service; pumping operations (on a volume of 80 m³) were to ultimately begin at the end of the day and be completed by the following morning. The increased volume of polluted water was due to the fact that the stormwater network also collects water from a small brook. The administrative investigation would reveal that the use of retention basins as intermediate storage tanks was a typical practice within the unit during maintenance work on installations or even during normal operations. The inspectorate also noted the following: the absence of both guidelines for maintenance tasks and an emergency response plan in the case of accident, unavailability of product safety data sheets, inadequate network drawings, and the inoperability of liquid detection alarms within retention areas. Lastly, the inspectorate noted the facts and proposed that the Prefect issue an official injunction imposing all necessary installation compliance work.

      **ARIA 31691 – 26/04/2006 - 60 - CATENOY**

      *20.14 - Manufacturing of other basic organic chemical products*

      Inside a chemical plant, a sulphur dichloride (SCl₂) leak on a pipeline supplying the boiler tube of a distillation column hydrolysed, thereby generating a strong emission of hydrogen chloride (HCl). This column was located in a building with a cladding that formed a sort of confinement.

      The internal emergency plan was triggered. Water curtains were activated and the external fire station was notified. 50 ppm of HCl were recorded inside the building (irreversible effect for 1 hr of exposure = 60 ppm), though readings remained below the detection threshold outside. Three in-house responders were assigned to hospital observation. Water from the activated curtain (100 m³) was collected in the fire water basin. Operating losses were valued at €270,000 (the downstream unit stayed idle for 18 days).

A pressure sensor was undergoing maintenance ; it had been diagnosed as defective after indicating a reading of 108 mbar of pressure at the boiler tube output (upper alarm threshold = 100 mbar), thus triggering closure of the valves controlling SCl_2 supply and regulating the vapour heating the boiler tube. Before replacing the sensor, the boiler tube contained 150 kg of SCl_2 and could not be drained due to the presence of glass stemming from degradation of the distillation column. This clogging situation had been known for 3 weeks, yet no remedial measures had been taken. Moreover, the pressure sensor shutoff valve, whose bolts were permanently seized and fastened, could not be closed; the technician was forced to disassemble the entire set-up, allowing air to be exposed to the DN25 tap. Since the sensor was not designed with positive safety, its electrical disconnection caused the vapour regulation valve to open, thus heating the boiler tube, whose temperature rose from 24° to 120°C in 30 min, and causing the emission of SCl_2 .

Several measures were adopted as part of the feedback provided : monitoring and intervention procedures in a degraded operating mode, modification of the sectional valve / pressure sensor assembly, introduction of a positive safety loop independent of the regulation, thereby prohibiting any automatic restart once the high pressure threshold had been reached.

This accident demonstrates that a process regulation system can in no way be equated with a safety device. More specifically, the programmable production automata satisfy a rationale and criteria that are not all known by response teams and that do not necessarily incorporate degraded modes and recorded situations.

 □ □ □ □ □ □ **ARIA 32016 - 24/07/2006 - 80 - AMIENS**

 □ □ □ □ □ □ *37.00 - Collection and wastewater treatment*

 □ □ □ □ □ □ A discharge of black wastewater polluted the Selle River and caused fatalities among the fish population.

 □ □ □ □ □ □ An alert was sounded during the morning of the following day. The pollution occurred subsequent to the

deficiency of a pumping station at the city's purification plant, leading to the direct spill of wastewater (discharged from a dry cleaners) into the natural environment via the overflow chamber.

The general station circuit-breaker, turned off at the time, was responsible for the accident. Once it had been turned back, normal operations could be restored. This malfunction would have been due either to vandalism (signs of forced entry into the electrical cabinet) or to the intense heat. Moreover, network remote monitoring was running in a degraded mode: a thunderstorm a few days prior had destroyed the remote transmission equipment at the pumping station, with information on system flaws not being relayed to the monitoring station. These safety devices could not be replaced due to an inventory shortage in the maintenance workshop, and many equipment replacements had to be carried out since the beginning of the month due to the frequent occurrence of thunderstorms.

 □ □ □ □ □ □ **ARIA 32484 – 08/11/2006 - 77 - GRANDPUITS-BAILLY-CARROIS**

 □ □ □ □ □ □ *20.15 - Manufacturing of nitrogenous products and fertilisers*

 □ □ □ □ □ □ In a fertiliser plant, ammonia (NH_3) emitted in a shop working with hot ammonium nitrate solution intoxicated 4 workers, 2 of whom were employed by a subcontractor. The unit was placed in a safe

operating mode and the local fire station was notified. The 4 injured personnel were hospitalised 5 hours for medical exams.

The workshop had been operating since the previous day. The nitric acid (HNO_3) flow rate regulation, which normally takes place automatically, was placed in manual mode due to the difficulties encountered in stabilising pH of the reactive media. A maintenance work order had been scheduled for 9 am on the day of the accident.

During the maintenance visit, both the low and high flow rate safety mechanisms were inhibited when tested. Following adjustment of the HNO_3 intake valve, acid flow stopped abruptly, causing excess NH_3 in the reactor. The technician attempted to reactivate the flow safety devices and then voluntarily restarted the reactor. Basic vapours were thus being discharged via the unit vents and by degassing the non-recycled condensates discharged into the gutters crossing the workshop.

 □ □ □ □ □ □ **ARIA 32679 - 04/11/2006 - 76 - PETIT-COURONNE**

 □ □ □ □ □ □ *19.20 - Crude oil refining*

 □ □ □ □ □ □ An incident on a German very high voltage network (Cf ARIA N°32455) caused disturbances in the power grid by generating a low frequency threshold causing several units in the refinery to switch over to the

safety mode. In line with the architecture of the power supply system, only the units supplied by the utility turbo-alternators were operating. These included the utilities, the CLAUS 4 hydrogen sulphide conversion

unit, SCOT tail gas treatment unit, the PLAT fuel catalytic reforming unit, the HDS gas oil desulphurization unit and the CRYO and HMP hydrogen production units.

The operator set up a crisis unit without triggering the internal emergency plan. The Propane Deasphalting Unit (PDU), Furfural Extraction Unit (FEU) and Viscosity Breaking unit (VBU) re-started on a priority basis. The operator decided to leave the CLAUS 5 unit shut while the CLAUS 4 was still operating. This loss of power supply resulted in a hot oil leak at the oil unit exchangers, spilling of the catalyst from the catalytic cracker unit FCC and the solvent (methyl-ethyl-ketone and toluene) initially onto the ground and then to the drains from the solvent dewaxing units. This accidental release resulted in the COD measured in the oily waters of the platform to exceed for several days. It is also responsible for significant flares (hydrocarbon rate > 110 g for 40 min) and the unstable load of the CLAUS 4 sending hydrocarbons for incineration (due to the overflowing of the amine tower), and triggering a high temperature alert. A sulphur dioxide concentration peak (823 $\mu g/m^3$) was recorded by the sensors of the air quality monitoring association in the town on 6 November since the SCOT unit treating the tail gases of the CLAUS 4 unit could be re-started only on 7 November due to poor load. Lastly, dispatch of butane and procurement of jet fuel from the refinery were stopped.

 □ □ □ □ □ □ **ARIA 34990 - 18/06/2008 - 971 - BAIE-MAHAULT**

 □ □ □ □ □ □ *52.10 - Warehousing and storage*

 □ □ □ □ □ □ In an oil depot, after unloading a ship, the security agent observed a leak under a fuel pipe connecting

the wharf to the depot. The agent installed a recipient to collect the drips and informed the operations manager who in turn informed the head of the depot. Less than 5 litres of fuel had leaked to the ground.

The head of the depot observed the leak and decided to install a water pipeline. He informed his superiors and the inspection authorities for classified facilities who visited the site the following day and observed several areas showing significant corrosion especially near each of the supports along the pipeline. Since the pressure in the pipeline was low during the leak, there was no significant impact on the ground.

The initial coating of the pipe was not adapted to the corrosive nature of the marine environment, temperature, high relative humidity, friction and drippings from the mooring ropes of ships. Moreover, according to the operator, the maintenance schedule of pipes was drafted following the recommendations of a specialised body that carried out thickness inspections in 2007 and that stated that the anomalies on account of corrosion were acceptable given the operating conditions of 10 bars. The facility overhaul procedure was underway but the leak occurred before the action plan could be fully implemented. On 19/06/08, the

pipeline was inspected by a company expert whose observations contributed to defining the operating conditions in degraded mode for all forthcoming unloading operations. The three other pipelines connecting the depot to the wharf were inspected a few days later (thickness measurement at areas showing external and internal corrosion detected during the 2007 inspection by the specialised body). An operations schedule was drafted based on these measurements: repair of pipelines and supports, installation of collars in sensitive areas, resistance tests, replacement of sections, application of bituminous coating, application of a coating using basic metal deposits obtained by welding, specific protection under mooring ropes, excavation of soil under the pipes running along the banks, etc. The operator decided to reduce the pressure in the pipeline in question to maximum 3 bars and reinforce surveillance until the operating conditions were back to normal. The operating procedures were accordingly modified.

      **ARIA 37440 – 23/10/2009 – PORTO RICO - BAYAMON**

      *19.20 - Oil refining*

An explosion occurred around 12:30 pm in an oil depot at a refinery ; 21 of the 40 hydrocarbon tanks caught on fire. Flames were visible several kilometres away, with a dense, black and toxic smoke released. A state of emergency was declared in five neighbouring municipalities ; a total of 1,500 people were evacuated, schools were closed and both air and road traffic was rerouted. Several drivers were injured by exploding car windows, while others were intoxicated from the smoke ; 3 rescue workers were also hurt. A shake measuring 2.8 on the Richter scale was recorded; dwellings and industrial premises were damaged at a distance of over 1.6 km from the explosion, and window panes were reported shattered several kilometres away. Local residents were asked to remain indoors due to the toxic smoke. The authorities prepared a stadium to accommodate up to 30,000 evacuees if necessary. Fire-fighters brought the fire under control on October 25th, at which time residents were allowed back home. Damages were estimated to run above \$6.4 million.

America's independent accident investigation commission (CSB - Chemical Safety Board) sought to identify the causes of this accident; according to initial findings, a gasoline tank was being filled from a boat. This tank had apparently overflowed, with gasoline spreading over the floor and forming an inflammable cloud 600 m in diameter prior to reaching an ignition source northwest of the site. The liquid level in the tank could not be determined, as the corresponding automated control system was not operational. Field technicians used a mechanical gauge on the outer tank wall, while control room technicians were unaware of the imminent danger resulting from tank overflow.

ARIA 37597 – 07/08/2005 - 76 - GONFREVILLE-L'ORCHER

19.20 - Oil refining

In an oil refinery, a leak was detected on crude oil tank A607 with a nominal capacity of 60,000m³ and filled at over 50%. Ground pollution covered several square metres from the extreme western edge of the tank until reaching the sump located a few metres from the tank shell. According to the operator, who was unable to visually observe any external corrosion either on the shell or on the visible section of the tank bottom and who relied on general renovation works conducted in 2000, with complete replacement of the tank bottom and foundation reconstruction and with feedback provided by other leaks (which had evolved slowly in a controlled manner), the tank's structural integrity was not considered suspect. The tank was kept operating under daily monitoring that took the form of rounds with : introduction of sand dams in the retention basin, regular pumping of spilled hydrocarbons, creation of a gutter to channel flow towards the sump, and replacement of the surface layer containing polluted gravel.

Six successive filling operations were conducted through Sept. 6th, when during the evening a sudden increase in the leak flow rate (20 m³/hr) was noticed at several points. On Sept. 7th, it was decided to drain the tank, and the crude oil was routed to the site's distillation units. The Classified Facilities inspectorate was informed of the event in the afternoon of the next day. In addition to verifying the tank's complete drainage, a technical inspection on Sept. 13th confirmed the presence of a few areas of seepage around the edge of the tank base, along with pollution over the entire retention basin surface area (and puddles of oil several centimetres thick in some areas). The inspectors also identified contamination in retention tanks A209 and 201, which were independent of tank A607. A decree ordered the issuance of incident reports on all 3 of these tanks as well as cleanup of the corresponding retention basins.

The expert appraisal of tank A607 revealed many internal corrosion pits on the tank bottom metal sheets and along welds with a leaky zone, plus the absence of a lining to protect against internal corrosion when replacing the bottom in 2000 ; two additional cases of leaks on this site's crude oil tanks would be identified in 2007 and 2009 (ARIA 33077 and 36502).

The operator installed an epoxy lining on the tank bottom prior to resuming operations and decided to extend this measure to all other onsite crude oil tanks. A penal court fined the operator €800 for failing to file the incident with the Classified Facilities Inspectorate.

      **ARIA 37720 – 08/01/2010 - 51 - MATOUGUES**

      *10.31 - Transformation and conservation of potatoes*

A pipeline burst around 2 pm at a plant devoted to the transformation and conservation of potatoes; 11 of the 13.5 m³ of the 32% hydrochloric acid (HCl) from a 30-m³ tank leaked, to a point of filling the retention basin.

      An on-duty watchman noticed a strong irritating odour around 10 pm and sounded the alert. HCl was discovered shortly thereafter in a gutter running parallel to a suppressor room located near the tank. A 20-m safety perimeter, demarcated by ribbons and metal containers, was set up around the installations. The stormwater basin outlet was plugged by an impermeable ball. Personnel working in the site's packaging zone were evacuated as a result of odours emanating from the stormwater drain pipes.

At 10:40 pm, two equipped individuals observed that the tank's retention basin was not well sealed and moreover that HCl began spreading on the ground along the suppressor utility room, over the adjacent lawn and onto the pavement. The tank leak was brought under control around 11 pm by successfully closing the bottom valve. The polluted stormwater remained confined while awaiting a decision regarding its disposal; this decision was made the following afternoon, in consultation with the Classified Facilities inspectors.

Also on the next day, pollution measurements at 3 points, conducted with fire-fighter assistance, showed no anomalies. The wind blew in a way that favoured dispersion of the emitted acid vapours, and fortunately the plant was located in the middle of a field with no dwellings within 1 km of the installation. The pH of effluent contained in the basin could be verified, as was the absence of chlorine gas in both the pipes and packaging sector. The Classified Facilities Inspectorate and local gendarmerie also made visits to the site.

The packaging zone was fully ventilated before personnel were allowed to return to work inside. The operator decontaminated the site by recovering a maximum quantity of HCl on the ground for tank storage. The bituminous pavement and utility room were both cleaned. The stormwater collector pipes were rinsed for 4 hours with abundant quantities of water. The pipe break was due to frost (-4°C at the time of the incident); moreover, the basin was not impermeable around the bottom slab / lower wall intersection. By undergoing maintenance, the tank was missing its antacid protective liner; HCl was thus spread over the pavement and adjoining land, before spilling into the collector connected to the stormwater drainage basin. A piping system made with more efficient material was installed. The basin was restored to good working order. The alarm warning of an abnormal drop in HCl inside the tank was upgraded. The damaged stormwater pipeline was placed under camera supervision, and the internal emergency plan was revised.

ARIA 37902 – 06/01/2009 - 72 - SABLE-SUR-SARTHE

21.20 - Manufacturing of pharmaceutical preparations

During a surprise inspection at a pharmaceutical plant, the Classified Facilities inspection authority noted that technicians were not complying with safety guidelines guaranteeing their radioprotection in the case of an incident when recharging radioactive sources. Such sources, implemented to sterilise medical accessories, were placed in 2 metal frames or holders at the bottom of a pool and in a safe position during the recharging operation. Sources were handled with poles, equipped at one end with a small chain to avoid any uncontrolled rise to within 3.5 m of the pool surface. During the follow-up visit held on December 9th, 2009, the inspector observed the same safety shortcomings and procedural noncompliance. According to the operator, the safety device was not being used given that its encumbrance impeded pole handling. The operator agreed on January 15th, 2010 to respect the conditions laid out in its guidelines and declared that the event had no consequences for personnel or the environment. Nonetheless, a Class 1 rating was issued on the INES scale due to the potential consequences of an individual's exposure to ionising radiation and noncompliance with the safety manual.