

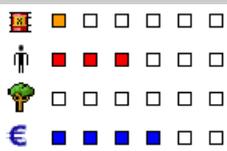


Heat insulators

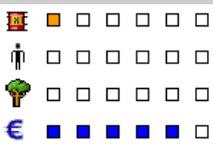
⑭ Explosions in a pharmaceutical plant

ARIA 25337 and 35822 - 13/08/2003 and 08/09/2004 - AUSTRIA - LINZ

21.10 – Manufacture of basic pharmaceutical products



In a chemical plant, 2 explosions occurred in a glyoxylic acid production line followed by a fire. The building in question housed a production unit for intermediate chemicals used in manufacturing antibiotics and crop protection products. The fire-fighters brought the blaze under control in a few minutes. Casualties include 20 cases of injury including a case of serious injury where the person was thrown off the scaffolding by the deflagration. The slight injuries mainly included cuts due to the projection of glass pieces and other debris. A company spokesman confirmed that the building was empty at the time of the accident. Projections were found as far as 150 m. The production line was completely destroyed but the neighbouring buildings only sustained light damage. The internal damage was assessed at 6 M euros. The media reported an operational loss of 15 M euros. Despite the investigations, the real causes of the accident were not known. The summer heat may have triggered a start of fire in a heat-insulated column imbued with peroxyde (reaction intermediate) and methanol (flammable solvent). The fire may have then spread to the two reaction columns causing them to explode. The new reactors installed are designed to resist explosions. Risk-curtailling measures were also implemented. Nevertheless, a second explosion occurred a year later when the facilities were re-started (ARIA 35822).



In a chemical plant, an explosion occurred when a glyoxylic acid production line using the ozonisation technique was re-started. The facility was destroyed a year ago by an explosion followed by a fire (ARIA 25337). The internal emergency plan and the external emergency plan were triggered and fire-fighters were brought in from outside. Since the site was implanted in an industrial zone, all neighbouring establishments in the zone were informed on the accident.

The unit, which has been rebuilt and reinforced (pressure proof) after the 2003 accident, is severely damaged. Nevertheless, the effects have been contained and no casualties were reported. Production was suspended until further notice. Despite several expertises that cost 400,000 euros, the causes of the accident were not known. The operator modified the process (use of air instead of ozone).

Heat insulators

The first of the two accidents described previously highlights the problems encountered in implementing heat insulating equipment (pipes, cold or warm storage, heat exchangers, etc.) and their regular inspection. Under normal operating conditions, insulating material and its protective sheath make it hard to detect any possible malfunction such as excess heating of an equipment part, leak of reagents, solvents or even the coolant. The risk of corrosion, fire or pollution, sometimes insidious is worsened when the leak has lasted for several days or even months before detection (ARIA 23839).

Several cases of start of fire in a heat insulator following an undetected leak and accumulation of a chemical in the insulating material have been reported (ARIA 20358, 24854, 26369, 26249, 27651, 30623, 31217, 32584, 32691, 33106, 34410, 35114, 35349, etc.). The fire can start upon contact with a hot spot (conditions made conducive by the heat insulator) or electrical equipment: electrical cabinet, heat trace cables, etc. (ARIA 29186, 31217)

During a fire, insulation can also complicate rescue operations by preventing facilities from cooling easily (ARIA 4460, 32163) and making the use of special equipment such as thermal cameras to detect hot spots necessary (ARIA 33713).

A heat insulator can promote (humidity, etc.) or aggravate corrosion due to no or late detection. This mainly concerns pipes (ARIA 6475, 24164, 32347, 32429, 34351, etc.) but also tanks (ARIA 6467, 35282) and columns (ARIA 25337, 26578). Pipes in rack run an additional risk and deserve special care as corrosion in heat –insulated pipes can result in domino effect causing other pipes to corrode (ARIA 35146) through condensation of atmospheric humidity, melting of ice and dripping of water.

The design and implementation of a heat insulator followed by its inspection are crucial for the safety of the facilities after their commissioning. Several accidents have occurred due to defects in equipment design followed by implementation of insulating material and the protective sheath (ARIA 25864, 31718).

Regular inspection of the facilities is vital to detect any possible malfunctioning at the earliest. Heat insulators can be equipped with “inspection windows” to verify the air-tightness of flanges, ensure presence of dedicated leak detection systems, facilitate regular checks, etc.

The accidents whose references are not underlined may be consulted at:
www.aria.developpement-durable.gouv.fr

ARIA 4460 - 27/04/1993 - 84 - SORGUES

20.51 - Manufacture of explosives

On 19 March, a tank glazed with 85% H₂SO₄ ruptured leading to a workshop to close down for five days. Given the waste acid storage autonomy period of four days for production, 3 tank trucks hired in February and not dispatched following a leak in the waste acid tank were reused and three additional tank trucks were hired. Tank truck 2 was half filled with waste acid from the production of dinozebe on 26/02, and completed on 23/03 with waste acid from the production of DNCTBB (dinitro 2-6 tertio-butyl 4 chlorobenzene), a crop protection intermediate. On 27/04, nitrous vapours were emitted from the manhole of tank truck 2. The internal emergency plan was triggered. The insulated tank truck was cooled with water hose nozzles. A water curtain was used to disperse the nitrous vapour cloud that was 30 m high and 180 m long. The tank truck exploded since the situation was aggravated by its insulation and closed vents. An acid aerosol was projected over 135 m, metal debris of 3 kg reached 195 m and 15 m³ of matter was spilt on the ground. Two technicians affected by the accident at the boundary of the site were treated onsite. Despite the projections, three lifeguards located at 25 m remained intact. Ground pollution in the town of OUVÈZE was limited and the spill was neutralised with calcium carbonate.

After an enquiry was conducted, it was shown that at room temperature and under adiabatic conditions, dinozebe starts to decompose after 15 days of contact with waste acids from the production of DNCTBB along with the formation of nitrous vapours. There was a slow decomposition reaction between the contents of the tank truck and the trace of dinozebe during the month of storage accompanied by an increase in pressure of the airtight and insulated tank truck. The accident resulted from inadequate cleaning between the two uses and the mixing of incompatible materials that triggered the sudden reaction. Measures were taken for other tank trucks containing the same acids: opening of manholes, cooling devices for tank trucks, etc. The use of temporary mobile storage containers without retention tanks was not allowed. Furthermore no risk assessment studies were carried out on the storage and treatment of waste acids. Material damage was evaluated at 0.36 MF.

ARIA 6475 - 14/03/1980 – THE NETHERLANDS - HENGELO

YY.YY – Activity not known

      There was a leak in polyurethane-insulated pipe transporting heated chlorine. The leak occurred due to the decomposition of polyurethane under the influence of heat (60 °C), and rain and an ambient pH of 2 that resulted in the external corrosion of the pipe.

ARIA 20358 - 10/12/1998 - 13 - MARTIGUES

20.14 - Manufacture of other basic organic chemicals

      Ethylene leaking from an approximately 12 cm breach below the cold insulation of a 4-inch pipe used to supply ethylene to a reactor manufacturing dichloroethane ignited and resulted in a fire that lasted 40 minutes.

ARIA 24854 - 01/04/2001 - NETHERLANDS - SITTARD-GELEEN-BORN

20.60 – Manufacture of artificial or synthetic fibres

      While re-starting the acrylonitrile units of a synthetic fibre plant, the facilities were flooded with water for 2 hours to test the resistance of equipment. A leak was observed in a steel pipe. Since chlorine was present in the heat insulators covering the pipes, corrosion due to chlorine was immediately suspected to be cause. Several samples were taken and analysed. However, the results excluded the above assumption as the cause of accident. Further investigations revealed that the leak occurred in an area that was often cleaned with sodium hydroxide to remove the frequent polymer deposits. This was confirmed by an expert analysis carried out by a third party. The steel pipe was replaced and as an additional precautionary measure the operator had to test the equipment resistance again by flooding the facilities with water or nitrogen to apply a maximum service pressure for 24 hours under the supervision of the inspection authorities. Since no further leaks were detected, the operator was allowed to re-start the units.

ARIA 26578 - 05/05/1975 - NC -

19.20 – Oil refining

      A fire broke out on the distillation tower of an atmospheric distillation unit operating normally in a refinery. The fire appeared on the valve spur of a naphtha stripper. The stripper was heat insulated till the spur. The naphtha leaked out and spread over the heat insulator that caught fire. The accident led to the temporary shutdown of installations and occurred due to the leak caused by a 6 mm crack in the ox-bow of the stripper. Corrosion was responsible for the leak.

ARIA 29186 - 31/03/1966 – UNITED STATES - LAWRENCE

ZZ.ZZ – Unknown origin

      The technician of a the nitrogenous solution loading station heard the safety valve open and saw a 2 to 3 m flame surge from the exhauster duct near the pump. An abrupt explosion occurred and the solution gushed out of the tank in huge quantities. The new team had just clocked in 15 min. back after the previous shift which had completed all loading operations, stopped pumps and had left all valves open except the valve in the loading station. An explosion occurred at the elbow of the 10 to 15 cm diameter, ascending steam-insulated and -traced part of the exhauster duct. This was due to the decomposition of the nitrogenous solution upon passing through the holes created by corrosion of the elbow weld into the insulating material made of aluminium. Furthermore, maintaining the steam tracing temperature contributed to the explosion. A similar explosion had occurred in a transfer pipe of the same unit on 25 May 1966 while the steam tracing was not commissioned.

ARIA 31217 - 29/12/2005 - 76 - NOTRE-DAME-DE-GRAVENCHON

19.20 - Oil refining

      In an oil de-waxing unit, a pool on fire was detected a little before 6.00 am at the foot of an oil/ammonia cooler that was neutralised the previous day following the detection of a hydrocarbon leak. The fire spread to an area of 50 m² and damaged the electric cabling, piping, neighbouring valves and fittings and four heat exchangers. The internal emergency plan was triggered and the fire-fighters brought the fire under control at 6.18 am. No casualties or pollution were reported. The economic impact, mainly due to the damage caused to the equipment and loss of production due to shutdown of facilities was assessed at 400 k euros. More than 12 hours before the fire, the technician had repaired a leak after draining and emptying hydrocarbons and crystallisable paraffin. The paraffin may have partially solidified in the heat insulator protecting the device thus retaining several hundred litres of solvent. During the previous night, heating with steam would have caused the most volatile substances in the insulator to evaporate. Heat tracing had triggered a wick fire phenomenon that liquefied the set paraffin and released around 2 tonnes of an already ignited mixture. The operator implemented measures to avoid similar accidents from reoccurring.

    **ARIA 31718 - 07/04/2006 - 74 - TANINGES**

10.13 – Preparation of meat products

   In a meat packing unit, 200 kg of ammonia (NH₃) leaked at 4.30 pm from a corroded pipe of a refrigeration unit (900 kg of NH₃) cooling two ham and sausage dryers.

 [...] According to [an expert], the corrosion was due to a flaw in the assembly of the heat insulator: the steel of the insulator was not protected by a petrolatum tape or a pitch layer. The corrosion went undetected since the heat insulator showed no signs of damage. The rusted pipes were replaced and the internal action plan was drafted into a written procedure. The operator planned to replace the refrigerant.

    **ARIA 32347 - 28/08/2006 - 61 - ARGENTAN**

10.52 – Manufacture of ice creams and sorbets

   In a deep-freezing tunnel of an ice cream manufacturing plant, 40 kg of ammonia (out of a total of 13 tonnes of NH₃ in the facility) leaked at 6.30 am from a pipe in the cone production line. The refrigerationist onsite was immediately informed by a technician. At the same time, the workshop's automatic detection system alarm was activated indicating a 300 ppm threshold and was deported to the control room triggering a siren [...].

The damaged pipe was covered with polyurethane foam that in turn was protected by a steel coating. Significant external corrosion was detected below the heat insulator. The corrosion could not be detected upon mere visual inspection and was responsible for the rupture of the pipe that operated in rough conditions in a humid atmosphere. This possibility was not taken into account during the safety assessment studies. The emitted NH₃ accumulated in the pipe between the closed valve and the point of leak. The operator had already taken steps to prevent corrosion especially when replacing pipes at regular intervals by systematically protecting them with petrolatum tapes to minimise the effects of humidity. A new round of inspection of all pipes in the deep-freezing tunnel was carried out to gradually replace the polyurethane-insulated pipes with petrolatum tape protected pipes as polyurethane speeds up corrosion.

    **ARIA 33106 - 14/06/2007 - 38 - ROUSSILLON**

20.14 - Manufacture of other basic organic chemicals

   In the cumene - cumyl hydroperoxide section of a seveso classified chemical facility, a technician on rounds detected a start of fire at 6.00 pm on a 6 bars steam line in the drain. The blaze resulted from the inflammation of a heat insulator imbibed with cumene / cumyl hydroperoxide (highly inflammable chemicals) insulating the pipe. The fire was quickly brought under control using two fire extinguishers and did not impact the rest of the facility.

    **ARIA 34351 - 16/03/2008 - 44 - DONGES**

19.20 - Oil refining

   The complete summary of this accident is presented in the sheet entitled "the effects of time on industrial facilities".

 "The examination of the pipe revealed an approximately 16 cm² longitudinal breach caused by corrosion localised under the heat insulator due to the leakage of water from a pipe situated vertically above. The water accumulated below the heat insulator and caused corrosion and then punctured the fuel oil pipe."

    **ARIA 35146 - 06/09/2008 - 76 - NOTRE-DAME-DE-GRAVENCHON**

20.11 – Manufacture of industrial gases

   Around 1.25 pm, a technician detected a strong smell of gas that he identified as propylene and noticed a cloud of fog at the centre of steam cracker without being able to precisely pinpoint the site of the leak. He then went to the control room and sounded the alert. The detection alarms of several gas indicators of the zone were activated on the safety panel [...]

Around 3.35 pm, a breach was localised on a 500 m long, 4" (101.6 mm) diameter carbon steel pipe carrying liquefied butane and operating under a pressure of 18 to 20 bar. At 3.40 pm, the contents of the line started to be released into the flare network and at just a little before 3.50 pm, the circuit was isolated and the leak reduced. The internal emergency plan was lifted at 4.00 pm. The operator published a press release. The total duration of the leak was estimated to have lasted for a little less than 2 hours and 30 minutes. The operator confirmed that the concentration of the gas had attained 20% of the LEL [...]

The examination of the pipe in question revealed an approximately 50 mm X 20 mm longitudinal opening in the upper generator with a diameter of about 30 mm. A significant loss of thickness was observed in the rupture zone. The non-insulated tube showed a generalised corrosion on the entire section.

Another rack housing a refrigerated ethylene pipe overhung the wrap containing the defective pipe. The corrosion resulted from the water droplets trickling down from the melting ice surrounding the ethylene pipe situated above the defective pipe.

[...] the operator indicated that the pipe was only inspected regularly but not overhauled. The next inspection was planned for 2009. [...]

ARIA 35349 - 31/10/2008 - 13 - CHATEAUNEUF-LES-MARTIGUES

19.20 - Oil refining

At 2.45 pm, a fire broke out in the heat insulator of a steam line in a pipe network inside a retention system without any storage tank. Following heavy rains, the heat insulator was imbibed with heavy hydrocarbons brought by the rain water.

The safety department took immediate action and put out the fire that released a cloud of smoke after several minutes. End of alert was sounded at 3.00 pm. The operator drafted a press release the very day.