



Mixing incompatible products



DR

17 Accidental generation of chlorine in a company trading in chemicals

ARIA 35830 – 05/10/2007 – GERMANY – FRANKFURT AM MAIN

46.75 – Wholesale of chemicals

	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>
	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

A cloud of chlorine gas was accidentally generated around 10.30 am while transferring hydrochloric acid (HCl) into a tank containing sodium hypochlorite (NaClO or liquid bleach) in a chemical wholesale company.

The accident happened during a period of rebuilding of the unit; the filling station and the delivery station were in the process of being renewed. At the delivery station for tankers there only one connection for all chemicals but FeCl₃. A pump transports the fluids via pipe to a connection battery / filling station for drums. At the battery, a worker connects the pipe, by using a hose, to the right tank. The technician chose the wrong tank at this point. Realizing his mistake, he stopped the transfer operation thus limiting the quantity of chlorine released to 200 kg. The employee was severely poisoned and died a month later.

The police stopped traffic in the industrial area and the residents within a perimeter of 200 metres were required to stay indoors for 2 hours. 54 people were treated by around 120 fire-fighters.

Further to this accident, the unit is rearranged:

- The delivery station for roadtankers was equipped with a separate filling pipe for hypochlorite. The adapter was equipped with left hand threads (mistake-proofing?).
- All adapters of the storage unit were locked off and keys will be released after analysis by the laboratory personnel.
- All connections were clearly labelled.
- The hypochlorite pipe is monitored by a pH-electrode.

Mixing of incompatible products

This tragic accident in a non-SEVESO German facility illustrates the frequent risk related to transferring chemicals between fixed or mobile tanks during both filling and emptying of reactors or any other storage containers used in the industry. This risk concerns accidental mixing of incompatible products (ARIA 10086, 10851, 15375, 14377, 17921, 17941, etc.).

This risk is ever more insidious as the mixtures generally involve so widely-used “standard” substances such as sodium hydroxide, liquid bleach, acids (hydrochloric, sulphuric, phosphoric, nitric, etc.) that the technicians “forget” or “underestimate” the potential danger. The risk of mixing incompatible products resulting in chemical (acid/base, ferric chloride/bleach, etc.) or physical reactions (exothermal dilution: concentrated acid/water, acid/acid, etc.) accidentally or due to lack of knowledge of the physico-chemical properties of the products involved is consequently increased.

The accidental mixing may suddenly result in the production of significant quantities of toxic or inflammable gaseous reactants or corrosive projections and even lead to the damage or destruction of the container due to either a significant rise of temperature of the liquid or accelerated corrosion.

Several accidents recorded in the ARIA database underline the importance of certain factors whose role is crucial in preventing such accidents:

- A sound risk analysis underlying such operations to identify a maximum number of triggering events and reduce their occurrence (11664, 27555, 29036, etc.).
- Appropriate ergonomics of installations with storage of incompatible products in distinct tanks, including their retention tanks (ARIA 6004, 15976), sufficiently spaced apart and as far as possible without common pipes (supply, gas phase return, etc.).
- Clear labelling, ID colour code on transfer hoses and related storage containers, mistake-proofing for filling devices (manifold, etc.) end pieces, etc. The risk of errors is increased in the case of unequipped facilities (ARIA 10851, 22217, 27555, 29036, etc.).
- Specific training of staff, employees of company or subcontractors performing operations (ARIA 167, 220, 21984, 27555, 32131, 32582, etc.). Regular reminders on guidelines and possible incompatibility between products or products and material maintain the awareness to risk underlying these operations deemed “simple” but that always require a certain degree of caution and care. Since risk prevention devices are relatively limited, the organisational abilities of the company mainly form the basis of measures for reducing risks.
- In addition to the deliveryman, the presence during the entire operation of at least one other person trained in the “receiving” company, who can guarantee the safety of facilities, effective transmission of information and smooth transfer, is strongly desired. Accidents occur when a deliveryman either on his own or just temporarily accompanied by a technician makes a mistake in identifying the tank or makes a wrong connection (ARIA 220, 22217, 27511, 27555, 29036, 30614, 32582, etc.).

Moreover, even though the kinetics of reactions involving incompatible products is generally very fast, some of them may be slow enough, at least in the initial phase, to go unnoticed or unreported at the time of the moment. This consequently results in accidents deferred in time (ARIA 4460, 34431, etc.). It is thus advisable to report all errors or accidental mixing even if they seem consequence free at that particular moment so that the potential risk of the situation can be analysed and appropriate measures taken at the right time if needed.

Lastly, for such type of relatively frequent accidents, whose prevention mainly depends on organisational measures, a global approach is ever more called for. Protective barriers formed by risk-reducing technical devices (valves, vents, personal protective equipment, etc.) or human intervention (emergency measures such as stop of transfers, alerts, neutralising accidental mixtures if needed, etc.) as well as limiting consequences by protecting people (confinement, evacuation, etc.) must be planned and regularly tested.

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

     **ARIA 167 - 17/07/1989 - 58 - NEVERS**
 29.32 – *Manufacture of other automobile equipment parts*
 While transferring sulphuric acid using compressed air, the driver cum deliveryman connected a hose to a pipe connected to a tank containing sodium hypochlorite. After the transfer of 15 litres of acid, a site employee, supervising the experienced driver delivering in the plant for the first time, heard an explosion and closed the compressed air valve immediately. The vent of the tank was ripped off. The chlorine released in the workshop poisoned the driver and 28 other employees (one case of serious intoxication) who were hospitalised. The accident occurred due to the presence of four similar pipes, transfer mode (air pressure --> inertia, etc.) and poor risk-awareness training of the driver cum delivery man. The delivery of products to the site was re-examined.

     **ARIA 220 - 12/07/1991 - JAPAN - FUJI-SHI**
 17.1 – *Manufacture of paper pulp, paper and carton*
 A tanker truck carrying 2 tonnes of aluminium chloride was emptied into a tank containing 11 tonnes of sodium hypochlorite. The driver came for delivery outside working hours and was misguided by the security guards. The mixture caused chlorine to be released. The emissions poisoned 46 employees, six residents and 58 employees of neighbouring facilities who were taken to 11 hospitals. 230 families were evacuated for 7 hours. The chlorine cloud impacted a surface of 4 km².

     **ARIA 4460 - 27/04/1993 - 84 - SORGUES**
 20.51 – *Manufacture of explosives*
 On 19 March, a tank glazed with 85% H₂SO₄ ruptured leading 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 tertibutyl 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 OUVÉZE 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 6004 - 03/11/1994 - 91 - LIMOURS**
 26.11 – *Manufacture of electronic parts*
 In a company manufacturing printed circuits, a tank containing hydrochloric acid overflowed onto a retention tank. The acid was mixed with around 100 litres of sodium hypochlorite or sodium chlorite already present in the tank. A cloud of chlorine gas was formed and spread to the entire building. Five employees were intoxicated and hospitalised. One of them was under observation for over 48 hours. The fire-fighters neutralised the chemical and aerated the premises. The accident may have resulted from the failure of a solenoid valve. This accident would not have occurred if the tanks containing two incompatible chemicals did not have a common retention tank.

     **ARIA 10086 - 08/07/1997 - 81 - CASTRES**
 46.75 – *Wholesale of chemicals*
 In a chemical depot, sodium hypochlorite and formic acid were accidentally mixed while transferring a product from a tanker truck to a fixed tank. Chlorine leaked from the vent of the tank until the valves were closed by the technicians. Ten people were poisoned (truck driver, depot staff and subcontractors) and hospitalised. A third party company analysed the conditions under which the truck was taken for delivery as well as the conditions for the treatment of the polluted tank.

     **ARIA 10851 - 26/02/1997 - 78 - LES MUREAUX**
 30.30 – *Construction in aviation and space sectors*
 A driver connected one of the three transported containers to a tank containing 400 litres of 35% sodium bisulphite solution. A technician observed bubbling of the liquid in the tank and informed the driver who promptly stopped the transfer. A 98% sulphuric acid container that was properly labelled but covered by a plastic cover was accidentally connected instead of the bisulphite tank. The 5 to 10 litres of transferred acid reacted with the bisulphite. An SO₂/SO₃ cloud entered a neighbouring building effecting eight people located between 15 and 30 m from the unit. The eight people took ill and were hospitalised (3 for over 24 hours) and 150 employees were evacuated for 4 hours. The tank was inspected. The isolation and ventilation of the premises were improved and safety guidelines made more stringent.

     **ARIA 14377 - 05/06/1985 - 69 - CHASSIEU**
 20.1 – *Manufacture of basic chemicals, nitrogenous chemicals and fertilizers, basic plastics and synthetic rubber*
 In a chemical wholesale unit, a cloud of chlorine was released into the atmosphere following the accidental transfer of hydrochloric acid into a tank containing sodium hypochlorite. Eight employees were poisoned. The facilities were moved and the storage tank organisation was consequently re-examined.

      **ARIA 15976 - 20/07/1999 - 45 - SAINT-CYR-EN-VAL**

17.22 – Manufacture of paper items for toilet and domestic use

      In a toilet paper production unit, a mixture of sulphuric acid and liquid bleach led to an exothermal reaction accompanied by the release of chlorine and hydrogen chloride. An absorbent product helped retain 150 litres of product that overflowed outside the retention area. Around twenty employees were evacuated. An outside company pumped the remaining product into two tanks. Failure of a valve at the foot of the sulphuric acid tank caused the acid to be spilled into the retention tank shared by the liquid bleach tank (inner separation wall not high enough). The acid damaged the transfer components of the tank causing the products to be mixed. No environmental impact was reported.

ARIA 21984 - 21/02/2002 - 59 - TOURCOING

13.10 – Preparation of textile fibres and spinning

While delivering 4 tonnes of sodium chlorite to a textile company (wool combing and lanoline production) at around 8.30 am, the driver read the loading plan upside down and emptied the wrong tank. About 50 litres of sulphuric acid was transferred to a tank still containing 700 litres of sodium chlorite. Chlorine dioxide vapours and a cloud of sulphuric acid were soon released. The area in the immediate vicinity was evacuated. The gas initially remained confined to a building housing the tanker truck as the mechanical extraction was insufficient. When the police and fire-fighters arrived, a safety perimeter extended to 200 m was set up around the site, all the staff evacuated and the residents informed (people were advised to stay indoors). The fire-fighters disconnected and emptied the transfer hose and broke a glass part of the roof to evacuate the gas. They subsequently sprayed 5 litres of caustic soda at intervals of 15 minutes to bring the pH to 12 – 13 which had dropped to 6.26. Around 3.30 pm, the pH was at 13.3 and the fire-fighters left the site. No casualties were reported and the weather conditions were conducive for atmospheric dispersion. Further to this accident, the operator was asked to prepare a report along with an impact study assessing the environmental consequences of the incident.

ARIA 27555 - 07/07/2004 - 59 - MARCQ-EN-BAROEUL

11.05 – Production of beer

In a brewery, the deliveryman transporting 2 tonnes of hydrochloric acid (HCl) connected the tank truck to the filling inlet of the sulphuric acid (H₂SO₄) tank, next to that of the HCl tank in the absence of a factory staff. Immediately after the pump was started, a cloud was formed and released via the blow off of the tank. The transfer was stopped after verification, but 500 litres of HCl has already been transferred to 1,500 litres of H₂SO₄. The staff from the buildings impacted by the cloud was evacuated. The zone was marked and entry prohibited. The tank was cooled with water until the arrival of a team from the transport company that transferred the contents into a tank pre-filled with 10 m³ of water, slowing down and subsequently stopping the exothermic reaction. A CMIC chemical emergency squad measured chlorine concentrations to be 0.5 ppm. An initial analysis of the causes showed the absence of a formal transfer procedure that required a factory staff to be present for all transfer operations. Moreover, the deliveryman who normally delivered H₂SO₄ was filling in for the delivery of HCl on that particular day. The filling inlets of the two acids were close to each other and were protected by the same locked cabinet.

      **ARIA 29036 - 26/01/2005 - 74 - THYEZ**

25.61 - Treatment and coating of metals

      In an effluent detoxication station of a surface treatment plant, chlorine was released when 800 litres of sodium hypochlorite (NaClO) was accidentally transferred into a tank containing 600 litres of sodium bisulphite (NaHSO₃). These products were used to treat some of the effluents of the site. The accident occurred when 1,000 litres of soda lye, 1,000 litres of liquid bleach and a container transporting 24 carboys of hydrochloric acid were being delivered by a company trading in chemicals. The truck driver accidentally connected the NaClO tank of the vehicle to the filling inlet of NaHSO₃ despite the clear labelling. This occurred during the temporary absence of a factory employee who was away to get a power lift truck to unload the HCl. The chlorine spread to the effluent treatment workshop, outside the premises and also to the production building connected to the wastewater treatment plant by leaking pipe ducts. The rescue services set up a safety perimeter and the company staff was confined to the entry of the production workshop. A day-care centre and five local companies were evacuated and the 98 people were accommodated in the town gymnasium. The inhabitants of neighbouring buildings were confined indoors. Four employees of the surface treatment plant who took ill due to the chlorine emissions were hospitalised for further examinations. They resumed work later on in the day. The rescue services pumped out the product from the tank and lifted the safety perimeter. Further to the accident, the operator has planned to install double-locked filling inlets on the cases requiring the deliveryman and an accredited company employee to be present at the same time, make the shafts connecting the production workshop to the wastewater treatment plant watertight, organise first-aid training for company staff and regularly carry out evacuation drills. Upon the recommendation of the inspection authorities of classified facilities, the prefect has issued an order on 15 February requiring the implementation of procedures setting out the conditions for receipt and transfer of chemicals within one month and preparation of a safety report on the risks relating to the delivery, storage and distribution of chemicals in the factory.

      **ARIA 34431 - 07/04/2008 - 49 - LE MESNIL-EN-VALLEE**

10.13 - Preparation of meat products

      In a meat products factory, a deliveryman emptied sodium hydroxide into a tank normally meant for ferric chloride. Both these products were used for treating effluents. The deliveryman left the site without realising his mistake. A few days later, the operator found out this error due to the malfunctioning of the physico-chemical treatment plant.

      A specialised company transferred the sodium hydroxide into a stainless steel tank brought onsite. During this operation, at around 11.30 am, an exothermic reaction took place in the tank and a light gaseous emission was released. The operator had not warned the specialised company that the sodium hydroxide had been polluted with ferric chloride, a product that strongly reacts with steel resulting in the production of hydrogen. The fire-fighters evacuated the 200 employees of the site and a set up a 100 m safety perimeter. The contents of the tank whose temperature had reached 55°C were transferred into three 1m³ plastic containers. The fire-fighters rinsed the steel tank and continued cooling and monitoring the containers where the reaction was in progress due to the presence of trace quantities of steel. Around 7.00 pm, when the temperature was back to normal, a specialised company took charge of the containers. The employees resumed work during the afternoon.

      The inspection authorities of classified facilities were informed of this accident. The operator had planned to secure and improve identification of transfer fittings of tanks and the products would be delivered in the presence a factory employee qualified to supervise the operation.