

Hazardous waste: beware of incompatibilities!

Accidents caused by incompatible mixtures are not limited to newly-produced chemicals! The end of their life cycle can also be a source of risk. Several recent events in France and abroad confirm this, sometimes with dramatic consequences.

All participants in the hazardous waste chain are concerned: from the private individual who unintentionally pours chemical substances into the sewer, generating toxic gases, to the manufacturer specialising in the treatment of hazardous waste.

Mixtures of incompatible substances most often occur during hazardous waste **grouping/unloading operations** (ARIA 51651, 52842, 52226) or during the **storage** of such waste, most often at landfills (ARIA 48039, 48274, 48393, 50867). While the **reaction kinetics** between incompatible wastes are generally quite rapid, some reactions may be slow enough to go unnoticed or unreported when they occur, thus creating accidents that are delayed over time (as is the case in numerous accidents that occur during storage or transport).

The analysis of such accidents reveals **recurring failures**, which are detailed below:

- **Insufficient checks at the time of acceptance:** incomplete identification procedure; inappropriate/non-representative test method (ARIA 35435, 42944)... leading to inappropriate waste management conditions, or even prohibited waste entering the site (ARIA 48393).
- **Inappropriate organisation of storage facilities:** prolonged storage of highly reactive waste without prior sorting; storage configuration unsuited to the risks (water-reactive waste exposed to inclement weather); storage of incompatible waste in proximity to each other (ARIA 48039, 48274, 48393)... The associated drift-related risks are accentuated in cases of **insufficient monitoring**, particularly during periods of reduced activity.
- **Inappropriate management of grouping or unloading operations:** lack of container cleanliness verification, which may lead to the presence of contaminants; unloading procedures that do not specify the order in which products are to be introduced... (ARIA 32574, 51651).
- **Insufficient training** leading to handling errors (ARIA 52842) or inappropriate behaviour in the event of an accident (ARIA 43204).

Incompatible mixtures and their consequences are not solely the fault of the treatment plant operator. **Some responsibility lies with upstream players.**

- Individuals: inappropriate behaviour on the part of waste collection centre users (ARIA 50866: hazardous waste containers mixed in with empty paint cans);
- Waste suppliers: missing or incorrect information about the composition and reactivity of the waste delivered (certificates, labelling, etc.) (ARIA 43204, 42944), unsuitable packaging (ARIA 52333, 50867, 52349: damaged packaging allowing products to come into contact with each other, opaque bags that complicate visual inspections, etc.);
- Transporters: no guarantee as to the quality of the cleaning performed (tanks), no history of the substances transported, etc. (ARIA 26864).

What dangerous phenomena are observed?

Mixing of incompatible waste results in a violent, often exothermic, chemical reaction which can lead to:

- an **explosion** (ARIA 52349, 52842, 50111, 52226),
- a **fire** (ARIA 51575, 52333),
- the **release of flammable** (e.g.: hydrogen), **toxic** (e.g.: HCN, H₂S), **asphyxiating** (e.g.: CO₂) or **corrosive** (e.g.: HCl) gases (ARIA 35996, 43204, 42944, 44417, 51651), and
- the formation of **unstable materials**.

What are the consequences?

Beyond the consequences for operations (safety perimeter, containment, etc.: ARIA 42944, 52349, 48039, 52649), the facility (ARIA 50111) and the environment (ARIA 48039), it is the **human consequences** that are most notable: residents inconvenienced by the emission of irritating gases (ARIA 1636, 15390, 52649), injury (particularly in the event of an explosion) or poisoning of technicians (ARIA 52842, 35996, 43204)... Even several fatal cases have been reported abroad (particularly involving the release of H₂S: ARIA 21081, 32574, 52226).

ARIA 52226 - 13-09-2018 - BELGIUM

An explosion occurred in a hazardous waste treatment plant while a lorry was unloading liquid waste into a pit. **One employee was killed** and 4 others were slightly injured. The pit exploded, causing pieces of concrete to be thrown onto the nearby motorway. The explosion is believed to have been caused by a mixture of incompatible substances.



Fire in pallets containing dangerous waste following an incompatible mixture (© DREAL Bretagne)



In the event of an accident, crisis management can prove to be complicated and the consequences exacerbated by the absence of an inventory log (ARIA 48039), an inappropriate neutralisation method (ARIA 42944), the lack of a system to capture and process the toxic gases released (ARIA 21081) or the presence of other potential hazards in the vicinity likely to create a domino effect (ARIA 48274).

All of these failures are linked to **incomplete risk analysis** (the scenario of an incompatible mixture not taken into account: ARIA 42944, 48274) or insufficient preparation.

It is regrettable to note that many accidents continue to occur at sites that have already witnessed similar events. How are the **lessons derived from feedback** taken into account?

Release of NO₂ (© SDIS 78)

ARIA 52649 - 26-11-2018 - ILLE-ET-VILAINE

One of three hazardous waste tanks transported on a lorry exploded at the intersection of 2 roads, and a leak of nitrogen oxide (NO₂) was detected. The fire brigade sprayed down the tank and set up a 300 m safety perimeter (in which 1,000 people were confined). The hazardous waste contained in the tank was transferred into small containers so it could be recovered by the shipper. Nine people were slightly affected by the incident.

An uncontrolled reaction, linked to **uncleaned residue from a previous load in the incriminated compartment**, caused the pressure in the tank to increase to the point where its rupture disc failed.

ARIA 52842 - 27-12-2018 - ESSONNE

An exothermic reaction was detected in a tank used to collect liquid waste in a hazardous waste treatment centre. Yellow/green fumes were released. Employees attempted to cool down the outside of the tank with hoses, but an explosion occurred, which ripped open the tank. The plant's internal contingency plan was initiated. Chlorine concentrations of 1.5 ppm were measured in the room. Spraying operations were able to rapidly halt the chemical reaction. A chemist, standing nearby at the time of the blast, was slightly injured.

It was determined that the event was caused by a **handling error**. A technician had poured a container of 30 l of sodium chlorite into a 1 m³ tank containing an organic substance (varnish or ink). The sodium chlorite reacted violently with this substance and chlorine gas was released. The **sodium chlorite had not been identified as an oxidizing substance** during the on-site identification tests. The technician had just completed his initial training period. The event took place during the lunch break, during a holiday week.

The operator has considered installing an emergency smoke discharge and suppression system. **Guidelines have been drafted concerning the transfer of mineral bases** and the safety guidelines have been reinforced regarding the sodium chlorite acceptance procedures. The **newcomer mentoring programme** has also been reinforced.

Several accidents involving incompatible mixtures had already occurred at this site in 2017 (ARIA 50866, 50867).

A few recommendations

- ✓ **Reinforcement of acceptance procedures** (ARIA 35435, 38299, 43204, 51398, 44417, 35435, 50867)
 - More stringent requirements for analyses conducted on the supplier's premises;
 - Increased attention to the condition of packaging in which the waste is placed;
 - Implementation of sampling and data archiving;
 - Increased vigilance when receiving waste from new sources;
 - Prohibition/limitation of deliveries of reactive waste before closing periods;
 - After receipt, the waste should preferably be quickly sorted (ARIA 31857, 48039).
- ✓ **Vigilance on the storage organisation**
 - Organisation based on the chemical nature of the waste (use of incompatibility matrices). For example, bases must be separated from acids, oxidising waste from reducing agents and oxidisers from fuels (ARIA 15390, 43204).
 - Adaptation of materials and physico-chemical storage conditions (temperature, humidity, light, etc..) depending on the waste. Provide a dedicated, closed room or cabinet for particularly reactive/toxic waste (ARIA 49393, 31857).
 - Limitation of the quantities stored, particularly prior to sorting (ARIA 48274, 51651);
 - Reinforced inspections before closing periods (ARIA 52333).
- ✓ **Vigilance concerning grouping/unloading/transport**
 - Verification of the cleanliness/cleaning of containers (ARIA 43204, 52649);
 - Definition of an unloading order to limit incompatible mixtures (ARIA 51651, 32574);
 - Monitoring by the operator during reception/transfer by an external company;
 - Work on ergonomics (labelling, colour coding, foolproofing) to avoid errors;
 - Waste transport: organisation of unloading operations according to chemical incompatibilities of the waste; after unloading, cleaning of the tank if the waste of the next load presents a risk of incompatibility or may have an influence on the waste treatment process.
- ✓ **Implementation of appropriate monitoring/control measures:** infrared detection/video-surveillance, sprinkling devices, gas capture/treatment devices, with regular operational testing (ARIA 48274, 51651).
- ✓ **Definition of the measures to be implemented in case of an emergency:** termination of transfers, neutralisation protocol, etc.
- ✓ **Training:** chemical hazard training for employees and subcontractors; exercises to improve responsiveness; raising awareness of waste collection centre users/communities (ARIA 48351, 50866). Teach contractors to report any accidental errors or mixing, even if they appear to have no immediate consequences, to analyse the potential risk of the situation and to take appropriate and timely action, if necessary.
- ✓ **Work on the completeness of the risk analysis:** updating of hazard studies while taking internal/external feedback into account (ARIA 48274).