

Degassing of a tanker truck containing waste 31 July 2007 Limay (Yvelines) France

Waste Degassing Tanker truck Exothermic reaction Decomposition Procedures / guidelines Internal Emergency Plan Oxygenated water

THE FACILITIES INVOLVED

The site:

The Limay processing centre for hazardous industrial waste, which features an annual capacity of 250,000 tonnes, utilises various treatment procedures depending on the type of waste received:

- combustion furnaces for liquid, paste or solid waste,
- an evapo-incineration furnace,
- physicochemical treatment unit,
- residue stabilisation unit,
- waste unpacking and pre-treatment units.

The involved unit: Incineration unit

Waste materials are received either in bulk or pre-packed and then moved to storage in designated zones: aboveground vats for liquids, ditches for solids and pastes.

For certain types of waste, it may be decided to treat them by direct injection as an incineration process from the tanker truck parked adjacent to the unit.

Waste is conveyed to the combustion furnace intake and then to a rotary furnace. A pre-treatment step (drying) is applied to the sludge according to its level of dryness, prior to introduction into the furnace.

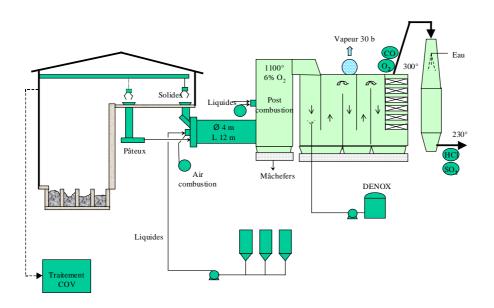


Diagram of the incineration process

The incineration process takes place over several stages: combustion, cooling of gasses, and gas treatment. Fume purification residues are then conveyed to the site's stabilisation-solidification unit.

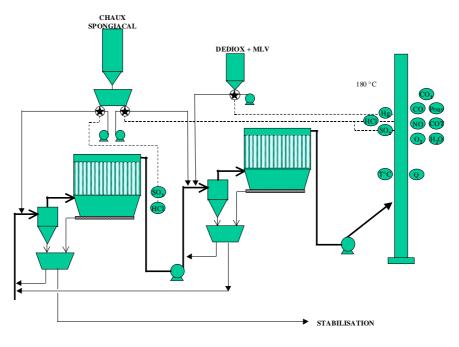


Diagram of the fume treatment process

Waste acceptance protocol:

The onsite acceptance protocol for hazardous wastes is as follows:

- The first step consists of identifying and characterising the specific type of waste before its arrival onsite, by means
 of a representative sample furnished by the waste producer, and offering judgment on waste suitability depending
 on both its characteristics and the site's capacity to provide treatment. A preliminary acceptance certificate is then
 sent to the client and an appointment set to receive the waste.
- Upon its arrival onsite, the shipment of waste must be accompanied by a waste tracking slip. Compliance of this slip along with the acceptance certificate is verified and a sample extracted for analysis in order to ensure a match between the waste received and the certificate and tracking slip details, ultimately with the aim of conducting specific analyses to refine treatment. The package of waste is then transferred to the appropriate installation.

Feeding the furnace with liquid waste:

The liquid waste is conveyed to the point of furnace injection by means of a set of pumps and racked pipes. The distribution array, laid out adjacent to injection points, feeds the injection tubes where the liquid is pulverised by compressed air. For each line of waste, the array recomposes the flow measurement and safety sectioning instruments. Each flow rate is automatically adjusted on the basis of furnace operating parameters.

THE ACCIDENT, ITS CHRONOLOGY, EFFECTS AND CONSEQUENCES

The accident:

Waste acceptance:

The waste at the origin of this accident was a mix of 30% hydrogen peroxide and 5% acid resins; it was the by-product of an unloading error that occurred on May 29, 2007 within a paper mill complex in Jouy-sur-Morin (Paris Region, Seineet-Marne Department). This error caused an exothermic reaction of the mix and necessitated the onsite presence of local fire and emergency personnel along with evacuation of the entire plant.

The waste processing centre was called on May 29 to undertake the immediate removal of 40 tonnes of waste involved in this incident; due to a lack of detailed information, the centre initially refused the request. After analysing a waste sample and stabilising the waste at room temperature, the centre agreed to an incineration-based treatment by direct injection into the furnace. A preliminary acceptance certificate was issued on June 1, 2007.



In an e-mail message sent on June 7, the paper mill requested the processing centre to suspend the outlined waste removal procedure as of June 11, since the mill was studying the feasibility of an in-house neutralisation solution as a means of limiting reprocessing costs. Following investigation, it was clear that neutralisation tests conducted on several samples of these wastes, at the production site, were not conclusive.

The mix contained in two of the vats was pumped on July 30, 2007 into a stainless steel, single-compartment tanker truck. The first vat could be completely emptied and the second to a partial extent.

The waste was delivered to the processing centre on July 30. A sample was extracted and, following acceptance, the tanker truck was routed to the site's direct injection zone for unloading into furnace no. 1.

Chronology of events:

On July 30, 2007 at 3:52 pm, the tanker truck arrived at the site.

At 5:45 pm, the direct injection line was rinsed with water before being connected to the tanker truck.

At 6:15 pm, incineration operations began.

At 9:00 pm, the direct injection line was obstructed. It was unplugged and nitrogen was injected via a vent on the truck, in an effort to "push" the waste through. The truck's valve was left open.

On July 31 at 3:00 am, leaks on the truck's second manhole were still ongoing. The incineration operation was halted. The underflow gate was closed and the nitrogen injection circuit isolated, yet the hose connecting the tanker truck to the direct injection pump was still hooked up to the truck.

At 4:00 am, the hose connecting the truck to the injection pump burst. The truck at this point was "very hot".

At 5:30 am, the truck was still "hot".

At 8:30 am, the temperature of the tanker truck sidewall was estimated at between 30° and 60°C. The ve nts were open and the truck was sprinkled by the spraying ramps located in the zone dedicated to direct processing operations.

By 12:00 noon, both the truck temperature and pressure were rising. The truck was moved outside the direct processing zone to install a "peacock fan"-shaped spraying device on each side of the truck. The valve on the site's industrial effluent and stormwater containment pond was then closed.

Around 1:30 pm, teams on the site's second shift arrived as a backup to continue spraying the tanker truck with fire hoses. In order to lower pressure, the truck was emptied of a few containers loaded with the mix, and these containers were placed adjacent to the truck. A safety perimeter was established.

The onsite teams chose to set up a water cannon in order to protect personnel from exposure. It was then decided to move the personnel to safety and call the emergency services unit.

At the same time, 2:30 pm, the internal tanker truck pressure rose and the manhole located on the back face of the truck broke open. The truck degassed all at once; then, both the truck and tractor were propelled some fifteen metres due to the effect of this pressure burst and came to rest when reaching the edge of the track.





Photographs of the tanker truck and the various spraying set-ups (reconstitution – Source: site operator)



Consequences of the accident:

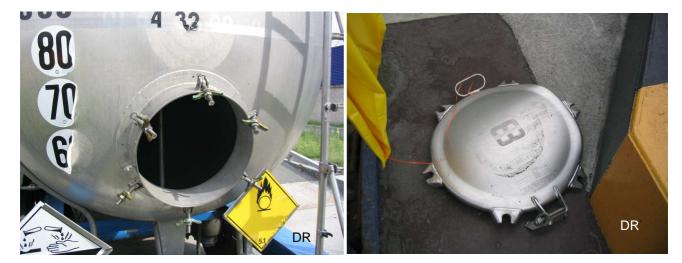
Just after the accident, a local evacuation notice for the zone was broadcast. Staff members at the nearby laboratory were evacuated to another zone on the same site, whereas office employees were told to remain indoors and not allowed to leave. Vehicle entrance bays were shut. A safety perimeter was marked off around the tanker truck. Truck cooling was facilitated using a fire hose. A message announcing the end of this alert was broadcast around 3:00 pm on the 31st.

Three employees were slightly hurt: facial irritations, and a partial foot burn; they were all taken to hospital.

Nine other people showed up at the site infirmary with benign injuries.

No major property damage was declared (deformation of some metal cladding), except for the tanker truck itself, whose braces and hood were bent.

The quantity of mix released into the atmosphere, in the form of droplets and O_2 remaining from peroxide decomposition, was estimated at less than a tonne (approx. 600 litres).



Burst manhole cover (Photos courtesy of the site operator)

The European scale of industrial accidents:

By applying the rating rules applicable to the 18 parameters of the scale officially adopted in February 1994 by the Member States' Competent Authority Committee for implementing the 'SEVESO' directive on handling hazardous substances, and in light of the information available, this accident can be characterised by the four following indices:

Dangerous materials released	1			
Human and social consequences	Ŵ			
Environmental consequences	P			
Economic consequences	€			

The parameters composing these indices and their corresponding rating protocol are available from the following Website: <u>http://www.aria.developpement-durable.gouv.fr</u>

The rating of the "hazardous materials released" index equalled zero since the 30% hydrogen peroxide is only considered to be a combustive substance as of a 50% concentration.

Level 1 of the "human and social consequences" index was reached due to the fact that three people were injured.

Environmental consequences were limited and very point-specific: degassing of the tanker truck. The water used to cool the truck, subsequently mixed with the waste contained therein, was confined (approx. 150 m³) by the retention basin.

The lack of accurate information on economic consequences of the accident makes it impossible to determine the index rating corresponding to the European scale.

THE ORIGIN, CAUSES AND CIRCUMSTANCES SURROUNDING THE ACCIDENT

Waste pumping at the production site:

The paper mill indicated that it had not modified the waste during neutralisation testing conducted solely on samples and moreover had not noticed any heating during waste loading into the tanker truck. The pumping stage using new hoses was carried out onsite.

Inspection of tanker truck contents upon arrival:

The sample taken from the truck, for the purpose of declaring acceptance or not at the processing site, was similar in composition to the one received for preliminary acceptance determination, yet showed slight instability (a few bubbles that were not mentioned on the material transfer form). Truck temperature was not verified by the sampling technician. The material transfer form listed the results of analyses performed and confirmed routing to the direct incineration unit. The tractor then towed the tanker truck to the required spot (direct treatment zone) and left it there.

Preparation for the incineration step:

Racking of this tanker truck could not begin immediately since the injection line was already in use for another vat. The incineration unit had been forewarned of the need to use a clean set of bleeding lines and buckets. The direct injection lines were rinsed with water prior to initiating tanker truck pumping.

Origin of degassing:

The decomposition of hydrogen peroxide led to a sudden degassing of the tanker truck. The H_2O_2 decomposition reaction is an exponential speed reaction. Defining with certainty the exact time when the product starts to react proves to be a difficult step, since inertia runs high in a tanker truck carrying 25 tonnes. This reaction was in fact able to begin prior to waste acceptance: before/during loading, at the same time as the transport?

A number of questions still remain:

- The waste was able to undergo modifications during treatment tests conducted by the producer, between the date of sample transmission and the date of waste acceptance;
- The mixing of both vats at the time of pumping also served to trigger the reaction. This information relative to the two-vat mix was only received after the accident at the processing centre.

An additional sample was extracted from the truck on the morning of July 31^{st} , as the temperature inside the truck was starting to climb. This sample revealed a lower H_2O_2 rate than that recorded the day before, which confirms a progression in the reaction, yet the analysis was undertaken following the accident. The incineration unit had been advised to use clean bleeding lines and buckets but had not been formally notified by the laboratory of an eventual risk of pressure rise.

The unloading method employed did not enable coping with the risk of waste degassing:

- The selected unloading line was operated by either suction or nitrogen thrust; it lacks a specific relief valve system that could have allowed releasing the gas formed during the reaction;
- Only the tanker truck valves could have ensured proper aeration and the requisite evacuation of gas bubbles; these valves however proved inadequate for this particular waste within this particular volume.

Internal Emergency Plan

The Internal Emergency Plan had not been activated since the various scenarios did not feature either hydrogen peroxide degradation or a tanker truck rupture as the consequence of an uncontrolled chemical reaction; the situation did not present any fire or explosion risk and the toxic risk was controlled by water curtains. Nonetheless, the set of actions actually initiated in response to the event did correspond to the measures indicated in this emergency plan.

ACTIONS TAKEN

Immediate measures adopted:

In order to avoid and limit the consequences of a similar accident, the operator decided to:

- introduce the systematic verification of tanker truck temperature at the time of material acceptance (with all pertinent information recorded on the material transfer form);
- refuse the acceptance of wastes containing hydrogen peroxide in bulk packaging exclusively for concentrations below 5%, and require wastes containing higher concentrations to be shipped in barrels or containers.

Prescriptions issued, request for remedial actions:

By way of Prefectural order adopted on August 22, 2007, the Yvelines Department Prefect's Office suspended the acceptance of composite wastes, either partially or fully, containing highly-concentrated combustive products, especially a mix of hydrogen peroxide and acid resins remaining on the paper mill site. This edict was issued while awaiting submission to the classified facilities inspection authorities of the summary report on an analysis of causes and deficiencies leading to the July 31, 2007 accident.

Inspection authorities stated that the set of measures specific to the internal emergency plan established by the Prefectural order approving the site were not respected.

Non-activation of the emergency plan meant that the fire and rescue unit was not informed and moreover that the unit's technical resources were not mobilised to prevent the exacerbation of an accidental situation. More specifically, air quality measurements in the vicinity of the tanker truck, in the case where the truck had been degassing for several hours, were not completed.

Subsequent to this accident, a number of site safety management system improvements were anticipated: re-evaluation of waste acceptability controls (including the physical magnitudes that enable tracking a potential evolution in loading behaviour), assessment of risks relative to tanker truck parking near industrial installations and high-risk zones, and re-examination of the decision-making process that leads to activation of the internal emergency plan.

Corrective actions undertaken by the operator:

- ⇒ Introduction of a guideline relative to the oversight of high-risk material deliveries that addresses the following points:
- acceptance of waste subject to agreement by the site's Safety Coordinator,
- preventive measures to be developed, disseminated and verified by the site's Safety Coordinator,
- a set of situation degradation indicators need to be defined,
- potential scenario(s) specific to the internal emergency plan are to be anticipated;
- ⇒ Stricter acceptance procedures for wastes containing hydrogen peroxide: accepted in bulk solely with concentrations of less than 5%. For higher concentrations, wastes are only accepted in barrels or containers;
- ⇒ Reinforcement of waste acceptance controls: a temperature control must be performed during sampling from the tanker truck. The result of this control step is to be formalised on the material transfer form;
- Modification of the internal procedure governing "emergency situations and reaction capacity", for the purpose of formalising how degraded (yet non-emergency) situations are handled. For all such modifications, a meeting must be quickly organised with the facility Director, Head of Operations, Unit Managers concerned and the site's Safety Coordinator, with the aim of determining: the measures to adopt, the degradation indicators to monitor, potential emergency plan scenario(s), and the measures and indicators tracked by the Safety Coordinator;
- ⇒ Enhanced formalisation of the emergency plan activation process;
- ⇒ Oversight of emergency plan training and exercises in order to familiarise all involved parties with emergency plan scenario management;
- ⇒ Reminder circulated to ensure that the zone assigned onsite for "suspicious" loads gets used whenever necessary. This zone resembles an isolated storage and is located in the north-western sector of the site; it is equipped with two fire hydrants and a fire protection system installed just opposite this storage zone.
- ⇒ Coordination of efforts with the emergency response units: modification of emergency plans, and addition of a new scenario involving the intervention of external rescue personnel. This scenario corresponds to deterioration in a treatment situation for a high-risk, yet controlled, waste. The inclusion of this scenario enables emergency units to record the event and implement suitable resources gradually without necessitating a critical accident situation.

LESSONS LEARNT

The primary cause of the sudden tanker truck degassing was the decomposition reaction initiated within the waste contained in the truck. The accident analysis has shown however that not only were the waste material acceptability controls insufficient, but the safety measures in place at the time were inappropriate.

The treatment of hazardous waste requires a safety management system that includes the following:

- characterisation of the targeted materials (pH, temperature, colour, viscosity, odour, etc.), controls and testing for chemical compatibility between substances, verification of the absence of phases within the mix, and any immediate undesirable chemical reaction or deviation in material characteristics over time;

- assignment of responsibilities to be more clearly specified and adapted to all operations planned by personnel or contractors involved at the processing site;

- technician training in hazard prevention, specifically for the steps of material unloading and transfer (with the possible presence of residual toxic or inflammable gas, etc.);

- indications of measures to be adopted in the event of an incident or deviation in operating procedure;

- introduction of measurement, detection and monitoring devices;

- documentation for the entire series of procedures, from acceptance of hazardous waste through its elimination, with recording of critical parameters and characteristics as regards safety.