## Incident

# Failure of a black liquor tank in a paper mill

## **Summary**

A complete rupture of a tank at a paper mill caused 4,100 m<sup>3</sup> of hot black liquor to spill. The wave effect caused the retaining bund walls to collapse, polluting approximately two hectares of the site's land area. A ditch cut 100 m from the tank to recover stormwater allowed 100 – 500 m<sup>3</sup> of the pollution to drain into a nearby stream and watercourse, killing approximately 300 kg of the fish population.

The exact accident causes are not yet known. Lessons learned from the accident relate to the ageing of installations in contact with liquors; the design of black liquor retention basins and tanks; and stormwater management.

Keywords: Tank, rupture, bund, spill



#### The site

The factory is a paper mill (in operation since 1928) specialising in producing unbleached Kraft paper for corrugated board from resinous wood, recycled cardboard, used crates and purchased bleached paper pulp. The Kraft paper pulp production amounted to 300,000 tonnes in 2011, yielding an output of 475,000 tonnes of paper. The factory employed some 450 personnel, including 240 in production activities (operating 24 hours a day, 365 days a year) and about 100 subcontractors.

This factory, located in France at the mouth of the Leyre River on the Arcachon Basin, is immediately adjacent to the Grande Leyre and Petite Leyre valley (listed as a Natura 2000 protected site). Effluent discharged by the onsite stormwater treatment plant as well as at municipal treatment plants around the Basin was being released into the Atlantic Ocean via a collector pipe operated by the Arcachon Basin Joint Municipal Authority (SIBA).

#### The unit involved

The installations where this accident occurred comprised:

- a non-insulated storage tank (facility index: RC15) containing black liquor concentrated at 18% dry matter originating from paper pulp cooking; the tank's specifications were:
  - diameter: 20 m height: 16 m volume: 5,000 m³
  - component material: carbon steel
  - date of construction: 1974;
- a 2,310 m<sup>3</sup> retention basin composed of earthen bund walls 2.10 m high.



Photographs of the tank taken before and after the accident -Source: DREAL Aquitaine (Environmental Agency)

## Black liquor

According to the Kraft process, caustic soda (NaOH) is used in the presence of sodium sulphide (Na<sub>2</sub>S) as a delignifying agent when heating wood at temperatures exceeding 160°C in order to obtain paper pulp. This cooking residue is called "black liquor" and contains approximately 15% solid matter, namely lignin, as part of hemicelluloses, and the resin found in maritime pine trees, which in conjunction with caustic soda forms a soluble soap. The liquor has a pH above 13 and high corrosion potential; it must have a concentration over 65% to combust. In its non-flammable state, black liquor releases hydrogen sulphide (H<sub>2</sub>S) whenever acid is present.



#### The accident

A complete rupture of the RC15 tank sidewall (a vertical zip tear) as well as on both the top joint (beneath the lid) and bottom joint (base of the chest) caused 4,100 m<sup>3</sup> of hot (80°C) black liquor to spill. The wave effect (upto 10 m high) caused the collapse of most of the retaining bund walls as well as damage to other parts of the site (though without triggering a secondary accident).

Most liquor was confined within the site boundary in the factory's retention basin (referred to as the "Saugnac" basin). Roughly two hectares of the site's land area were polluted.

A ditch cut 100 m from the tank to recover stormwater allowed 100 - 500 m<sup>3</sup> of the pollution to drain into the Lacanau stream and then into the Leyre watercourse, turning it a brownish colour. The Leyre reached a pH of 11.15, killing approximately 300 kg of the fish population.

A municipal order was issued to temporarily prohibit swimming and boating on the Leyre as well as at a nearby beach. The water quality was closely monitored at beaches on the south side of Arcachon Basin.

#### Accident causes

The exact accident causes are not yet known. The expert commissioned by the factory operator reported that an instantaneous pressure surge caused the tank damage, but the origin of the pressure surge was not determined.

The Classified Facilities Inspectorate, with approval from judicial authorities, requested that the operator perform another round of sampling and undertake additional analyses on:

- the "zip" tear zone;
- an intact metal sheet, so as to assess the material's intrinsic characteristics;
- swelling previously recorded during a routine site inspection held in February 2012.

During the follow-up inspection, a leak was identified at the level of a strake on top of the tank; this convinced the operator to schedule regular inspections (in-depth visits by an external body) beginning on 9 July 2012.

## Actions taken

Two local authority orders oversaw the recovery and disposal of products stored in the "Saugnac" basin, specifically by authorising their treatment at the onsite plant (returned to service for this purpose), under discharge conditions established in the 2010 plant permit approval.

The need to accelerate drainage of the "Saugnac" basin, to avoid heavy rains causing a new pollution incident and to resume normal factory activity, led the operator to propose adding several new treatment processes, namely:

- batch treatment with a solution that precipitates the lignin present in the effluent, performed in an onsite basin;
- treatment by oxidation and filtration/absorption on activated charcoal, performed on a mobile physicochemical system installed on the site;
- incineration using authorised external processes.

Prior to facility restart, the operator's Certified Inspection Service proceeded with controls on:

- all tanks containing black liquor, caustic soda and acids (regardless of their volume, i.e. 17 tanks of black liquor) - routine inspection, followed by external or internal inspection depending on the conclusions drawn from the routine inspection;
- all tanks (with the exception of new ones) with a capacity above 100 m<sup>3</sup> (i.e. 66 tanks) - routine inspection, with thickness measurements at the tank bottom (for any carbon steel and stainless steel tanks in a poor state of repair or corroded), control of verticality, settlement and the measurement chain, combined with an external or internal inspection depending on the conclusions drawn from the routine inspection.

A number of more detailed control procedures had to be deferred until after restart. These procedures were based

- conclusions of the routine inspection visits;
- the volume and type of products contained in the various
- maintenance work performed on certain tanks (shell replacements, two sheets of metal reinforcements, stronger tank bottoms, etc.);
- countervailing measures (load limitation on some tanks, including the site's other 5,000 m³ black liquor tank until its replacement – scheduled for 2013);
- the economic consequences stemming from this shutdown (over €300,000 a day).

Facility restart was approved on 23 August, in light of the full set of controls, repairs and countervailing measures adopted regarding tank operations.

In total, 1,500 tonnes of contaminated earth were excavated and stored while waiting for an appropriate pollution clean-up operation. A further 6,200 tonnes of other wastes generated by the accident were removed from the site and treated by specialised subcontracted processes.

As regards pollution outside the site boundaries, initial findings have revealed locally acute fish mortality in both the Lacanau and Leyre watercourses; however, no significant impact on Arcachon Basin flora and fauna was identified.

## Lessons learned

## Ageing of installations in contact with liquors

The various site inspections performed on tanks, along with the bibliographical review conducted by the Inspectorate, confirmed the corrosive nature of the liquors involved in the Kraft process on tank material (even stainless steel), especially in the vapour space and the levelling zone or upon exposure to turbulence (stirrers). These inspections revealed numerous punctures in the tank lids due to corrosion, in addition to thickness losses (as evidenced when the measured thickness falls below the design thickness). The bibliographical review indicated that the rate of corrosion was capable of reaching 2.5 mm a year.

While the operator has definitely become aware of



the corrosive nature of these products, wider knowledge would be useful on the corrosive properties of black liquor and similar substances (e.g. white liquors, green liquors) depending on their storage conditions (tank materials, temperature, etc.). For this reason, the 23 August 2012 restart authorisation prescribed a search for information on the potential degradations caused by black liquor and special substances used in the Kraft process (green and white liquors). The Inspectorate later acknowledged the additional elements required following analysis of the submitted documentation.

During this waiting period, it proved necessary to conduct investigations in the part of the tank exposed to the vapour space during operations, with emphasis placed on introducing enhanced monitoring in black liquor tanks until the phenomenon became better known.

Furthermore, for all new tanks installed at the site, corrosion test samples have been placed in the liquid compartment, as well as in both the fluctuating part (gas/liquid boundary) and vapour space.

## Design of black liquor retention basins and tanks

The operator has undertaken works to replace both 5,000 m<sup>3</sup> black liquor tanks according to the following layout:

- reduction of storage volumes to 3,250 m<sup>3</sup> and 3,275 m<sup>3</sup> respectively, for a 35% decrease;
- use of stainless steel to improve corrosion resistance;
- introduction of corrosion test samples to identify any type of degradation;
- a shared reinforced concrete retention basin: with a volume corresponding to that of the tank with the largest capacity; designed to resist the wave effect and fitted with an "anti-spill" rim to contain the product in case the shellbottom joint breaks.

### Stormwater management

Prior to the accident, a ditch running along the site boundary had served to discharge stormwater in the direction of the Lacanau stream. On the day of the accident, pollution drained via this ditch to the watercourse.

The operator has subsequently modified stormwater management practices by blocking the ditch and creating an infiltration zone with an overflow in the event of high flow rates. With this modification, stormwater is now diverted to the site's treatment plant.

## National action plan targeting paper mills

In response to this accident and a previous release of black liquor on a storage tank in Saillat-sur-Vienne in July 2011 (ARIA 40542), the Ministry for Sustainable Development hosted a meeting in December 2012 for all of France's paper industry representatives in order to establish a national action plan. According to this plan, which is not exclusive to black liquor storage, operators were requested to:

- list the storage facilities devoted to pollutants, including those outside the scope of the 4 October decree<sup>1</sup>;
- define an initial set of measures in terms of prevention and protection, i.e. routine inspections, in-depth inspections during both operating and idle periods;
- plan medium term actions dedicated to tank monitoring following these early measures (guide for developing inspection programmes and plans);
- initiate longer-term actions to complement the safety reports for all targeted sites so as to better incorporate wave effects.



<sup>&</sup>lt;sup>1</sup> Decree on the prevention of accidental risks on ageing-related risks of specific equipment