

Failure of a black liquor tank in a paper mill

5 July 2012

Biganos (Gironde)

France

Releases
Paper mill
Corrosion
Rupture
Fixed storages (tank)
Pollution
Health (impact)

THE FACILITIES INVOLVED

The site:

The factory involved in this accident was a paper mill that had been doing business since 1928 in the town of Biganos; it was specialised in producing unbleached Kraft paper for corrugated board with the following raw materials:

- ♣ resinous wood;
- ♣ recycled cardboard;
- ♣ used crates;
- ♣ purchased bleached paper pulp.

The firm was manufacturing substantial quantities of food packaging. 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.

The site was subject to special authorisation by virtue of French regulations applicable to classified facilities and moreover was required to comply with Heading 6.1.a of the IPPC Directive relative to industrial installations intended to produce paper pulp directly from wood or other fibrous materials.

This factory, located 2 km from the Biganos Port 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).

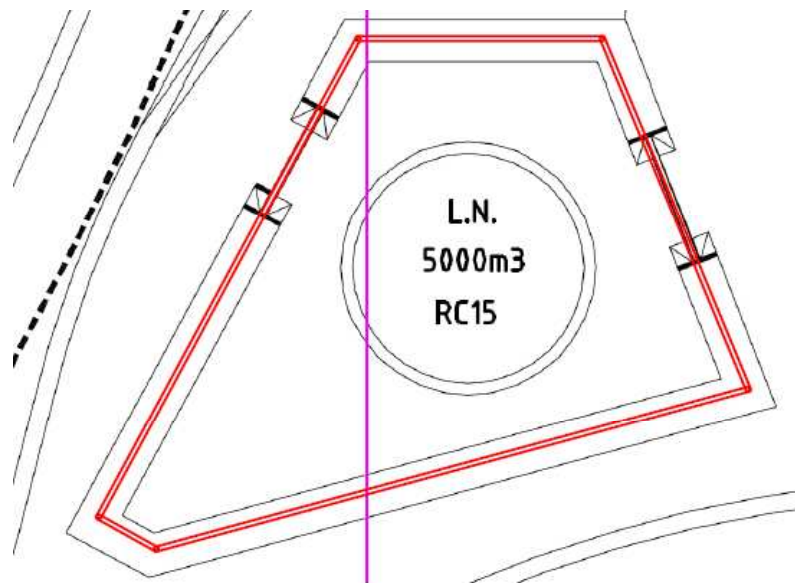


Map of the vicinity

The specific 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-m³ retention basin composed of earthen bund walls 2.10 m high.



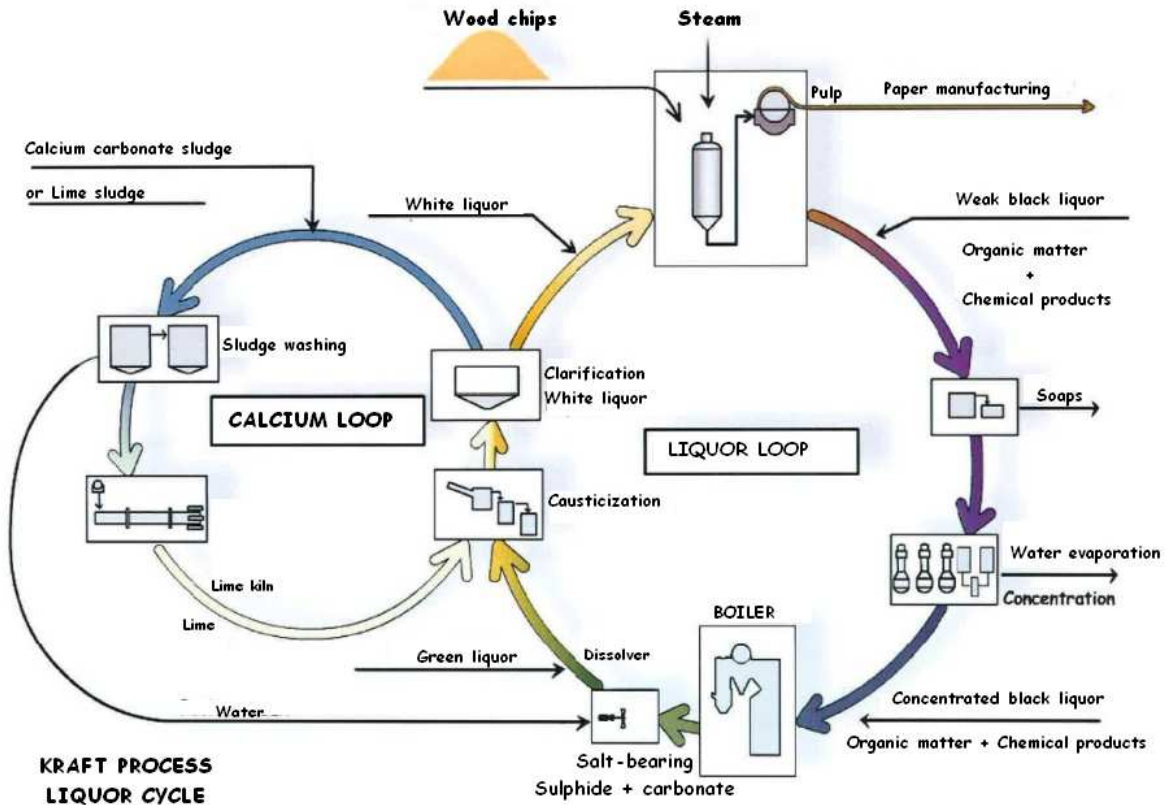
The tank and the retention basin



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 (Na₂S) 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 approx. 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. This liquor features a pH above 13 and high corrosion potential; moreover, it must be concentrated at over 65% to combust. In its non-flammable state, black liquor releases hydrogen sulphide (H₂S) whenever acid is present.



The black liquor cycle within a paper mill - All rights reserved

THE ACCIDENT, ITS CHRONOLOGY, EFFECTS AND CONSEQUENCES

The accident:

On 5 July 2012 at 2:28 pm, a complete rupture on 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 m³ of black liquor to spill at approx. 80°C inside the site boundary. A portion of this discharge reached the Lacanau stream and ultimately the Leyre River.

Consequences of the accident:

The wave effect of this sudden spill caused the collapse of most of the retaining bund walls. This wave, which started out 10 m high, spread across the site destroying installations, yet without triggering a secondary accident.

The majority of liquor was confined within the site boundary in the factory's retention basin (referred to as the "Saugnac" basin). However, a ditch cut 100 m from the tank to recover stormwater wound up draining a portion of the pollution into the Lacanau stream. The facility operator evaluated this discharge into the natural environment at between 100 and 500 m³, based on pH increases observed in the Leyre. Roughly 2 hectares of the site's land area were polluted.

The gendarmerie was mobilised first, before the fire-fighting unit, by the town hall, which itself had been notified by neighbours. The Deputy Prefect proceeded to supervise the Operational Command Post response directly at the site.

At 3:15 pm, the black liquor diluted in the Lacanau stream reached the Leyre watercourse, turning it a brownish colour. The Lacanau water pumping station, part of the factory's processing equipment, was placed in manual override mode to collect the maximum amount of water being diverted to the stream. This collected water was then channelled through the factory's sewer system and eventually transferred to the "Saugnac" basin.

pH measurements were recorded by fire-fighters, working in coordination with the operator, for the purpose of monitoring the evolution in pollution in the Lacanau and the Leyre as well as at the Biganos Port (a total of 8 measurement points).

At 4:34 pm, the Leyre had reached a pH of 11.15, immediately killing fish populations (approx. 300 kg of dead fish), as observed at the mouth of the Lacanau and halfway along the length of the Leyre.

By 5:34 pm, the pH of the Leyre had dropped to 7.6.

At 8:30 pm, with low tide being responsible for significant water inflow, pH at the port showed a value of 7.49.

Measures were also adopted to address human health concerns, namely:

- ⤴ a municipal order temporarily prohibiting swimming at the Teich's beach;
- ⤴ Prefecture-level order temporarily prohibiting swimming and boating on the Leyre at 8 pm, for a full 24 hours. As of 4 pm, canoe rental office employees had been notified;
- ⤴ water quality monitoring at beaches on the south side of Arcachon Basin.

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 information available, this accident can be characterised by the four following indices :

Dangerous materials released		<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Human and social consequences		<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Environmental consequences		<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Economic consequences		<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

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

Despite the extensive discharge of black liquor in nearby watercourses, the "Dangerous materials released" index was not scored because the pollutant involved was not included in the list of substances appended to the Seveso Directive.

The "human and social consequences" index was rated a "2" since 3 individuals required psychological treatment for 3 months following the accident (parameter H9). Cases of chemical burns to the feet or legs and respiratory tract irritation were also recorded during site cleanup operations.

The "environmental consequences" index was assigned a "3" given a volume of polluted water equal to between 10,000 and 100,000 m³ (parameter Env 12).

The "economic consequences" index was rated a "4" due to production losses that topped €10 million (parameter €16) and pollution cleanup costs evaluated at over €1 million (parameter €18). Onsite property damage was estimated in the range of €2 million to €10 million, while offsite property damage / production losses remained less than €50,000.

THE ORIGIN, CAUSES AND CIRCUMSTANCES SURROUNDING THIS ACCIDENT

The deputy public prosecutor visited the site and requested the Court to appoint a legal expert to lay the groundwork for an appraisal conducted on 10 July 2012. Conclusions of the judicial investigation (still underway as of January 2013), specifically appraisal results on the initially damaged tank, should provide a better understanding of the accident causes.

The expert commissioned by the factory operator reported that an instantaneous pressure surge caused an immediate opening of the tank at both the top and bottom, along with a "vertical zip" type of tear. This instantaneous pressure surge would have been triggered by a shockwave whose origin has yet to be determined.

An initial metallurgical appraisal of the damaged tank was assigned to the Classified Facilities Inspectorate by the gendarmerie. The content of this appraisal mainly focused on openings with crack lips observed on the tank. The break was exhibited by a "vertical zip-like" tear crossing metal sheets without following any weld lines, offset in a step-like pattern between each sheet. The appraisal also uncovered local buckling and the presence of a lower-quality steel.

After completing a thorough examination however, this study raised a number of questions. The sheet metal sample had actually been extracted quite far from the zone of the tear (6.5 m from the "zip"). Hence, the conclusion drawn regarding the phenomenon taking place could have been further refined by analysing closer samples on several shells. Moreover, no thickness measurements were conducted over a given part of the tank.

With the tank no longer sealed for inspection as of December, 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 shell on top of the tank; this discovery convinced the operator to schedule regular inspections (in-depth visits by an external body) beginning on 9th July 2012.

ACTIONS TAKEN

Immediate response to the accident:

As of 6 July, a Prefectural emergency order was enacted, requiring the factory operator to:

- ⌘ recover and remove all products that had spilled and spread;
- ⌘ monitor the environments adversely affected by the event;
- ⌘ submit a study of the impact of this discharge on surface water resources, sediments, groundwater and soils;
- ⌘ propose a series of remedial measures;
- ⌘ identify accident causes and implement corrective measures prior to reactivating the site, while addressing in particular the state of repair of all tanks storing substances potentially hazardous for the environment.

Two orders, issued on 9 July and 3 August respectively, were intended to oversee 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 very mission), under discharge conditions strictly established in the 2010 plant permit approval.

The need to accelerate drainage of the "Saugnac" basin, which was critical both for preparedness in the event heavy rains caused a new pollution incident and for resuming 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.

Site reactivation:

A Prefecture order issued on 20 July authorised partial and temporary facility restart by allowing for the tanks under inspection to be drained, along with the shutdown of all factory equipment for control purposes. In reality, these machines had been turned off while the process was ongoing (just after the accident) and still contained by-products.

Another partial resumption was authorised by a Prefecture order issued on 14 August to ensure draining the boiler as part of the maintenance procedure for black liquor injection pipes. This equipment could not be drained during the partial restart at the end of July.

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

The factory immediately resumed activity that very same evening by turning back on the evaporator and paper pulp cooking equipment. The other machines were placed back into service during the evening of 24 August. The facility reactivation procedure proved difficult to implement after such a long unplanned down time.

Moreover, the restart approval of 23 August 2012 created a monitoring commission for this paper mill and another nearby industrial site operating a biomass boiler.

Industrial safety:

The Classified Facilities Inspectorate organised a site visit on 25 July in order to lay out the protocol for inspecting the tanks identified in the 6th July Prefecture order (routine verifications, external or internal, controls performed on the tank bottoms, verticality and angle of inclination, etc.). A follow-up visit was scheduled for 10th August with the aim of evaluating the results of previous inspections and specifying facility restart conditions.

The tank verification criteria were defined by the Inspectorate on the basis of "Section I: Prevention measures dedicated to ageing-related risks of specific equipment" contained in the 4 October 2010 Ministerial decree on the prevention of accidental risks at classified facilities subject to authorisation. Even though only 12 of the site's 194 tanks contained substances (sodium hypochlorite, liquors, fuel oil, turpentine) of actual relevance to this decree, it was nonetheless decided to apply the control methodology to all tanks both before and after bringing them back online.

Prior to facility restart therefore, 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 visits depending on conclusions drawn from the routine visit;
- ⌘ all tanks (with the exception of new ones) with a capacity above 100 m³ (i.e. 66 tanks): routine inspection, with thickness measurements at the tank bottom (for all carbon steel and stainless steel tanks should they be in a poor state of repair or corroded), control of verticality, settlement and the measurement chain, combined with an external or internal visit depending on conclusions drawn from the routine visit.

A number of more detailed control procedures had to be deferred until after restart (delayed no later than issuance of the factory's technical memorandum at the end of 2012); these procedures were based on:

- ⤴ conclusions of routine inspection visits;
- ⤴ the volume and type of products contained in the various tanks;
- ⤴ 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 shut-down (over €300,000 a day).

Environmental impact:

The operator was not yet able to fully comply with the prescriptions set forth in the 6 July Prefecture order regarding both the impact of this accident on the environment and the remediation measures. This event caused soil pollution on those areas of the site where black liquor had spilled, as could be detected by effects on pH, sodium and sulphates.

1,500 tonnes of fouled earth were ultimately excavated and stored on a sealed onsite platform while waiting for an appropriate pollution clean-up operation. 6,200 tonnes of other wastes generated by the accident were also removed from the site and treated by specialised subcontracted processes.

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

Nonetheless, government authorities are still anxiously awaiting additional findings, whereby analyses on the biological quality of watercourses are expected to confirm this diagnosis. A long-term flora and fauna monitoring protocol has been established by the operator, in collaboration with nature protection associations and the regional natural park.

These additional inputs will make it possible to decide on eventual application of the Environmental Responsibility Law (no. 2008-757, enacted 1 August 2008) and its accompanying decree (no. 2009-468, issued 23 April 2009).

LESSONS LEARNT

Ageing of installations in contact with liquors:

The various site inspections performed on tanks, along with the bibliographical review conducted by the Inspectorate, have 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 visits revealed numerous punctures in the tank lids, in addition to thickness losses (as evidenced when the measured thickness falls below the design thickness). The bibliographical review also 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, no findings have yet to be provided on phenomenon kinetics relative to stored products. It would also seem pertinent to expand the state of knowledge 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-m³ black liquor tanks according to the following layout:

- ⤴ reduction of storage volumes to 3,250 m³ and 3,275 m³ 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 from the operator's perspective to resist the wave effect; and fitted with an "anti-spill" rim to contain the product in case the shell-bottom 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 was being drained via this ditch until reaching the watercourse.

Since then, the operator has 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 being 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 (department 87) 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 are being requested to:

- ⤴ list the storage facilities devoted to pollutants, including those outside the scope of the aforementioned 4 October decree;
- ⤴ define an initial set of measures in terms of prevention and protection, i.e. routine inspections, in-depth visits during both operating and idle periods;
- ⤴ plan actions over the medium term 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.