

## Rupture of a black liquor tank

8 July 2011

### Saillat-sur-Vienne (Haute-Vienne)

France

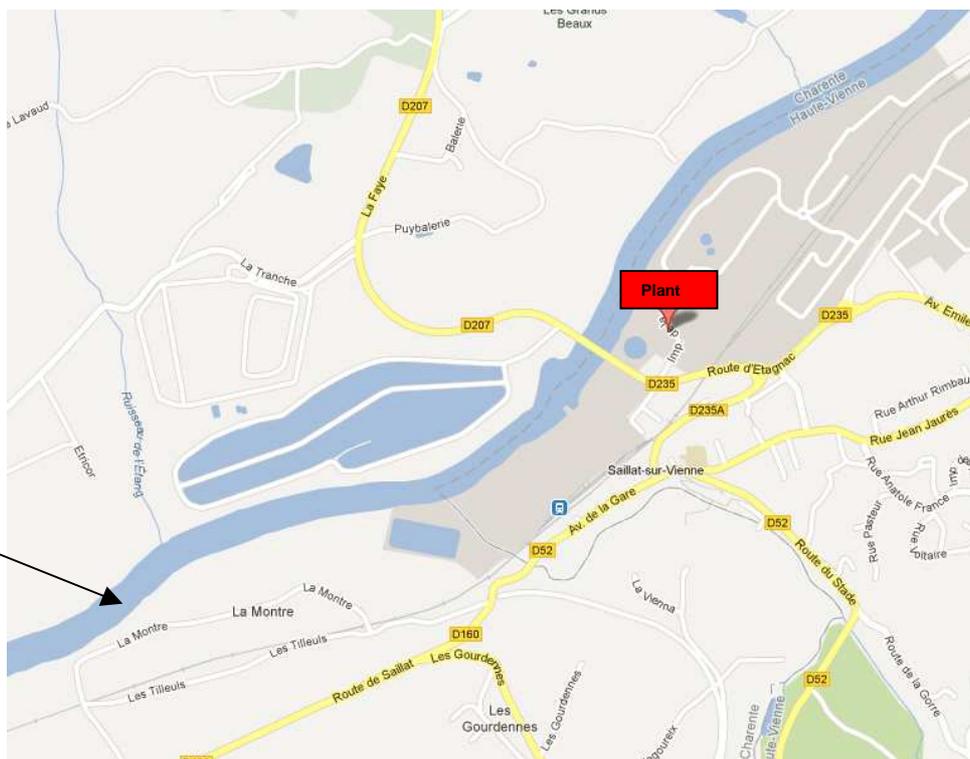
Releases  
Paper mill  
Corrosion  
Rupture  
Fixed storages (tank)  
Pollution

#### THE FACILITIES INVOLVED

##### The site:

The paper mill involved in this accident had been operating since 1894 within the municipality of Saillat-sur-Vienne. The site encompasses 104 hectares on both sides of the Vienne River. Moreover, this facility is part of an industrial complex that employs 550 people. All stages of the paper manufacturing process, from wood treatment to the distribution of paper reams across Europe, are included among the site's activities.

Assigned a lower-tier Seveso rating since 2005, essentially due to the onsite storage of combustible materials like sodium chlorate, the company was required to implement both an Internal Emergency Plan and an External Plan. A Prefecture order, issued on 12<sup>th</sup> July 1990 and then "consolidated" during August 2009 in order to incorporate modifications resulting from the various subsequent orders, served to authorise mill operations.



Site map - Source: Google Maps

##### The specific unit involved:

The unit giving rise to this accident housed a storage tank with a cone-shaped bottom, referenced TB7, containing black liquor, at a 52% concentration of dry matter stemming from the paper pulp cooking process. This tank's characteristics are as follows:

- diameter: 7 m
- height: 21 m
- volume: 600 m<sup>3</sup>
- material: carbon steel
- date of construction: 1988.

This tank had been equipped with heat insulation and an opening at the base; it was placed in the older part of the mill within a 705-m<sup>3</sup> retention basin protecting a total of 8 tanks. "Process" drains had been installed outside the basin.



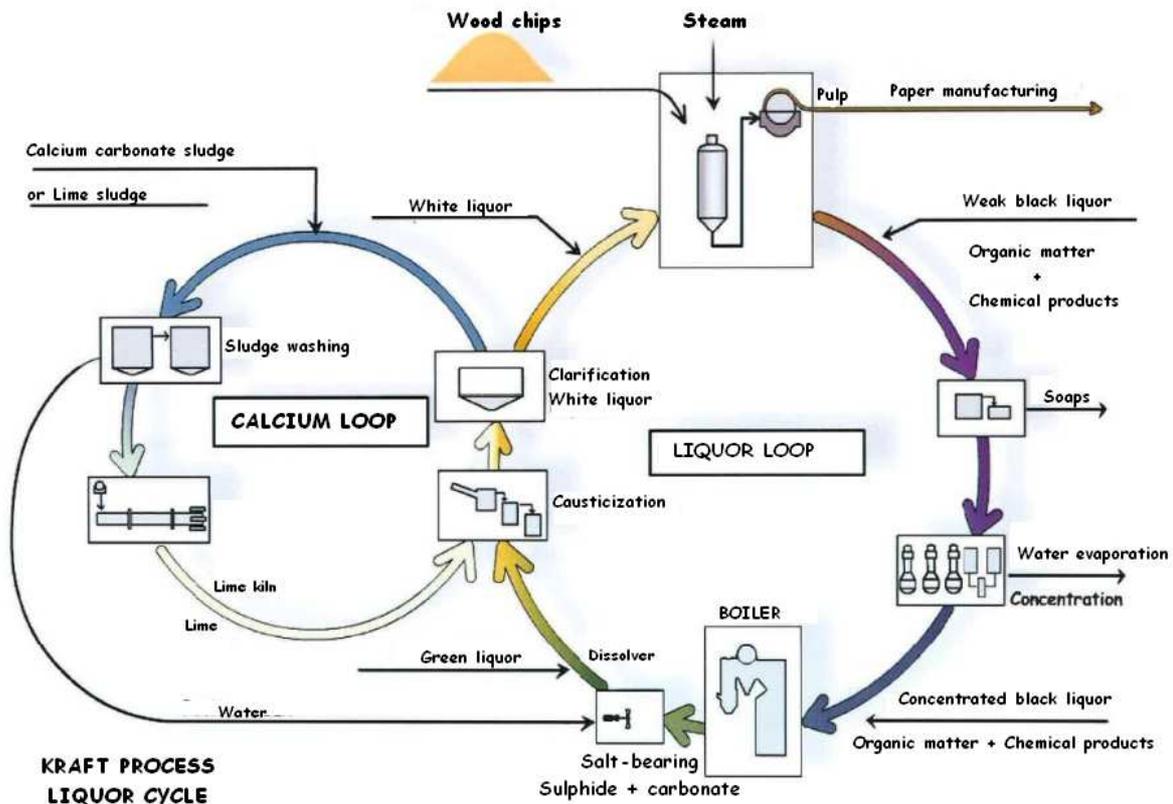
Low wall on the tank TB7 retention basin - Source: DREAL Limousin (Regional Environmental Agency)



Cone-shaped bottom of tank TB7, as seen from the opening of its shell - Source: DREAL Limousin

### **Black liquor:**

According to the Kraft process, caustic soda ( $\text{NaOH}$ ) is used in the presence of sodium sulphide ( $\text{Na}_2\text{S}$ ) as a delignifying agent when heating wood at temperatures exceeding  $160^\circ\text{C}$  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 ( $\text{H}_2\text{S}$ ) whenever acid is present.



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

## THE ACCIDENT, ITS CHRONOLOGY, EFFECTS AND CONSEQUENCES

### The accident:

- 8:47 am: Tank TB7 experienced a mechanical rupture of its cone-shaped bottom. At the time of the accident, this tank was holding 500 m<sup>3</sup> of black liquor and emptied all its contents in less than 30 s.

While most of the black liquor spilled into the "process" sewers located underneath the bleached pulp storage towers, a portion (due to the wave effect) seeped onto an internal road and flowed towards a water tower located at the site's low point. The black liquor then made its way into the fresh water preparation system before ultimately reaching the Vienne River via the stormwater drain network.

The energy/regeneration control room operator, who was assigned to remotely manage and supervise this installation, noticed activation of an alarm on the TB7 tank, indicating that it had abruptly emptied, and duly notified his foreman.

- 9:04 am: The Internal Emergency Plan was triggered and a field command post established in conjunction with the departmental emergency and rescue services.

A neighbouring paper mill downstream of the site was informed of the presence of black liquor in the Vienne.

The town halls of Saillat-sur-Vienne, Chassenon, Chabanais and Confolens were also kept apprised, as were the environmental protection associations listed in the Internal Emergency Plan. The Upper Vienne Prefecture alerted France's downstream jurisdictions, specifically the Charente and Vienne departmental authorities.

Measures set forth in the Internal Emergency Plan were immediately implemented so as to limit black liquor discharge into the Vienne.

A plate was placed inside a manhole and valves were adjusted in an attempt to divert flow into the process effluent network while awaiting installation of an inflatable balloon at the last manhole prior to discharge into the Vienne.

Vienne River water quality monitoring was undertaken right after accident occurrence; sampling was initiated at 9 am on 8<sup>th</sup> July and continued until 13<sup>th</sup> July at the request of the Classified Facilities Inspectorate. Results were transmitted to the various State agencies as they became known.

- 9:30 am: Fire-fighters installed floating booms. The efficiency of these devices was limited given the high level of miscibility of black liquor in water. Nonetheless surface foam could be partially retained.



Floating boom set into place and Vienne River pollution - Source: Departmental Fire Services

- 9:40 am: The production of both paper pulp and paper was halted.
- 10 am: The paper mill immediately down-stream of the site shut down production operations as a preventive measure.
- 10:30 am: The discharge of stormwater containing black liquor was completely stopped.

End of the morning: the Internal Emergency Plan was lifted given the latest situation updates (mill shut down, all flows stopped, Vienne River water quality deemed "satisfactory").

**Consequences of the accident:**

No human consequences were reported. The mill's equipment, outside of tank TB7, sustained practically no damage. Outside the site, more than 80 m<sup>3</sup> of black liquor spilled into the Vienne without killing any fish.



Condition of installations after the accident - Source: County Fire Services

Subsequent to the accident, calculations were performed to determine the whereabouts of the 500 m<sup>3</sup> of black liquor present in the tank prior to discharge:

- o 100 to 120 m<sup>3</sup> remained in the retention pit and were recycled into a storage tank;
- o 300 m<sup>3</sup> were collected and channelled to the mill's effluent treatment pond via the process drains;
- o the remainder, some 80 to 100 m<sup>3</sup>, headed into the Vienne between 8:50 and 10:30 am.

The most blatant visual sign of this incident was the formation of foam due to the presence of soaps in the black liquor, corresponding to the saponification of fatty acids contained in the wood during paper pulp production. The foam rising to the water surface was quickly diluted but still allowed tracking the movement of river pollution. The increase in both pH and conductivity remained limited, and the concentration of dissolved oxygen did not surpass the level known to cause consequences on local flora and fauna.

As a precautionary measure, the Haute Vienne Prefecture issued an advisory to refrain from fishing, swimming, boating and piping water from the Vienne River during the period of 8<sup>th</sup> - 13<sup>th</sup> July.

Production at the downstream paper mill had to be shut down for roughly 30 hours, at an appraised cost of €200,000.

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

Despite the heavy discharge of black liquor into the Vienne River, the "hazardous materials released" index could not be scored because the identified pollutant was not included on the list of substances in the Seveso Directive appendix.

The "human and social consequences" index was not rated either since the event caused no impact to any individuals.

The "environmental consequences" index was scored a "2" given that fire-fighters observed the formation of foam along the Vienne over at least a 500-m stretch (parameter Env 14).

The "economic consequences" index was assigned a "4" due to the costs involved in both production stoppage and cleanup, which were estimated at €2 million (parameter €18).

**THE ORIGIN, CAUSES AND CIRCUMSTANCES SURROUNDING THIS ACCIDENT**

Rupture of the cone-shaped bottom on the tank where black liquor was being extracted occurred as a result of gradual wear due to the effects of corrosion/erosion.

This TB7 tank had undergone an internal control in 1998 by an independent body. The findings of this inspection had led to adding a second steel sheet to the bottom and then performing a dye penetrant inspection.

Based on expert appraisal, it turned out that the black liquor had infiltrated between the original plates and reinforcement plates following repairs. This infiltration served to substantially accelerate plate corrosion phenomena while continuing to corrode the original tank wall.

According to the mill operator, no corrosion issues on the cone-shaped bottom could have possibly been anticipated, especially given that during regularly-scheduled external inspections, no early warning signs had ever been detected.

Moreover, the raised and outlying position of the TB7 tank retention basin, coupled with its 21-m height and sudden rupture of its cone-shaped bottom, caused the tank to be blasted outside the retention structure (due to the wave effect).

## ACTIONS TAKEN

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### Immediate response to the accident:

On 8<sup>th</sup> July, the Prefect signed an order imposing emergency measures intended to:

- predicate service restart on the completion of a number of specified actions: recertification and renovation of equipment, such as electrical installations, valves, emergency shutoff switches, and tanks similar to the one involved in the accident; plus the update of mill procedures and structural works;
- monitor the mill environment (pH, dissolved oxygen) through the conclusion of installation cleaning and renovation operations;
- remove and transport waste generated by the accident to authorised waste handling facilities.

### Site reactivation:

Pulp and paper production was shut down as of 8<sup>th</sup> July at 9:40 am, subsequent to contamination of the mill's fresh water treatment system.

The restart routine was gradual and contingent upon completion of the cleaning, repair and control steps, which focused on:

- installations and machinery located outside the retention basin, e.g.: racks, foundation bolts, heat insulation, walkways and staircases, crinoline, fittings;
- electricity and instrumentation;
- fire safety equipment.

Successful execution of these controls made it possible to restart the facility on 11<sup>th</sup> July.

### Industrial safety:

The other two black liquor storage tanks TB3 and TB4, located in the same retention basin, were drained and then taken offline in order to proceed with an early in-depth inspection of their internal as well as external integrity. These tanks differed from TB7 to the extent that they had been designed with flat bottoms.

Following this inspection step, no structural weakness potentially similar to what had been identified for TB7 was observed at the level of TB3. Nonetheless, these verifications led the operator to strengthen the structural integrity of the tank bottom. The restart of tank TB3 received Prefecture authorisation on 12<sup>th</sup> August 2011.

The drainage and cleaning of tank TB4 were completed on 29<sup>th</sup> August. After inspection by a specialised body, welds were repeated so as to remedy an initial bonding defect.

### Environmental impact:

The precautionary advisories relative to sailing, swimming, fishing and irrigation on the Vienne downstream of Saillat-sur-Vienne were lifted on 13<sup>th</sup> July at 9 am. As regards water pollution, the measurements taken at several points downstream of the site suggested that the natural environment had returned to normal. No indication of an impact on flora and/or fauna was apparent. Detailed observations were recorded with the assistance of the water control authority.

## LESSONS LEARNT

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### Control of storage facilities:

The industrial operator had verified the structural integrity of the site's storage tanks and proceeded by improving maintenance procedures, in adopting the conditions outlined in the 4<sup>th</sup> October 2010 order relative to accidental risk prevention within listed Classified Facilities for environmental protection. The operator was also requested to widen the scope of application of this order to all tanks containing pollutant substances.

The set of actions implemented to avoid recurrence of a similar accident pertained to:

- scheduling of inspections, especially in-depth internal controls (tank TB7 had been scheduled for August 2011);
- more in-depth inspections, in light of the fact that no early warning sign had drawn attention to the possibility the TB7 tank would break;
- the choice of repair methods in the event of corrosion or structural defects.

### Stormwater management:

This accident has effectively illustrated the difficulty involved in quickly blocking stormwater networks, especially when using inflatable balloons in case of an accident.

From that point forward, 2 automatic shutoff valves fitted with an alarm relay to the control room have made it possible to divert stormwater to the process effluent network. This system of valves had already been installed in the mill's more recent part.

### **Efficiency of retention basins:**

Beyond the mere presence of retention basins, their operational efficiency needs to be examined. For this accident, the magnitude of the wave effect, correlated with tank configuration and location (placed near the low retention wall), exceeded the capacity to retain the entire quantity of black liquor. As such, the mill operator was requested to evaluate the efficiency of existing retention basins to identify potential improvements and undertake remedial actions.

### **Improved site safety report:**

The site's safety report (conducted in 2009) exposed 2 plausible accident scenarios at the level of the liquor regeneration unit, one pertaining to a boiler explosion the other to an explosion of the unit's dissolver. On the other hand, the scenario of a storage tank rupture had not been raised.

### **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<sup>th</sup> 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.