Bursting of a high-pressure steam pipe

28 June 2010

Le Grand-Quevilly (Seine-Maritime)

France

Pipes
Steam
Construction defect
Inspection program
Internal emergency plan

THE FACILITIES INVOLVED

The site :

The plant is located within a large industrial zone along the banks of the SEINE River to the west of the Rouen metropolitan area ; the facility is specialised in the production of fertilisers using 4 raw materials: natural gas, ammonia (NH_3), sulphuric acid and phosphoric acid. It contained 4 manufacturing units clustered on the site's southern and eastern zones, featuring:

- an ammonia production unit, with a capacity of 1,200 tonnes/day,
- two nitric acid production units, totalling a capacity of 3,000 tonnes/day,
- an ammonium nitrate production unit, with a capacity 2,100 tonnes/day,
- a special fertiliser (NS/NP) production unit, with a capacity 2,000 tonnes/day.

The site employs a total staff of 340 and comprises on-site storage facilities for both end products and raw materials : 24,000-tonne capacity of cryogenic ammonia storage, 2 ammonia spherical tanks totalling 550 tonnes, 5 nitric acid tanks offering a cumulative 10,000-tonne capacity, a zone dedicated for solid ammonium nitrates either in bulk (12,500 tonnes) or packed in big bags (2,000 tonnes), 4 tanks of ammonium nitrate in hot solution accounting for 4,000 tonnes, another 140,000-tonne zone for special fertilisers as well as various sulphuric acid and phosphoric acid tanks.

The plant layout includes a series of lorry loading/unloading installations for fertilisers, fertiliser and ammonia railcars, and maritime terminals for ammonia, sulphuric acid and phosphoric acid. Site operations is required to comply with the *Seveso II* European directive for the storage of ammonia, ammonium nitrate in hot solution and solid fertiliser made from ammonium nitrate. The main technological risks identified by the site operator are : toxic leaks of ammonia or nitrous gas, explosion of an inflammable gas cloud subsequent to a natural or process gas leak , overpressure within an equipment, or detonation of out of specification ammonium nitrate material. A town of 27,000 population is located less than 1 km east of the site.

Figure 1 : External view of the site (source: Google)

The specific unit involved :

Figure 2 : Ammonia synthesis unit (source: Google)

The unit involved in this accident is responsible for manufacturing ammonia by means of natural gas steam reforming (see Fig. 2). The ammonia produced by this unit is being used onsite or shipped to clients, as a complement to the ammonia delivered by sea or rail, for the purpose of manufacturing nitrogenous fertilisers.

Inside this unit, ammonia is being synthesized from nitrogen and hydrogen according to the HEURTEY process, whereby nitrogen is supplied by atmospheric air while hydrogen is produced from natural gas (Fig. 3).

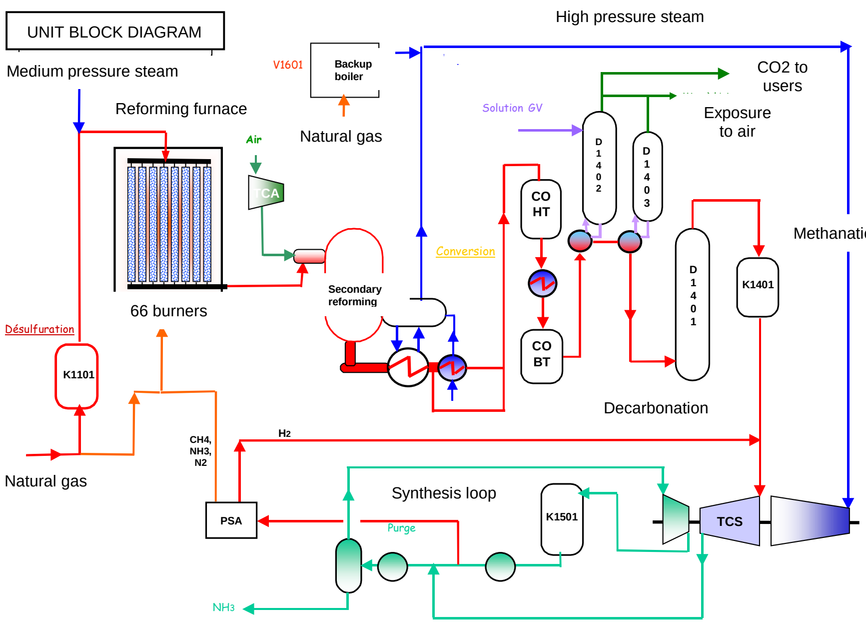

Figure 3 : The HEURTEY ammonia synthesis process (source: GPN)

The three major steps involved in this process are the following :

① In both the reformers and conversion chain, the previously-purified methane (through a desulphurization process) reacts with the water vapour in contact with a nickel oxide catalyst: the methane and a portion of the water vapour are then transformed into carbon monoxide and dihydrogen.

Primary reforming:

$$CH_{4(g)} + H_2O_{(g)} \rightarrow CO_{(g)} + 3\ H_{2(g)}$$

Secondary reforming of the methane that has not reacted with air inflow:

$$2\ CH_{4(g)} + O_{2(g)} \rightarrow 2\ CO_{(g)} + 4\ H_{2(g)}$$
$$CH_{4(g)} + 2\ O_{2(g)} \rightarrow CO_{2(g)} + 2\ H_2O_{(g)}$$

The carbon monoxide is then converted into carbon dioxide, which in turn is recovered to be compressed and liquefied, with the intention of external reuse: $CO_{(g)} + H_2O_{(g)} \rightarrow CO_{2(g)} + H_{2(g)}$

② The small quantities of CO and CO_2 remaining in the synthesis gas are capable of poisoning the ammonia synthesis catalyst. For this reason, the gas is decarbonated in order to eliminate CO_2 ; as a next step, the remaining CO/CO_2 is hydrogenated into CH_4 inside the methanation reactor:

$$CO_{(g)} + 3\,H_{2(g)} \rightarrow CH_{4(g)} + H_2O_{(g)}$$
$$CO_{2(g)} + 4\,H_{2g()} \rightarrow CH_{4(g)} + 2\,H_2O_{(g)}$$

③ The synthesis gas (a N_2/H_2 mix) is then compressed to replicate the physical conditions required for ammonia synthesis. This step takes place in the presence of a high-pressure iron catalyst (100-200 bar) and high temperature (400°-550℃): $N_{2(g)} + 3\,H_{2(g)} \leftrightarrow 2\,NH_{3(g)}$. Since these equilibrium conditions are not conducive to the reaction, only 20-30% of the synthesis gas is actually converted into ammonia. The synthesis gas that has not entered into reaction then resumes the synthesis loop following extraction of the formed ammonia. The gaseous ammonia formed is liquefied inside the unit's receiving bottle.

The large available quantity of surplus heat stemming from the reformer's burnt gases, change conversion and ammonia synthesis serves to generate high-pressure steam (> 100 bar) and high temperature (> 400℃) through he at exchangers. This high-pressure steam feeds the steam turbines, thus driving several compressors. A proportion of the steam is then extracted from the turbines to supply medium-pressure steam (40 bar) for the steam reforming reaction and for driving other compressors, pumps and fans in some of the neighbouring units (nitric acid production, etc.).

THE ACCIDENT, ITS CHRONOLOGY, EFFECTS AND CONSEQUENCES

The accident :

28 June 2010, at 11:07 pm : A violent blast is heard over several kilometres centred at the ammonia production unit, while the unit was operating in a steady state without any prior incidents, followed by a continuous decompression noise. Two employees on the premises noticed a leak fed by pressurised steam at the level of the chamber roofing on the steam reforming system's smoke chain.

11:07 pm : Technicians placed the unit in safe mode by automatically triggering the equipments shutting down (reforming furnace and other unit processes).

11:10 pm : Dispatch of the plant's fire-fighting crew to the damaged unit for an initial damage inspection.

11:15 pm : Notification of the on-call manager and site supervisors. On their side, public emergency services (Departmental Fire and Safety Office) were alerted following several phone calls by local residents worried by the decompression noise from the affected pipe. The operator chose not to activate the internal emergency siren or even the "mini sirens", given the absence of physical injuries or toxic leaks. The emergency crisis team was activated internally with reminders issued to all on-call personnel. Some neighbouring residents, concerned by the fire-fighters' siren, went out onto their balconies or walked toward the site to watch the accident.

11:27 pm : End of the decompression incident on the damaged pipe and pressurisation of the unit's steam boiler to the atmosphere; the noise noticeable outside the facility has stopped.

11:30 pm : Second inspection conducted by plant fire-fighters in order to assess damage; arrival of the first public fire-fighters emergency vehicles.

11:50 pm : The operator formalised with outside resources the activation of its Internal Emergency Plan; public fire-fighters officers and a municipality representative showing up for a site visit. A command post was established in the site's southern control room.

12:12 am : Plant fire-fighters performed an atmospheric monitoring of ammonia outside the site boundary using a portable analyser. The entire public fire-fighters team (55-person crew) was mobilised but did not intervene onsite.

12:18 am : Following the measures implemented, the absence of an ammonia leak was confirmed.

12:30 am : Telephone exchanges took place with the civil security's emergency room of the local government authorities.

12:41 am : Third inspection by plant fire-fighters, accompanied by members of the management, to evaluate the extent of property damage.

1:15 am : Fourth inspection, this time accompanied by plant supervisors, public fire-fighters officers and the municipality representative, to remove any lingering doubts.

1:50 am : Subsequent to the final field inspection, a joint decision was made to lift the internal emergency plan.

Consequences of this accident :

No hazardous substance listed under the *Seveso* Directive was released, since the leaked substance was overheated pressurised steam. This steam leak caused the asbestos cement cladding to be ripped off the breeze block wall of the machine room located opposite the blast zone. A 40-kg dished bottom was found onsite at a distance of 230 m from the damaged unit (Fig. 4).

Figure 4 : Photograph of the dished bottom projected on the day of the accident (source: GPN)

The projection of this piece of equipment led to no injuries, yet still caused damages inside the unit: a grated walkway was torn down, and a safety ladder sustained damage. The dished bottom was ejected above the ammonia receiving bottle (placed at the end of the synthesis process) and above an ammonium nitrate conveyor belt to come crashing down between two railway lines. Though these lines happened to be empty on the day of the accident, they were often used to park railcars loaded with ammonia awaiting construction of a full ramp (Fig. 5).

On 6 July 2010, the operator provided the local environmental authority with a metallurgical appraisal of the dished bottom.

On 12 July 2010, the government authority, at the behest of the local environmental authority, issued an order requiring as a precondition to unit restart the introduction of controls to enable detecting similar defects on any of the unit's equipments which might have been damaged, including an analysis of steels quality used for manufacture and the execution of all necessary repairs. Any anomalies identified during this inspection were to undergo repairs prior to unit restart.

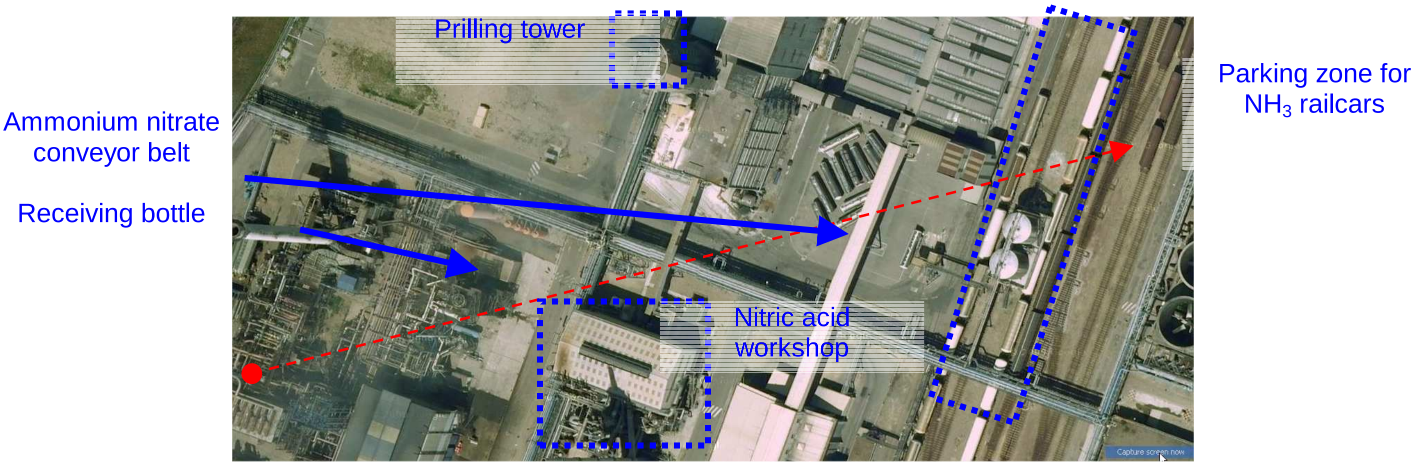

Figure 5 : Trajectory travelled by the dished bottom shown in red (source: Google and DREAL HAUTE NORMANDIE)

The damaged unit had to be shut down for 10 weeks. Given the existing storage capacity and the possibilities for ammonia deliveries by water or rail, shutdown of the site's nitrogenous fertiliser production has been avoided. Nonetheless, the damaged unit had become unable to feed the rest of the plant in medium-pressure steam, specifically to enable unit restart. An auxiliary boiler within the damaged unit was actually capable of supplying steam throughout the site; however, its high-pressure steam pipes needed to be inspected before any attempt at plant restart. The local environmental authority, in considering that all necessary elements and controls had not yet been fulfilled, rejected the operator's request to restart the boiler 3 weeks after the accident.

The nitric acid production unit was finally restarted thanks to steam delivered by a second nitric acid unit that had remained in service, to the detriment of steam supply to the ammonium nitrate and special fertiliser units, both of which had been temporarily shut down. The operator suffered major operating losses, on the order of several million Euros, as the result of a drop in production but chiefly due to the purchase of ammonia on the international market in order to maintain the production of nitric acid and nitrogenous fertilisers. This production was necessary to secure the operator commercial commitments.

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

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

The "hazardous substances released" index is rated 1 due to the phenomenon of a pipe bursting.

The "economic consequences" index was rated 3 as a result of property damage sustained by the unit, coupled with significant production losses resulting from the imposed plant shutdown, whose total exceeded €2 million yet remained below €10 million.

The other indices were not rated owing to the absence of human, social or environmental impacts.

THE ORIGIN, CAUSES AND CIRCUMSTANCES SURROUNDING THIS ACCIDENT

The dished bottom was convex and welded with a tulip-like shape on a weld-free drawn tube made of P22 type steel (cross-section with 2 dished bottoms). This tube served as a collector for a 14-inch pipeline (DN 350, thickness: 44 mm), conveying the 520℃ water vapour at high pressure (120 bar) between a superheater and turbines. The superheater is a heat exchanger that enables recovering excess heat from the unit's reforming furnace in order to increase temperature of the steam produced by the boilers (Fig. 6). The piping was insulated and removed from all machines generating vibrations; it was placed high above ground on the smoke chain chamber roof, at the level of the unit's steam reforming installations (Fig. 7).

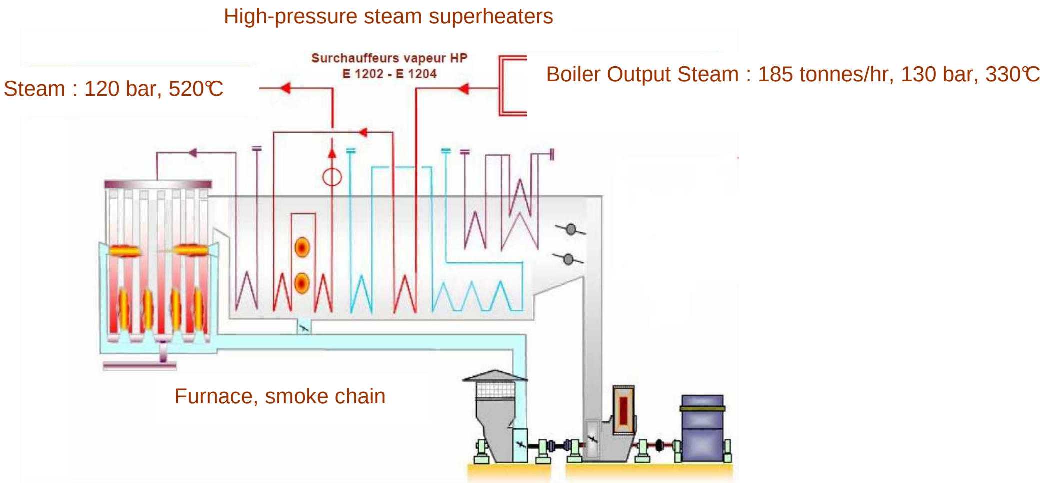

Figure 6 : The unit's overheated steam production circuit (source: GPN)

A break was detected along the bottom weld seam on the tube, over the bonding zone thermally altered by the weld, on the bottom side. The weld has remained fastened to the tube. The operator observes that the only visible flaw was a slightly oxidized surface condition at the level of the break on the dished bottom.

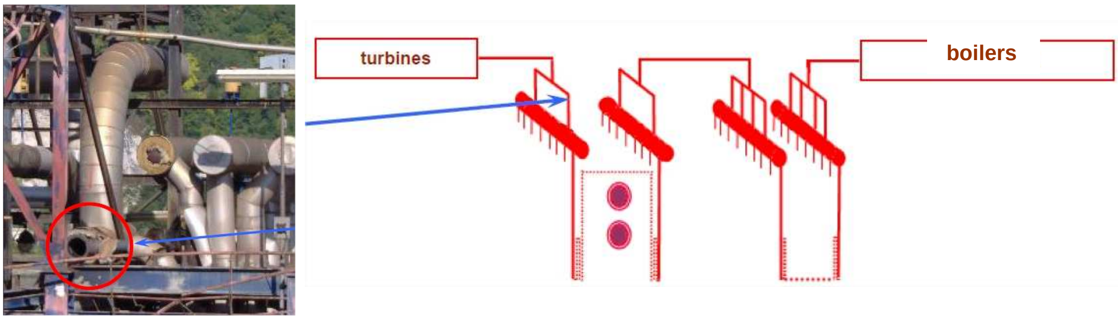

Figure 7 : Localisation of the damaged pipe (source: GPN)

The complete collector tube was built in 1978, but it is not known whether both dished bottoms were welded in the workshop or onsite during unit assembly. This welding operation required preheating at 250°-300°C followed by a heat treatment at 720°-740°C, although no document providing traceability of the bottom welding procedure applied onto the tube has ever been produced. The same shortcoming was observed for pipe manufacturing specifications. Only a radiographic inspection, when the bottom was built, and a hardness verification at the weld surface following heat treatment had been conducted at the time.

Formal pipe monitoring elements first appeared by the end of 2003, during a periodic recertification of the piping performed by an authorised certification body. The report mentioned thickness controls executed by the operator using ultrasonic probes, in addition to visual inspections of assembly surfaces and welds, without detecting any defects. The piping was recertified through 2013, in compliance with the 120-month periodicity set forth in the regulation relative to pressurised equipment.

Between 2006 and the day of the accident, pipe controls were performed on a regular basis in accordance with the periodic inspection plan adopted, i.e.: external visit under normal operating conditions every 18 months, and periodic inspection of the unit during down time every 60 months by the site's internal inspection team which has been approved by the administrative authority (Certified Inspection Department). Since the main objective of this protocol is to detect eventual leaks, the majority of these controls are indeed visual and take place under difficult conditions while the unit is up and running (pipes located high above ground, hot temperatures). The primary anomalies observed pertain to the state of heat insulation, which in certain spots had become detached and deformed. The non-destructive control procedure, undertaken when the unit was down during December 2008 and applied to the dished bottom, did not reveal any loss of thickness. At the time of the most recent shutdown, a section of pipe was cut in order to insert a trial bottom to carry out a periodic recertification of the bundle associated with this pipe. Following testing on this bundle (at 80°C), the pipe was restored to a compliant state and the welds were fully x-rayed after heat treatment. According to the operator, the bottom and its weld were also tested at the same time as the pipe bundle. A search for cracks by means of magnafluxing conducted 3 months prior to the accident on 5 pipe welds did not indicate any anomalies, although the suspected cross-section was not targeted as part of this search.

The pipe inspection plan, adopted in May 2007, focused on the degradation modes by erosion, abrasion and cavitation, while corrosion under the heat insulation has been discarded (service temperature: 520°C). In October 2009, the internal inspection department had requested that this plan include degradation by vibrations subsequent to the recent rupture of a bleed valve on a high-pressure steam pipe in the unit, due to vibrations (water hammer hits) during unit restart sequences. On the day of the accident, this plan had still not been updated accordingly (no specific control of vibration-induced degradations). The dished bottom was sent for metallurgical appraisal to a specialised firm, the outcome of which revealed that rupture was due to the type of steel used to manufacture the bottom. This steel was of the ordinary carbon variety and not adapted to pipes operating at temperatures above 425°C, even though the original specification called for a lightly alloyed steel of type P22 (2.5% Cr and 1% Mo), capable of resisting temperatures above 530°C and pressures on the order of 130 bar. It is important to mention that the pipe and metal used for the weld were indeed made of P22-grade steel.

Furthermore, damage had started to slowly progress on the outer skin of the dished bottom and was gradually entering into the thickness of the zone thermally altered by the weld (slow creep), without any apparent deformation. The metallographic inspection of rupture on the bottom side revealed the presence of oxidized microcracks running parallel to the weld bond zone. The technical appraisal also underscored the fact that the heat treatment performed after welding might have accelerated damage, since the temperature selected had been adapted to a P22-grade steel and not to an ordinary carbon steel.

ACTIONS TAKEN

The administrative authorisation to place the damaged unit back into service was contingent upon an exhaustive control of the installation.

The operator proceeded with an inventory of all pipes potentially containing noncompliant steel or subject to the risks of cracking corrosion due to hydrogen (synthesis gas). An analysis reported 65 critical equipment that would give rise to 969 material analyses involving a portable X-ray analyser (portion of pipes, welds and equipment of the boss, T-section and elbow type, etc.). All of the unit's dished bottoms underwent a materials inspection as well as magnafluxing on their welds, amounting to 12 bottoms made of P22-grade steel and 7 containing P11 steel. Three of the unit's pipes, subjected to vibrations subsequent to poor operations of the steam turbine regulation system, were included in this weld inspection campaign by use of magnafluxing. An accident analysis allowed the operator to conclude that none of the threshold operating conditions were exceeded.

This inventory exercise was completed on 21 September, 2010 and led to identifying ;

- 4 elements made from higher-grade material than indicated in the original specification (stainless steel coupling, plug and boss), they were all left in place ;
- 3 elements made from lower-grade material than the original specification (a T-section, elbow and tube using P11 steel), they were also left in place since actual operating conditions were not hindered (medium-pressure steam pipe section and pressure surge protection by safety valves) ;
- 12 elements made from lower-grade material than the original specification (carbon steel instead of P22 steel), and were replaced. These elements included a dished bottom on another of the unit's high-pressure steam pipes, boss, a valve and a flange on three steam pipes connected to the backup boiler, and two taps on the damaged pipe. Moreover, a pipe had combined several anomalies on its high-pressure part, where several sections and a valve made from P11 steel were discovered, as well as a carbon steel tube and bleed valve on the neck.

The replacement of noncompliant and damaged equipment was completed on 21 September, 2010, thus making it possible to restart the ammonia synthesis unit. The site returned to a normal production mode, yet the operator was unable to find the original manufacturing specifications for the damaged pipe (since construction records were apparently not kept).

As regards the quality of accident response, the operator held meetings with entities responsible for safety and civil protection (municipality, government authority, etc.) in order to improve coordination in the event of another accident . The plant's communications strategy in the event of an accident is revamped; this new strategy included :

- a specially dedicated phone line to alert the public fire-fighters emergency response service ;
- information within 5 to 10 min to all municipalities in the vicinity through a grouped dialling system, followed by additional messages specifying the instructions to be delivered to neighbours according to the type of accident.

LESSONS LEARNT

Even though the severity of this accident remained rather mild given the absence of domino effects, several lessons can still be drawn, relative to both the causes and circumstances.

As for causes, this accident highlights two significant organisational flaws :

- Deficiency in the control of equipments materials at the time of unit installation. Even though material certificates were verified by an independent control body according to the operator, the steel used on the bottom and 12 other pieces of equipment was not compliant with specifications, and the original pipe construction documentation could never be found.
- Incomplete traceability of pipe monitoring given that until 2003, formalisation of the steam pipe condition monitoring protocol had only been partial (restricted to unit drawings). Formalisation of monitoring procedures was not initiated before the first periodic recertification, in application of the 15 March 2000 decree, though the unit had already been operating for 25 years. Nonetheless, the French regulation relative to plant pipelines (issued on 23rd January, 1962) stipulated in Article 13 that "*the documents, drawings or diagrams, testing and retesting reports, notes from inspections prescribed in Article 12, relative to a pipeline or set of pipelines, are to be archived…*".

From a broader perspective, this accident stresses the difficulties found by the internal and external control entities in detecting such non-compliance in steel. As demonstrated in the inventory of all unit's pipes, this non-compliance does not represent an isolated case. It would be useful to mention that a verification of the steel quality had taken place in 1987 but was limited to those elements prone to hot hydrogen damages. Even if the initial recertification had been conducted in compliance with current regulations (without any imposed hydraulic test, no imposed exposure, original drawings forwarded to the authorised certification body), the question can still be raised whether it was reasonable to limit this verification to just the regulatory control steps in the absence of construction specifications. The organisation of these controls, shared over time among several distinct actors (internal inspection team, certified control authorities and the various external firms subcontracted to perform specific tasks), was not designed to promote efficient monitoring given the lack of rigour in their formalisation.

The operator also conducted verifications on the type of materials found on the most sensitive parts of the site's other units. The local environmental authority requested an operator of similar units located just a few kilometres away to undertake the same kind of verification. Feedback was addressed at the national level to all local environmental authority offices.

As regards the consequences of this accident, it can be considered that a 40-kg steel projectile propelled through an operating ammonia production unit, passing close to an NH_3 receiving bottle, missing the nitric acid unit and a bulk ammonium nitrate conveyor belt only to land in a zone where railcars loaded with ammonia were likely to park, all while causing relatively minor property damage, lies within the realm of “divine intervention”. This assessment was underscored in a letter written by the local environmental authority to the operator: "… *the caps, which are massive pieces of equipment weighing some forty kilograms, most likely crossed the most sensitive installations found in the AM2 unit, namely the R1501 bottle, to ultimately land between 2 railway lines at the location of switch 371. These elements attest to the potential seriousness of this incident…*".

This potential seriousness was also fully perceived by the operator, with some testimonials suggesting that some plant employees became aware of the risks related to pressurised steam. It goes without saying that the site's safety reports were focused on the most common hazardous phenomena for this kind of activity, as well as those causing potential effects outside the site boundaries, though domino effects caused by pressurised steam equipments were not included. The scenario with most third-party exposure is based on a toxic ammonia leak (up to an 8-km radius around the site). This scenario recently became more predominant in employees mind given the repetition of accidents of this type arising just a short time earlier at one of the Group's sister facilities located less than 200 km from Grand Quevilly (three months before the accident : ARIA 38959; and one year before with the evacuation of 300 employees receiving significant media attention : ARIA 36660).

Besides, a flaw in the implementation of instructions issued by the internal inspection team has to be pointed out. Following the incident that occurred in October 2009, when the water hammer associated with a restart had caused the rupture of a bleed valve on one of the unit's high-pressure pipes, this team had requested that the pipe inspection plan incorporate the mode of vibration-induced degradation. Eight months later, on the day of the accident, this mode had still not been included even though it would have perhaps allowed to detect the surface defect or the onset of microcracking at the level of the weld (had for example a magnafluxing inspection been carried out on the suspected weld).

On the other hand and despite the communication efforts engaged by the site operator and authorities over major accidents behaviour in the past few years, this potentially serious outcome has gone unnoticed by all neighbours. Several local residents actually went onto their balconies to observe the actions of fire-fighters, while others walked up to the site boundary even though safety guidelines called for residents to remain indoors (Fig. 8).

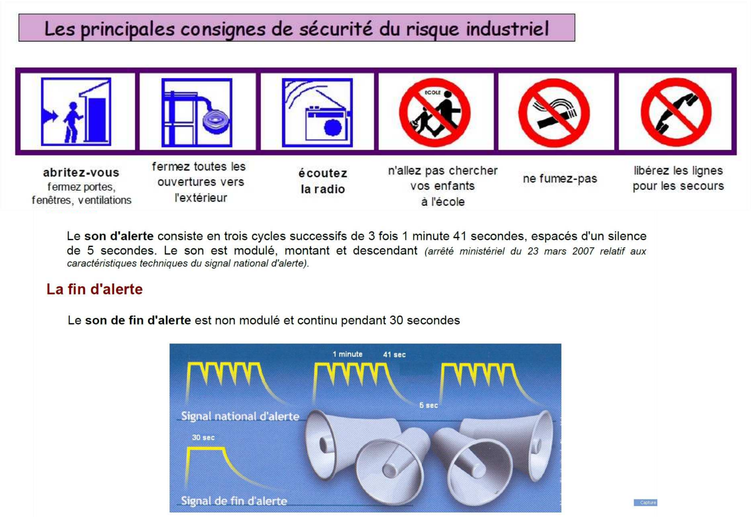

Figure 8 : Extract from the municipal safety guidelines distributed to localities adjacent to the site

In defence of local residents, the operator's decision to activate the internal emergency plan would have alerted them to the potential seriousness of the incident. Instead, the operator waited for 50 minutes before triggering this emergency plan jointly with the municipality and local authorities. Fire-fighters were notified well before this period, but this notification came from local residents calls, and fire-fighting crews were unaware of the exact situation when they arrived at 11:30 pm in front of the site. Moreover, the decision made at 11:15 pm not to activate the emergency siren on the grounds of an absence of toxic leaks only further sparked the curiosity of some residents upon hearing the leaking steam noise between 11:07 and 11:27 pm, inciting them to get closer to the site. In reality, the operator could not have been completely certain of the absence of toxic leaks until around 12:18 am, after the second inspection of the damaged unit and negative controls of air toxicity around the site. A final inspection of the unit with authority representatives was even considered necessary at 1:15 am to remove any lingering doubts.

Alerting local residents and requesting them to remain indoors, even if not really necessary, would have provided the added benefit of reminding residents that a major accident can occur and would have tested their ability to apply correctly the preventive guidelines.

In conclusion, the operator was late in informing local emergency response teams and neighbouring municipalities, which were unable to notify individuals with information regarding the accident, a shortcoming that further incited the inappropriate reaction of some residents. And yet the plant's locality happened to be one of the few in France to be equipped with an automated call system to quickly and simultaneously alert residents living near the site.