Gas explosion in the cat cracking and gas plant units of a refinery

9 November 1992

La Mède [Bouches du Rhône]

France

Explosion
UVCE
Gas
Catalytic Cracker
Gas-plant
Piping
Rupture / Corrosion
Victims
Material damage

FACILITIES CONCERNED

The facilities concerned have been set up since 1935 on the La Mède site in the towns of Châteauneuf-les-Martigues and Martigues and are located on the banks of the Etang de Berre water body at 40 km to the west of Marseille.

The banks of this water body are home to several Seveso facilities. (see figure 1).

At the time of the accident, the refinery occupied 250 hectares of the lower part of a rocky dale open eastwards with an annual processing capacity of 6.6 millions tonnes and employed 430 persons.

The site has an internal contingency plan and is subject to a risk prevention plan which are both regularly updated and operational.

The accident occurred in the Fluid Catalysed Cracking Unit (FCCU) CR3 with a 4,800 tonne capacity.

The cat cracking operation breaks down the heavy molecules of atmospheric distillates in vacuum and transforms them into easily recoverable lighter products such as certain fuels and thinners. The operation is performed at temperatures around 500°C in a pressure conditions slightly greater than atmospheric pressure. The operation produces fuels, gas oils, gases, heavy products and coke deposits on the catalyst.

The latter is constantly regenerated by combustion via injection of air.

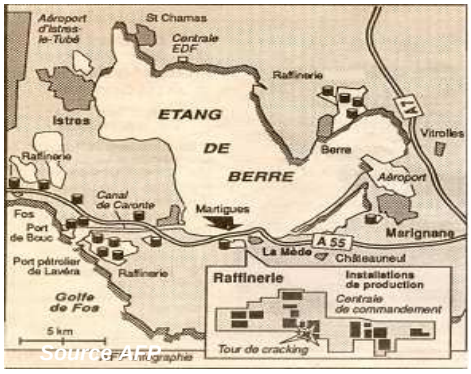

Figure 1 **– Geographical location of the site**

The non-condensable gases serve as fuels. The cryogenic unit commissioned in 1986 at the gas exhaust is used to recover virtually all the contained butane and propane. (see figure 2)

The gas plant unit commissioned in 1953 is located after the FCCU and is used to fractionate gases (operated at 290°C under 20 bars) in different cuts (C1 to C4).

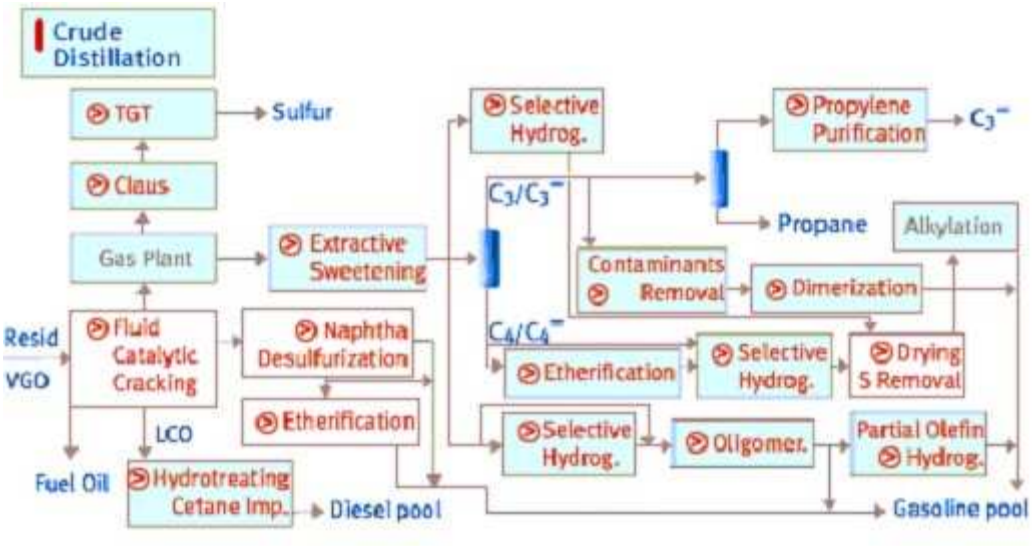

Figure 2 **– Working diagram of a catalytic cracker**

THE ACCIDENT, ITS CHRONOLOGY AND CONSEQUENCES

The accident:

On Monday 9 November 1992 at 5.20 am, a violent open air explosion was heard within a radius of 30 km around the site.

The various events succeeded in the following order:

- Between 4.00 am and 5.19 am: the units were operational and stable: the staff signed off without noticing any unusual incident.

- A little before 5.20 am: a major gas leak occurred in the gas plant. An explosimeter near the pump detected the leak at 20% of the LEL and triggered the alarm in the control room.

- At 5.20 am: an explosion was heard followed by a flashover in the gas plant and cryogenic units.

- Between 5.30 and 6.00 am: due to direct and indirect cascade effect, new explosions occurred and the fire spread to the adjoining facilities. Two tanks in the vicinity caught fire, as well as two liquid and gaseous hydrocarbon pipe racks. The emergency services arrived and the refinery rolled out the internal contingency plan. At 5.48 am, the prefecture triggered the disaster plan and the deployed the pre-alert phase of the risk prevention plan.

- Between 6.00 am and 9.50 am: the emergency services got organised and the command posts were operational right from 7.00 am in the prefecture.

- At 9.50: due to thermal radiation, the fire aggravated on a tank containing a mixture of used sodium hydroxide and fuel resulting in the last explosion.

- At 1.00 pm: the fire was brought under control. However the flare network was damaged and the firemen decided to let a few furnaces burn under controlled conditions to avoid the non-inflamed gas from spreading and forming a cloud. The facilities under high pressure were thus decompressed under minimal risk.

The implemented actions were limited to the supervision of the two operating furnaces in the site (on the piping) to complete degassing of the destroyed unit and protect technicians carrying out safety operations in the zero-risk facilities.

The firemen of the refinery administered first aid to the victims of the shift while awaiting reinforcement from the adjoining Seveso facilities. In all over a hundred firemen from the Bouches-du-Rhône and neighbouring regions (Gard, Var and Vaucluse) took part in the rescue operations.

Significant fire extinguishing measures were used to put out the flames including several dozens of fire engines and wagons and around 150,000 litres of foam compounds.

The organisation and management of the emergency services was carried out according to the guidelines contained in the internal contingency plan.

During the afternoon, the fire fighting teams from the region took off gradually. Only the firemen attached to the facility stayed on site while the firemen from the neighbouring facilities were on alert until 12.00 noon of the following day.

Consequences:

The final human casualty included 6 deaths and one case of serious injury among the refinery staff. 37 other persons including two firemen sustained minor injuries. Most of the victims were in the control room that was destroyed during the explosions (see. figure 3).

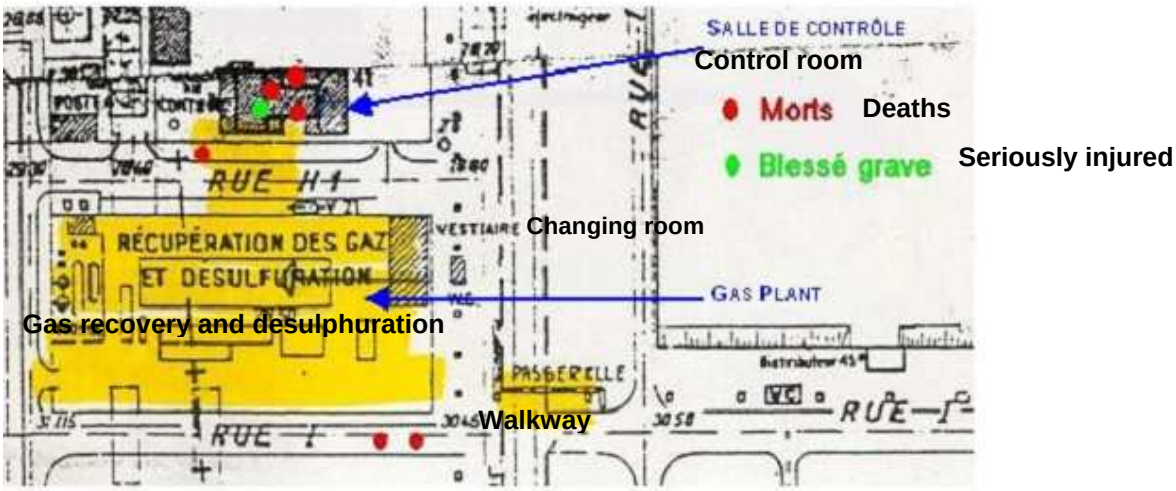

Figure 3 - Disposition des victimes
Location of victims

The refinery facilities were devastated further to successive explosions and fire approximately within the radius of 2 hectares around the catalytic cracker no. 3. In particular, the control room common to the cracker and all associated units, the gas plant section as well as the propylene fractionating facilities attached to the cryogenic section were all severely damaged. Shattered glass was found around a radius of 1 km around the site with some isolated fragments around 8 km. The roofs of buildings within a few hundred kilometres around the site in the towns of Martigues and Châteauneuf-les-Martigues sustained damage.

Figure 4 **– View of the control room at 9.00 am**

Figure 5 **– View of the cryogenic unit**

The most severe damages related to the fire were directly on the gas-plant and cryogenic units, the adjoining piping and a heavy gas oil tank near the B20 tank whose roof was ripped apart due to excess pressure resulting from the explosion. The C24 tank, whose main function is to receive used sodium hydroxide from units for an alkali wash, sustained severe damage in the upper part despite a protective bund wall covering 2/3rd of its height. At the time of the accident the C24 tank contained a mixture of 1,700 m³ of sodium hydroxide and light hydrocarbons. The shell of the A38 tank also sustained some damage following the fire

Figure 6 **– View of the B20 tank**

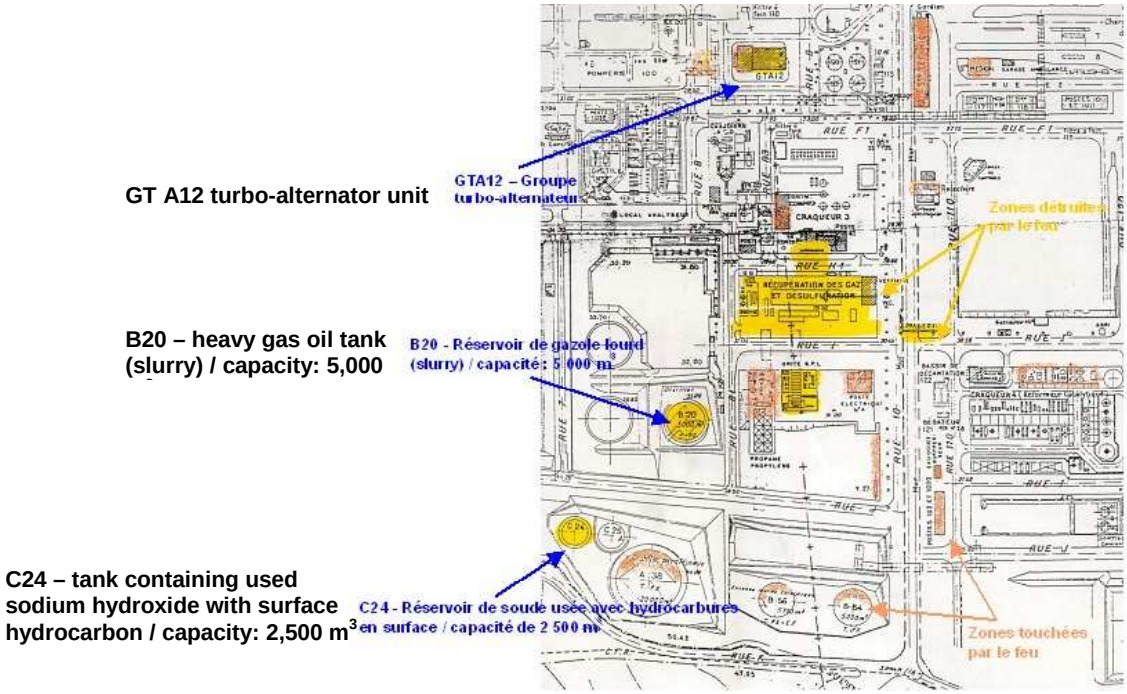

Figure 7 **– Diagram of accident zones**

The facilities affected by the fire include:

- Gas plant + Cryogenic units: 4,000 m²
- GT A12 turbo-alternator unit: 600 m²
- B20 tank: 450 m²
- C24 tank: 200 m²
- Piping racks: surface area hard to estimate.

The shock wave resulting from the first explosion in its two successive phases shattered structures (positive over pressure – impulse) and then drew in light structures (depression - negative phase). The explosion was accompanied by a rain of debris of which some were projected as far as 135 m from their initial location (such as the fairing of the cooling tower weighing 340 kg). The resulting cascade effects ripped out and destroyed various piping networks, the metal structure of the GT A12 turbo-alternator unit and caused the resulting fire and set fire to the B20 and C24 tanks.

The explosions secondary to the main one resulted from the indirect cascade effects. In fact, some piping networks weakened by the mechanical and/or thermal effects of the initial explosion gave in and resulted in new explosions.

***Figure 8* – Facilities destroyed by the explosion**

Environmental pollution was significantly limited. In fact, most of the water used to put out the fire and cool down the units was collected in the refinery's storm water retention basin. The retention capacity is 30,000 m^3. The water containing oils were subsequently treated in the site's treatment plant before being released into the Rhône river's Marseille canal.

The floaters in the Etang de Berre water body and in the various canals around the site reduced the consequences of the accident on the adjoining superficial waters.

With regard to air pollution, the network monitoring the air quality around the Etang de Berre water body did not record any significant and sustained increase in the concentrations of controlled air pollutants namely sulphur dioxide (SO_2), nitrogen oxides (NO_x), hydrocarbons, ozone (O3) and dust particles.

Lastly, the accident did not have any major impacts on the environment.

The estimated cost of the material damage resulting from the accident is assessed at 230 million euros. This cost mainly comes from the consequences of the cascade effects of the disaster

The site gradually resumed partial functioning in the beginning of the year, i.e. three months after the disaster and subsequent to obtaining the official prefectoral go-ahead upon the recommendations of the inspection authorities of classified facilities.

European scale of industrial accidents

By applying the rating rules of the 18 parameters of the scale made official in February 1994 by the Committee of Competent Authorities of the Member States which oversees the application of the 'SEVESO' directive, the accident can be characterised by the following 4 indices, based on the information available.

The parameters that comprise these indices and the corresponding rating method are available at the following address: www.aria.developpement-durable.gouv.fr.

Level 4 attributed to the «dangerous materials released» corresponds to an equivalent of 5 to 50 t of TNT (shattered glass found within a radius of 1 km around the site – Q2 parameter).

The death of six technicians in the accident justifies level 4 attributed to the "social and human consequences" index (H3 parameter).

Level 6 attributed to the "economic consequences" index represents the recorded material damage worth 230 million euros (€15 parameter).

THE ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

A massive leak in the gas phase followed by a rapid flaring up in contact with a hot point may be the origin of the accident.

The extent of the damage can be classified in 3 zones in the refinery that have been impacted:

- accident zone
- expert zone subject to special checks
- low exposure zone with no damage

Based on the observations in the various zones and several testimonials, the experts concluded that the explosion was a UVCE (Unconfined Vapour Cloud Explosion) type explosion. The effects of an UVCE type explosion are mostly mechanical (often at large distances from the epicentre) and result in pressure waves produced by the explosion and thermal effects arising from the flames.

Calculations of the gas hydrocarbon mass in question (empirical method said to be the "TNT equivalent" based on the damage observed caused by the over pressure explosion peaks) have shown that at least 5 tonnes of a light mixture (C3/C4 cut – propane, butane and propylene mixture) were involved in the explosion. This reactive mixture may be increased to include the unburnt and ignited masses without deflagration. Therefore, experts estimate between 6 and 12 tonnes of gas hydrocarbon mass to be involved in the accident.

The observation of damage in the closer range (radius less than 30 m) and in a wider range confirms that due to partial confinement resulting from an over congested floor area, the UVCE was triggered locally. The explosion speed was assessed at over 2,000 m/s.

The explosion of the gas cloud required an ignition point. A precise study of the various hot points, electrical substations and other furnaces pointed to the F301 furnace of the catalytic cracker. In fact, traces of fire beneath the furnace and only outside the electrical cabinet confirm the presence of a fire in these points before explosion. Moreover, this phenomenon bears out testimonials that indicate wicking ("flash" propagation) from the furnace to the passage I (passage separating the gas plant from the cryogenic unit). Thus the epicentre of the explosion was definitely located in this zone where maximum damage was caused.

Out of the 41 accident scenarios considered during the investigation, 29 were rapidly discarded following simple observations and 9 declared unlikely further to visual inspection by experts. There remained 3 possible scenarios of which two were supported:

- opening of crack in gas plant transport pipe showing signs of corrosion.
- breaking of a spur with a small diameter on the oxbow of the same piping network.

Further to analysis, the piping network in question supplied the first tower of the gas plant of the cat cracker no. 3, tower DA101. This "absorber-stripper" tower receives the entire light product yield (gas and light essence) obtained from the cat cracking reaction. The operating flow was at 110 t/h at the time of the accident. The fractionating tower DA 101 operates at a service temperature of about 40 °C en viron and under a relative pressure of 10 bar. The tower comprises 3 parts:

- 1 lower stripper that “strips” light gases, i.e. light fuel mixture + LPG (Liquefied Petroleum Gas: propane + butane).
- 1 primary absorber that scrubs the gases in fuel and absorbs propane and butane to prevent them from absorbing too much of LPG
- 1 secondary absorber at the head of the tower that performs the last scrubbing operation of the gases with a product heavier than fuel

Since the absorption reaction releases heat, a water cooler (EA 103), in which a mixture of fuel + LPG flows, is used to absorb the heat produced.

On 20 cm (8") of the return piping of the water cooler the following were observed:

- 2.5 cm diameter (1") spur broken at the boss of the piping network (figure 9).
- An 80 x 20 cm serrated crack in the internal generator of the by-pass of the heat exchanger EA 103, de (figure 10). On the piping network, a longitudinal stretch of corrosion was observed on the internal generator with a significant decrease in thickness (humid hydrogen sulphide medium maker the metal more fragile).

Figure 9 **- 1" spur**

Figure 10 **– 8" by-pass**

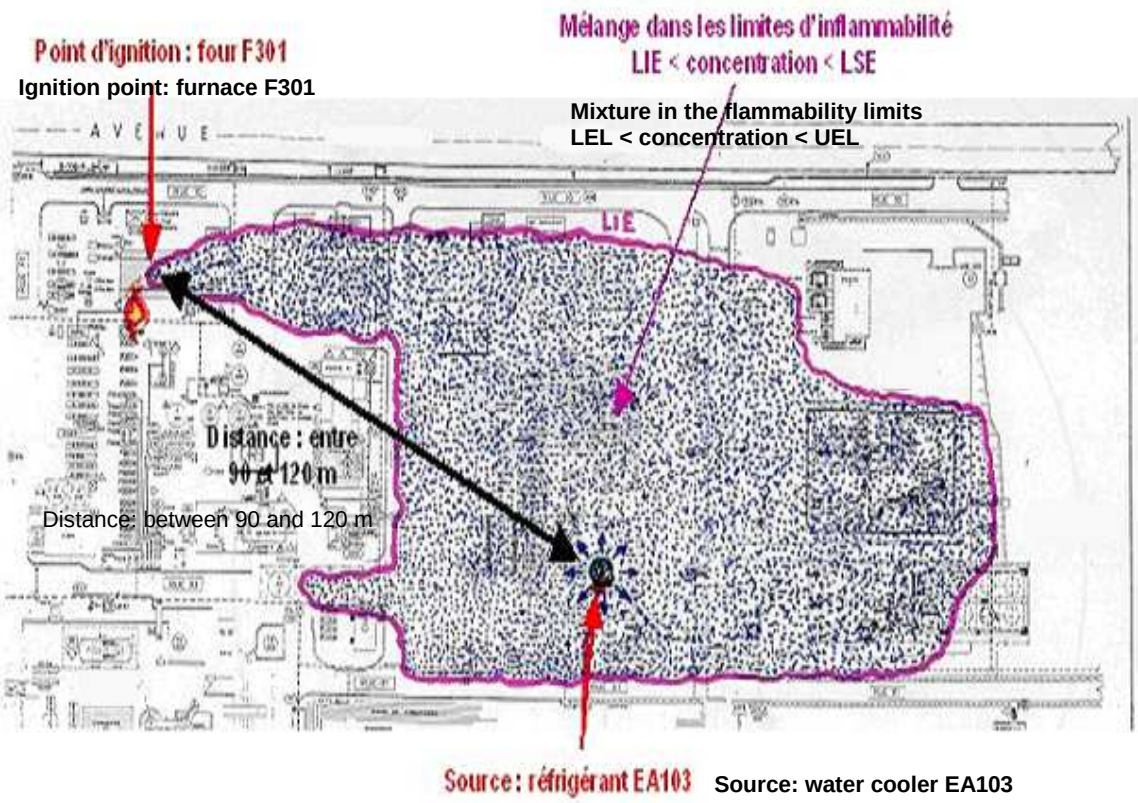

Figure 11 **– Gas cloud propagation diagram**

Expert analysis has revealed that a crack on the piping released 12 tonnes of LPG in 10 minutes as opposed to 5 tonnes released through the spur hole of which only one thirds of the quantity vaporises. The spur hole is thus not wide enough to vaporise the quantity of gas required to trigger the accident (quantities greater than 5 tonnes). The crack in the piping seems to be the cause of the accident.

The approximately 70,000 m^3 gas cloud (gaseous hydrocarbons + combustion air) was spread out over an area of about 14,000 m² and had a variable height of 4 m (cryogenic, propylene fractionating and furnace F301 zones) and 6 m for the gas plant zone.

Three successive phases could be identified during the initial explosion. The other explosions resulted from the cascade effects.

- The initial "flash" travelled at a low speed of around 5 to 12 m/s. Both air blast effect and over pressure was absent as long as the fire front did not encounter an obstacle. The involved surface was around 3,300 m². The flammable volume represented a volume of around 13,500 m^3. The first phase can be compared to the functioning of a wick.
- The second phase involved the deflagration phenomenon. The presence of a gas concentration gradient within the cloud, disturbances due to the various obstacles and the partial confinement accelerated the slow deflagration into a fast one (speed estimated at approx. 200 m/s) and hastened the UVCE phenomena. The over pressured generated by the deflagration was weak at around 0. 6 bar and the surface in question was approximately 7,200 m². The flammable volume was about 44,000 m^3 and contained nearly 3.6 tonnes of gaseous hydrocarbons.
- Lastly, the shock wave from the gas plant compressed the cool gas in the cryogenic unit and amplified by the local phenomena of focusing and reflection, locally triggered one or several detonations (speed > 330 m/s). The weight of the cloud at this stage was relatively low (less than 200 kg of gaseous hydrocarbons). The supersonic spherical waves collided with the propagation of rapid deflagration from the gas plant probably at passage I, the zone designated as the epicentre of the explosion. The over pressure generated is in the order of 2 to 3 bar. The surface in question is estimated at 3,400 m² and the flammable volume represented around 13,500 m³.

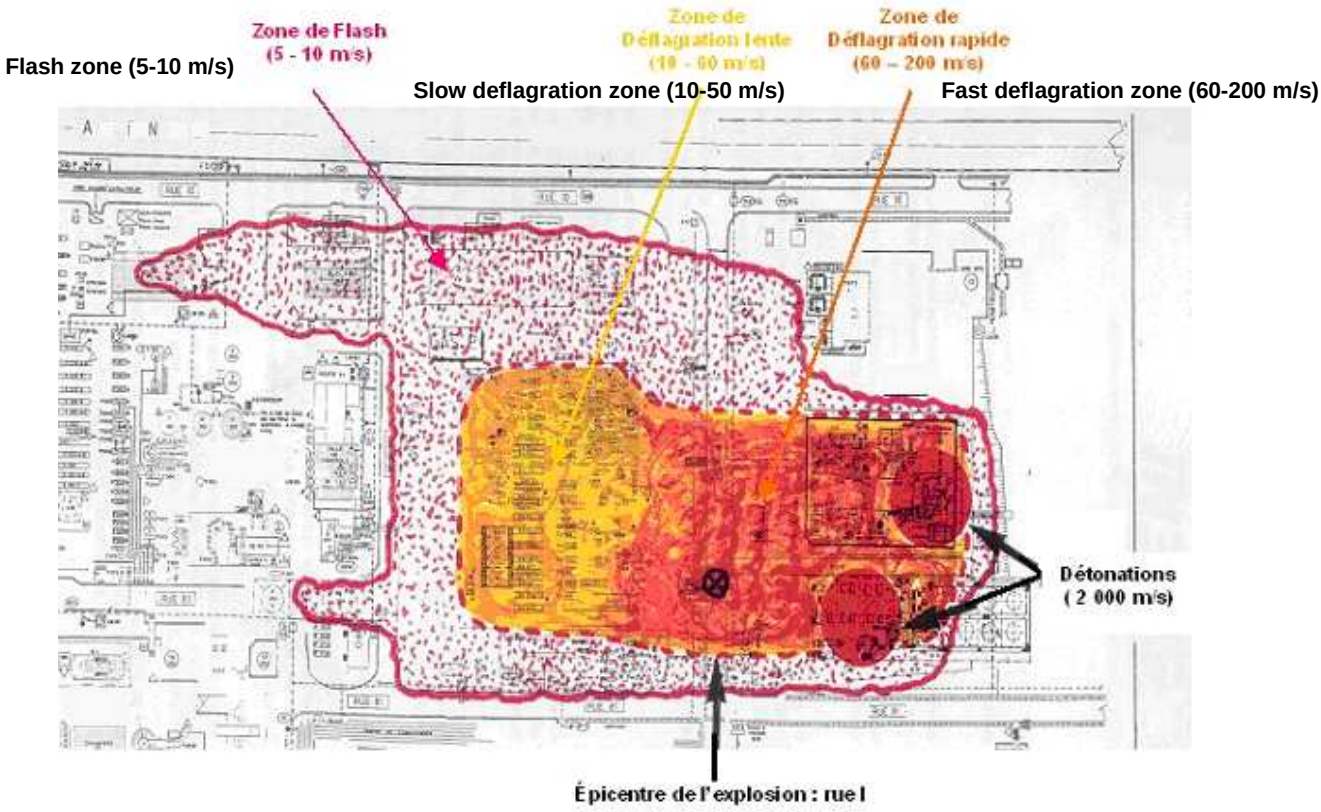

Figure 12 **- Illustration of the different phases of explosion**

In a summary, it seems that the gas cloud formed at the leak from the crack in the piping of the tower DA 101 drifted for a few minutes before catching fire at a distance of about 100 m upon contact with the furnace F301. The cloud caught fire at its fringes with lower concentration of hydrocarbon and close to LEL. The fire then spread to zones in the centre of the cloud with higher concentrations of hydrocarbons and finally in a zone with the required stoichiometric concentrations, the explosive UVCE phenomenon was triggered.

ACTION TAKEN

Subsequent to the accident, three enquiry committees (technical, administrative and legal) were dispatched and expert reports drafted. The study of the reports revealed shortcomings in the inspection and maintenance of the industrial facilities of the refinery of which some were obsolete and non compliant with the standards

After about nine years of the accident, the trial started on 29 January 2002 in the criminal court of Aix-en-Provence. On 24 April 2002, seven employees of the operating company including three former managers were given a suspended prison sentence from 4 to 18 months and fined for amount ranging from 1,500 to 4,500 €.

The refinery was fully re-commissioned in July 1994, i.e. 21 months after the disaster. The studies and work done on the site to re-build the damaged portions (setting up a new gas treatment unit) and modernise the cracker lasted 18 months. The entire project required 2 million working hours and an average of 1,000 people per year. The chief aim behind reconstructing and modernising the site is to enhance the level of prevention and curtail potential risks (safety of facilities and staff) by:

- increasing the number of gas detectors which are placed closest to the potential sources of emission to detect leaks as fast as possible
- setting up sprinkler system networks in “sensitive” areas
- conducting investigation on control room operations and effects of over pressure. The new control room has been designed like a bunker to resist shock waves. It is equipped with a new centralised control station designed along with ergonomists. This station provides the shift teams with information on operating and adjusting the units.
- installing robots that manage safety systems in addition to these measures.

In addition, pipeline inspection schedules at regular intervals were also put in place.

LESSONS LEARNT

The complete analysis of the accident is rich source of vital information on updating the best practices followed in industry and refinery.

The principles involve:

- control room location and construction criteria: set up outside the sensitive unit areas, design taking into account the thermal effects and impacts of over pressure ("blast proof" or "blast resistant" type construction)
- tightening the regulatory framework on construction, follow-up and regular inspection of the plant piping networks and accessories in both operating and non-operating conditions
- general lay-out of the site and units: spaced out units to reduce the cascade effect, creation of obstacle free areas to reduce the propagation speed of over pressure waves and keep safety measures (location of internal backup devices, etc.) and utilities (flare networks, boilers, fire fighting water network, water vapour and nitrogen piping network) in the event of an accident
- decongesting units: besides contributing to reduce speed in the event of a UCVE, a well designed lay-out facilitates rescue operations, maintenance, inspection and checking of equipment and accessories
- increasing the efficacy of risk curtailing means: number, location, calibration and reliability of gas detectors
- enhancing and increasing security of internal and external communication means
- promoting discussions with the press and other local players even during absence of crisis.

In terms of intervention, the implementation of backup measures was successful in both the internal contingency plan and in the pre-alert phase of the risk prevention plan. These plans that have been tried and tested by the various parties of the rescue team before the accident have increased the efficiency and coordination of the emergency services. These results bear out the utility of training and informing the actors concerned by these plans and making each individual aware of the configuration of facilities and their specific risks through drills jointly performed by the operator and external emergency services.