Explosion and fire in a hydrogen peroxide plant

22nd April 1992

Jarrie - [Isère]

France

- Chemical industry
- Hydrogen peroxide / Metals
- Automation / Controls
- Regulation valve
- Non-return valve
- Design / Redundancy
- Emergency stop / Fail-safe
- Organization / Procedures
- Human failure
- Crisis management

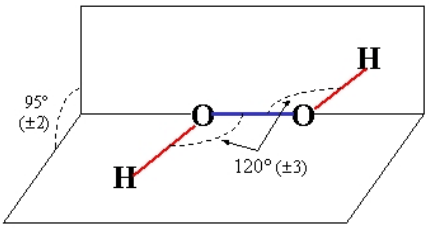
THE INSTALLATIONS CONCERNED

The site

Built in 1956, the chemical plant started up its first hydrogen peroxide (H_2O_2) production unit (OS1) in 1961 then a second unit (OS2) in 1973; these two units being controlled from a single control room which also contained common equipment for the decontamination and collection of the H_2O.

The site, authorised by decrees from the Prefect, employed around a hundred people in 1992 and had one of the largest peroxide production capacities in the world. At that time the site had a storage capacity for H_2O_2 requiring a study of risk as specified by the 2nd amendment of directive n° 82-501 commonly called « SEVESO »; the management had thus made a declaration concerning this storage capacity in October 1991.

The principal substance involved



Hydrogen peroxide (H_2O_2) was discovered in 1818 by Baron Louis-Jacques Thénard from a solution of barium peroxide activated by dilute sulphuric acid in the presence of hydrochloric acid (as a catalyst). Two chemical reactions are involved::

$$BaO_2 + 2\,HCl \rightarrow BaCl_2 + H_2O_2$$
$$BaCl_2 + H_2SO_4 \rightarrow BaSO_4 + 2\,HCl$$

Known in industry under the name of perhydrol, or occasionally by the public as oxygenated water, (H_2O_2), this pure peroxide (100 %) is a syrupy liquid with a volumetric mass of 1,45 kg/l, which can be mixed with water in any concentration. While chemically stable, it can easily and sometimes rapidly react in contact with numerous substances, releasing water and, according to the concentration, more or less important quantities of oxygen (O_2). This decomposition is the source of special dangers:

- *Major over-pressure in enclosed spaces with possible breach of the containing vessel, if the gas resulting from the decomposition is not released to the open air,*
- *Release of heat and O_2, H_2O_2 can spontaneously ignite in contact with certain combustible materials (wood, rags, paper…),*
- *Release of O_2 which may cause fire / explosion in contact with inflammable materials or increase combustion in the event of a fire in the vicinity.*

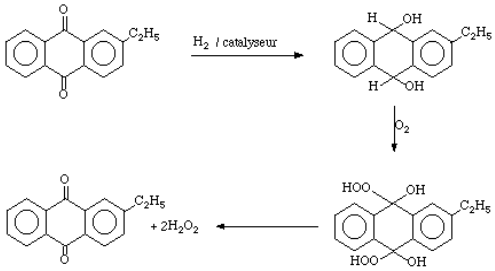
H_2O_2 must therefore be handled with very clean equipment made of aluminium, stainless steel glass or certain plastic materials

The concentration in volume of a solution of H_2O_2 corresponds to the volume of O_2 in litres at 0 °C and 1 atm released by one litre of this solution at 20 °C.

The stability of solutions of H_2O_2 is influenced by temperature, light, its concentration, the pH (> 5) and by the presence of decomposing agents, iron and chromium in particular, which are always present as trace elements in solutions. This stability constitutes one of the specifications for commercial products and corresponds to a maximum admissible decomposition of between 2 and 5 %.

The procedure used

The procedure used is based on the reduction of alkylanthraquinone to anthraquinol followed by its oxidation. During this reaction, the anthraquinone is regenerated and hydrogen peroxide is formed. Pressures are close to atmospheric pressure. The hydrogenation and oxidation temperatures are between 60 and 80 °C and the output as aga inst the hydrogen is above 95 %. (in the illustration H_2 catalyst)



The synthesis of the peroxide is achieved in three successive stages from a "working solution" of solubilised alkylanthraquinone in a mixture of organic solvents which can not be mixed with water. The hydrogenation of the solution to form hydroquinone is performed in the presence of a catalyst (palladium / alumina), the hydrogenated phase is then oxygenated by free oxygen from atmospheric air to form a mixture of hydroxyhydroperoxides. The hydrogen peroxide attached to the quinone (equivalent content in H_2O_2 close to 10 g/l, 1 % of the weight) is finally extracted by distilled water. The raw H_2O_2 obtained is finally distilled and stored, prior to delivery in concentrations of 50 or 70 % according to the clients' requirements. The working solution freed of peroxide is recycled to the hydrogenation.

THE ACCIDENT, THE SEQUENCE OF EVENTS, ITS EFFECTS AND CONSEQUENCES

The accident

On April 22nd, units OS1 and OS2 were in normal operation at the nominal production rate when an alarm sounded at 22h15 ; 20 valves moved to the fallback position including the valve for release to the open air of the largest compressor for the oxidation stage (noisy). The cooling water circuit valves also closed, in particular on the exchangers positioned between the oxidiser and the extraction column to cool the working solution circulating in OS2.

At 22h19, an unsuccessful attempt to put the installation back into service caused a general failure of the automatic command and control systems. All the mobile control elements (valves, activators, gas struts…) "stuck" in their current positions.

The absence of pressure control caused uncontrolled two way flows of solution between the oxidation and extraction stages of the OS2 unit.

At 23h09 and in less than 5 min, the temperature in this section rose suddenly (70 → 200 °C) as did the pressure. The pipeline linking the oxidiser to the extractor burst and the equipment emptied. The "working solution" released from the installation ignited almost immediately.

An explosion was heard tens of kilometres away and a raging fire propagated itself in the drains. During 2h15, this fire ravaged the oxidation/extraction installations of unit OS2. There was a fear of domino effects as the production unit of 4 000 m² surface area was close to the hydrogen and chlorine reservoirs. The internal emergency plan (POI) was initiated and the first emergency services arrived at 23h30. A safety perimeter was set up.

The intervention mobilised 34 in-house firemen, some hundred external firemen of whom 15 came from a factory close by as well as 35 vehicles. 10 m^3 of foam and almost 2 600 m^3 of water were used to fight the fire and to protect nearby installations. The fire was declared to be extinguished around 1h29.

The consequences

- Human consequences

One employee was killed and two others were seriously injured.

- Environmental consequences

The consequences observed to the environment were limited. A foul smelling odour was noted during the incident, but the emergency services did not mention any serious atmospheric pollution and the local air pollution surveillance network did not detect any peak of pollutants (SO_2, NO_x, HC…).

The retaining tank for the emergency basin on the site being of inadequate volume t (1 500 m^3), 1 000 m^3 of extinguishing water was released into the natural milieu; the mixture of organic solvents, non-miscible with water, remained on the surface but no die-off of fish was observed.

- Activity and economic consequences

A quarter of the unit was destroyed (1 000 m^2). Material damage and operational losses were estimated at between 74 and 110 M€ (1992) according to the sources. An entirely new installation entered service on January 1st 1994 ; the corresponding investment amounted to nearly 46 M€.

- Other consequences

During the intervention, the sound alarms in the plant and the spectacular external effects (explosion, flames, smoke) led to inappropriate behaviour by the population (curiosity, panic…).

European scale of industrial accidents

In using the scoring rules of the 18 parameters on the scale approved in February 1994 by the Committee of Competent Authorities of the Member States for the application of the 'SEVESO' directive and taking into account the available information, the accident can be qualified by the following 4 indices:

The parameters for these indices and the scoring methods are available at the following address http://aria.ecologie.gouv.fr

Hydrogen peroxide is an oxidant and the "working solution" consisting of a mixture of inflammable organic solvents is cited in the Seveso directive with respective thresholds of 200 et 20 000 t. Given the absence of any precise measurement of the materials released, the index is evaluated at 1 by default (parameter Q1); this same level of 1 is characteristic of the initial explosion which was evaluated at the equivalent of 3Kg of TNT (parameter Q2).

One death and two serious injuries being unfortunately recorded among the employees, the index for "human and social consequences" is equal to 2 (parameter H5).

The material damage and the operating losses from the accident being evaluated as between 74 and 110 M€ (1992), the index for "economic consequences" is equal to 4 (parameter €16).

THE ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

As in numerous cases, this accident was the result of **a chain of material and human causes** :

- The first was the failure at 22h15 of the power supply circuit board (DPXI) for the n°2 Input/Output (I/O) panel (covering generators 3 and 4) in one of the three technical cupboards of the Digital Control Command System (DCCS)..
  1. A simple interface between this site and the DCSS, this n°3 (FIO) station receives and supplies all the analogue measurements (excluding regulation) plus the regulation measurements, the status of the pumps and partial data on the status of the all or nothing (AON) valves. From the FIO are distributed all commands for all the remotely controlled valves some of the AON valves and those of the regulating valves. The cupboard also contains the microprocessor ensemble
  2. The panels contain two groups of I / O cards and the microprocessor part of the FIO, while ensuring the + 5 V et + 20 V power distribution and protection from a power module (Multiplex Power Module or MPM)

This failure was what originated the initiation of the sound alarms and the passage of the 20 valves to the fallback position.

- Around 22h19, the FIO was placed in the hold position; the valves controlled by the station were then "frozen" in their current position and could no longer be piloted from the DCSS; the OS1 and OS2 units and the common components were affected. According to the designer of the system, only a command given at the operations work station, which is furthermore protected by a key, can lead to this hold position, a possible operator error in reaction to the sound alarm had thus been anticipated.
- The operators attempted to halt the production on OS2 around 22h21 specifically by stopping the circulation of the working solution, but the automatic failsafe of the installations (normally followed by local manual commands) was interrupted following a discrepancy detected by the system and sounding of the alarm for non-closure of the isolating valve of the oxidiser. This fault was linked to the information loop

which should have been relayed by the FIO which was then in the hold position. As the manual command passed also through this work station, the default non-closure situation persisted.

However the steam valve can be directly controlled outside the DCSS from the console; but this action was not taken at the time.

- The aborted failsafe did, however, allow for the closure of the valve upstream from the extractor (discovered later not to be fullyleak-proof) and for the halting of the circulation pumps. Following the fall in pressure on the oxidation section linked to the opening to the air of the compressor at 22h15, the halting of the pumps caused a 1st return of H_2O_2 from the extractor to the oxidiser (50 m^3/h) ; the non-return valves to prevent the pumps from major flow-back were not designed to provide complete seals and the valve upstream from the extractor leaked. The flow-back continued, the H_2O_2 being pushed towards the extraction column until the pressure automatically stabilised in the oxidiser through the function of a regulating valve.
- Around 22h20, the operators alerted an engineer on standby and an instrument specialist. On his arrival, the latter observed the facts and contacted the help-desk of the company which had designed the automatic systems. He then put back into service, around 22h50, the FIO cupboard (position «UNHOLD») to take back control of the OS1 unit which had been operating "blind" for 30 min. A progressive temperature rise was observed at the entry to the extraction column.

  Attempts to arrange for the safety shutdown of OS2 were continued in parallel. Two operators outside the room thus received by radio the order to stop the two compressors of the oxidiser, the flow-back from one of them still being released to the open air.

  The halting of the last compressor remaining in service on the oxidiser at around 22h59 had the immediate result of a lowering of the pressure at the top of the oxidiser and of the temperature at the entry to the extractor column. A further flow-back of H_2O_2 towards the oxidiser was however made possible by the upstream extractor, the open valve at the base of the oxidiser creating suction of the liquid.
- Around 23h06, the isolating valve at the base of the oxidiser was closed by remote control from outside the DCSS from the control room. Observable as from 23h04, an exponential temperature rise at the entry to the column was noted within 5 min during which it reached 200 °C. .

  During the 2 or 3 minutes preceding the explosion, a radio call from an operator informed the standby engineer that "something is going wrong". An internal operator left the control room and went on a bicycle to check out the situation, (his body was later found on the site). He was followed by the engineer on foot.
- Meanwhile, the 2 flow-backs of H_2O_2 from the extraction stage to the oxidation stage following the uncontrolled variations of pressure in the installation, favoured the progressive build up of metallic contaminants (deposits, rust…) in the peroxide, these being powerful destabilising agents.

  These agents initiated and then accelerated the exothermic decomposition of the H_2O_2 (exponential temperature climb to 200 °C), the formation of O_2 (1 l d'H_2O_2 to 48 % weight → 187 l of O_2 released) and the rise in pressure between the downstream valve of the oxidiser and the upstream valve of the extraction column, both closed.


Source : exploitant

- The stainless steel piping (diameter. 273 mm, thickness. 2mm) connecting the oxidiser to the extractor burst at 23h09, the extraction column emptied into the retaining basin and then the reacting mixture ignited on contact with a heat source.

Following the initial breakdown of the control system, further material and human failures and design faults in the unit were therefore also at the origin of the accident and causes of its aggravation:

- Interventions by operators on the control system / commands which aggravated the disturbance,
- Control and safety systems acting on the same components,
- Partial automation of the emergency stop limited to the hydrogenation component,
- Insufficient control of the sequence of events for the failsafe shutdown of the installations coupled with several manual operations which were not performed by the operators to safely shutdown the unit,
- Imperfectly sealed systems (automatic and non-return valves),
- Linking piping not equipped with pressure valve,
- Difficulties in analysing the situation, even for the management,
- Absence of specific standing orders for the safe shutdown of the installations and lack of clarity in the existing standing orders and procedures.

The operators seem to have detected the flow-back of the hydrogen peroxide. This flow-back could have been halted using one of the two isolating valves in the reaction section, but the one piloted by the control system did not close

(computer breakdown) and the second was not leak proof. Finally the manual valves, which require local intervention by the operators of the installation were not closed. A logical tree of causes of the accident is to be found as an appendix.

THE MEASURES TAKEN

The operation of the seriously damaged unit OS2 (oxidiser / extractor assembly destroyed…) was suspended. An emergency decree required the management to safely close down the damaged installations as well as evacuate the debris and treat the water polluted by the fire.

Although they had no direct relationship with the accident, the inspectorate of classified installations noted that there was poor protection of the drains against the propagation of flames, insufficient dimensions for the retaining tanks and the emergency basin, absence of a file of standing safety orders as well as a list of the equipment and parameters which were important for safety.

The reconstruction and the start-up of unit OS2 were made conditional on a new application for authorisation including moreover a "safety report" presenting the results and actions taken following the enquiries undertaken.

Prior to the new start-up of the OS1 production chain, not affected by the accident, the operator had to put into effect the technical and organisational improvements required to avoid any repetition or this kind of accident:

- Technical measures required to

  - Prevent flow-backs of H_2O_2 in the oxidation stage by the insertion between the oxidation stage and the extraction column of at least two leak proof cut-outs (AON valves…), of tried and proven design with failsafe security and capable of being periodically tested, self-closing automatically in the event of weak flow of the working solution, detection of a stoppage of the circulation pumps or of voluntary act in the control room.
  - Protect the sections of piping which could contain the oxygenated working solution subject to decomposition from overpressure, by installing a protection device (with collection of any effluents that could be released), operating immediately on isolation of the piping to be protected. A report to the control room providing information and an alarm system was also planned. .
  - Improve the command and control system:

    In various sites within the installation where the risk of decomposition is to be feared, continuous measurement of at least 2 parameters influencing the stability of the solution (temperature, pH, metallic impurities).

    All remotely controlled operations allowing for the rapid shut-down of the unit (emergency shutdown) had to be backed up so as to be operable outside the normal control of the operation. The automation of operations required for this emergency shutdown requiring only the action of a single button (punch type) is under study.

    All partial/total breakdown or all unavailability, even temporary, of part of the control system now generates a visual alarm on the control console screens.

    The controlling components of units OS1 and OS2 being grouped in the same control room, the control tables and screens displaying the alarms the control and safety devices for OS2 are neutralised before the re-start of OS1 to avoid all confusion for the operators and interference with the control devices between the two installations (in particular the alarms).

    A feasibility study is in hand to examine the possibility of installing two technically independent systems.

    - The first to control and regulate the parameters which ensure the safe operation of the unit within the limits of its "safety envelope" with alarms and automatic safety shutdown in the event of exceeding the previously established safety thresholds.
    - The 2nd safety system with alarms and automatic safety shutdown of the unit in the event of exceeding the previously established critical thresholds.

    Alarms relating to important security parameters (IPS) are re-grouped and displayed on a specific interface (panel or screen) allowing operators or foremen to make an independent diagnosis of the safety risk for the unit the event of an anomaly in the system. All IPS equipment can also be operated independently from the control system.
  - Increase the retention capacity for the installations and protect the drains. The global retention capacity of the plant is increased to 5 000 m^3 (a 6 hour fire) ; an emergency basin of un 3 000 m^3 was specially built for this purpose.

    The retaining tanks below the units and storage sites were modified, (protection of gutters, increase in height of the walls, flame arrestors at the exit of the tanks...)

    The drains were to be protected against the propagation of flames by the installation of 3 firewalls on the storm drain, each of them being equipped with a vent to eliminate the risk of explosion.

- Protect sensitive installations nearby: fixed banks of sprinklers (10 l/m²/min) to protect compressed hydrogen tanks from thermal radiation and also fencing capable of blocking projections of metal fragments in the event of bursting of the tanks while preventing the confinement of a potential hydrogen cloud…

- Organisational measures to

  - re-define the missions of those concerned and improve their knowledge and training. Operators responsible for managing the process via their computer terminals will no longer have access to the central system even in the event that it should break down.

    Any intervention by a qualified person on the central system must be brought to the attention of the operators managing the production units.

    A company employee should be specially appointed to supervise the quality and the follow-up of the training of operators and their practising to provide an improved reaction to accident situations. Specific training is also implemented for those who only occasionally intervene on the installations (instrument specialists, maintenance personnel, standby foremen…)
  - Draw up well adapted standing orders. Independently of standing orders for normal operation, "safety" orders, defining precisely either the procedure for emergency shutdown, or the measures to be taken in the event of a deviation of the process from normal safe operating conditions. These standing orders are to be drawn up with the participation of the operators.
  - All the elements comprising the safety file should be included in a single document.
  - Risk studies were undertaken concerning the production, transfer and storage of hydrogen peroxide (explosive nature of mixtures of H_2O_2 / corking solution …).

As regards the damaged unit, it was rebuilt taking into account the following objectives:

- Allow for the return to the former production capacity of the site,
- Facilitate the control of the installations of the entire plant and enable their safe remote shutdown: new control room further away from the production equipment, safety system allowing for the emergency shutdown independently of the control system, improvement of the ergonomic and comfort aspects of the workstations.
- Limit the extension and the consequences of possible fires, improved airing of the destroyed premises, increase of capacity of the retaining tanks for fire-fighting water, application of the principle of remote tanks, gravitational emptying of the reactors,
- Reduce the environmental impact, principally as regards waterborne waste and noise pollution: biological treatment of waste, noise reduction devices on the compressors.

THE LESSONS LEARNED

Particular points highlighted by this accident

- The negative points

  - Specific risks linked to the process (instability of peroxide, flow-back of H_2O_2 and poorly sealed circuits) of which the operator was perfectly aware: a regulating valve thus provides no guarantee of absence of leakage (according to the sources, up to 10% leakage for certain valves).
  - As few stoppages as possible for the units and, when they are necessary or indispensable, isolation of the installations solely by manual valves.

    Throughout the safety shut-down of the installations, local actions (valves and purges to be closed) were thus planned in the procedures, not all these actions were taken, or were doubtless taken too late.
  - Emergency safety precautions and shutdown procedures for the installations were poorly adapted.
  - A control system designed to ensure at the same time the regulation of the parameters guaranteeing the correct operation of the units and the management of the security systems.
  - Possible access by operators to this system to modify the parameters in the event of certain failures.

- The positive points

  - The operation of the fixed sprinkling and extinction devices,
  - The enslavement of these devices to detectors (fuse wires…),
  - Firewall devices to equip the overflow of the retaining tanks,
  - Assistance from outside factories,
  - The collaboration of the fire-brigades from the various mobilised fire-stations.

- The retention of the fire in the initially affected zone,

Lessons as regards technical and human aspects

- In the field of prevention

  - The value of an analysis of risks and failure modes, as well as the technical and organisational measures, as detailed as possible, for the various "operating" modes.
  - A control system for a procedure in no way constitutes a safety device and can not be treated as such. In particular, programmable production robots correspond to a logic and criteria which are more or less well known by operators and do not necessarily take into account degraded modes and situations covered by standing orders.
  - The role and the limits of intervention assigned to operator, as well as their training and rehearsals to deal with crisis situations should be once again underlined.
  - The close attention that should be given to the design and drafting of the standing orders and operating modes, particularly as regards organisational measures, (isolation/de-isolation…) to ensure improved effectiveness and reliability.

- A regards the special difficulties of intervention

  - The violence of the fire linked to the combustible power of H_2O_2 reduced the effectiveness of the foam projectors,
  - The proximity of other dangerous installations (storage of hydrogen under pressure…),
  - The blockage of the drains in the retention basins and the overflow of these in zones without collectors caused a propagation of the fire in drains without fire-break siphons,
  - An under-dimensioned emergency basin.
  - Management of information,
  - The reception of external personnel (administration, elected officials, judicial police).

- As regards the behaviour of the populations

Being very spectacular both as regards the noise intensity of the explosions and by the size of the fire, the accident of 2nd April was widely perceived by the inhabitants of the communes of Jarrie and Champ-sur-Drac. Conversely, the management, considering that the accident presented no special risk to the surrounding population, took no special steps to inform the public during the first instants. This absence of information was widely criticised during the following days.

Facing a disaster of considerable scope and taking into account the co-existence in the same industrial site of another plant presenting "major" risks, it is understandable that the populations, imagining the worst case scenario, were worried and awaited information concerning the measures to be taken to ensure their safety. This sensitivity can also be explained by the fact that the neighbouring factory had been subject to concrete measures taken in application of the "SEVESO" directive and of the law of 21st July 1987.

For several years numerous information campaigns had been directed at the public in the department as a result of concerted action by the industrial concerns, the local authorities and the government (Operation Isère, pilot department) and following the completion of risk studies concerning the local "SEVESO" installations. The risk perimeters in the event of accidents were known and the control of urban planning, negotiated with the local authorities was in the process of completion with a view to their integration in urban planning documents. (Land Occupation Plans at the time of the events). During the information campaign conducted throughout the department concerning technological risks, over 90 000 leaflets had been distributed and confinement exercises had been conducted.

Despite this information, a large part of the population had not followed the classic safety instructions provided for just such a situation. Thus, according to witness statements gathered after the accident, people reacted in various ways in leaving their homes and moving, sometimes to watch the incident, sometimes to flee in a car or in confining themselves in their homes… sometimes until the following morning while awaiting radio messages which were indeed planned in the framework of a PPI (special intervention plan), where, in the event, such a plan was not launched.

Such reactions demonstrate that the public had been made aware of the technological risks but that the initiation and the function of intervention plans needed to be further explained. This accident therefore served to support the discussion during a public meeting several days later.

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Logical tree of causes of the accident of 22nd April 1992