Fire in a hydrodesulfuration unit of a refinery

June 26, 2004

Feyzin – [Rhône] France

Furnace
Detection
Intervention
Communication
Inspection plan

THE INSTALLATIONS IN QUESTION

The refinery was commissioned in 1964 to provide the Rhône-Alpes region with a variety of fuels.

It produces a full range of conventional petroleum products (LPG, kerosene, petrol, diesel fuel, domestic heating fuel oil, …) and also has a significant petrochemical activity (including the production of ethylene and propylene).

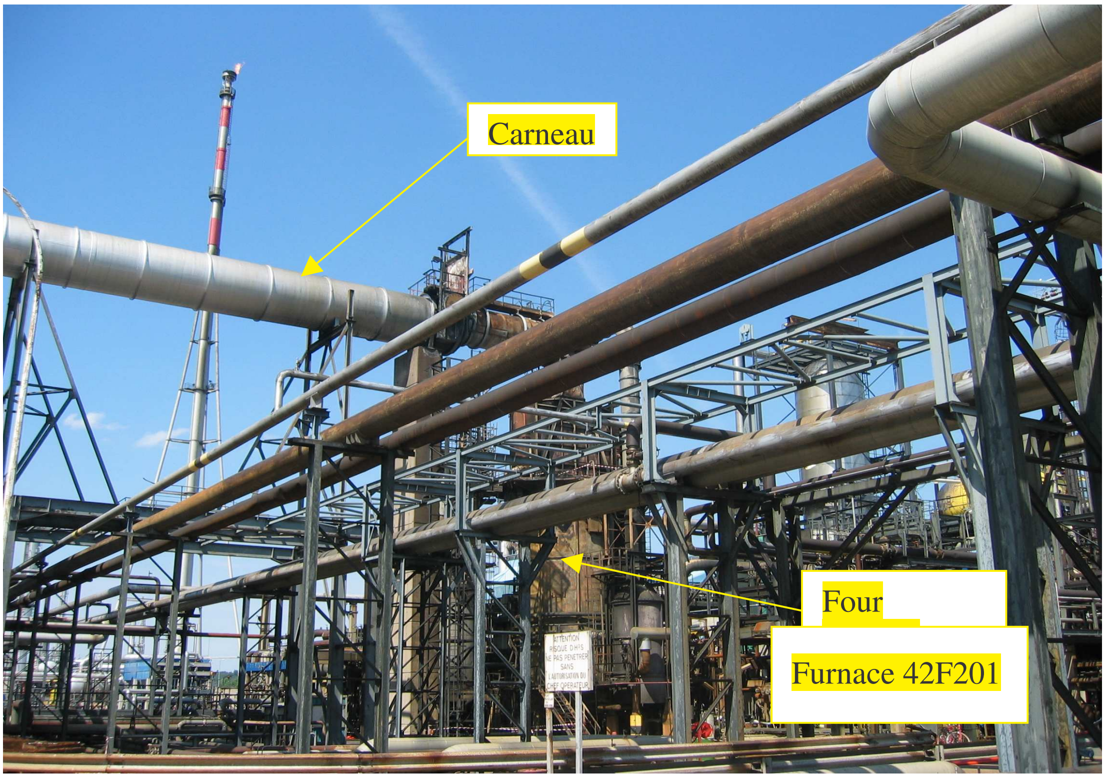
It produces roughly 6 million tons per year and has a storage capacity of 1 million m^3 for liquids and 34,000 m^3 for liquefied gases.

The plant employs approximately 600 people, including 150 for the petrochemical sector.

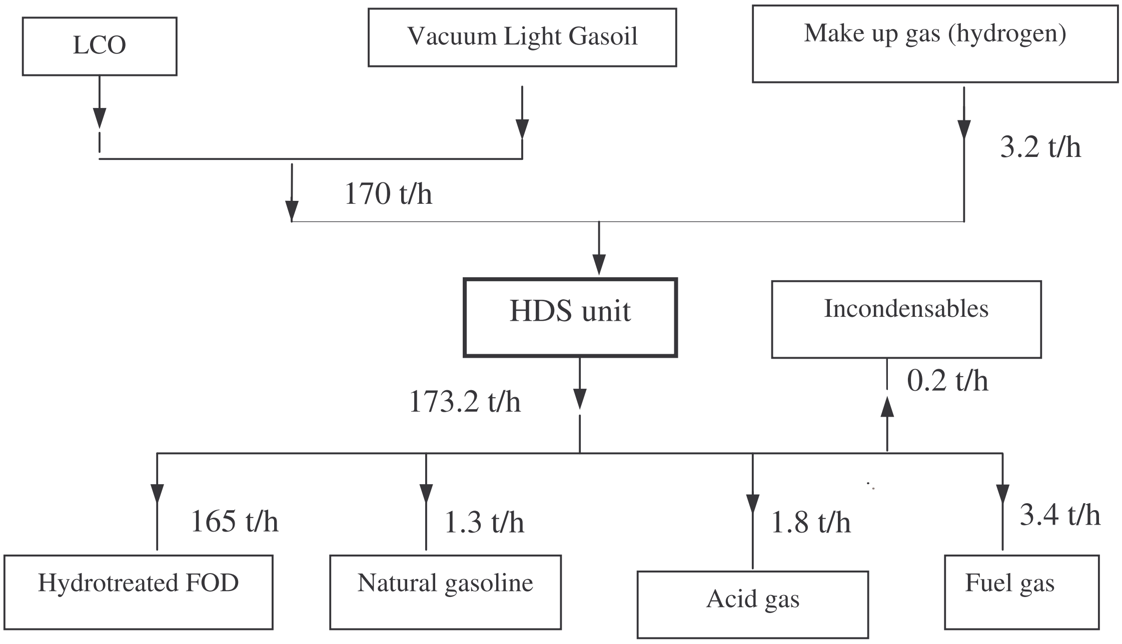
The refinery is located to the south of Lyons in "Chemical Valley" on a narrow site covering 143 hectares. It is bordered to the west by the Rhône Canal and to the east by the A7 motorway (except for the loading zone located on the other side of the A7), the Lyons/Marseilles rail line, the Sibelin railroad yard and an urbanized zone.

This establishment is governed by the SEVESO II Directive (High Level). In addition, an inspection department for pressurized equipment at the site was "recognized" by the DRIRE in 1995.

The fire occurred on the load preheating furnace (42F201) of the hydrodesulfuration (HDS) unit located on 5,300 m^2, to the southeast of the zone dedicated to the refining units.



Overall view of the HDS unit (after the fire)

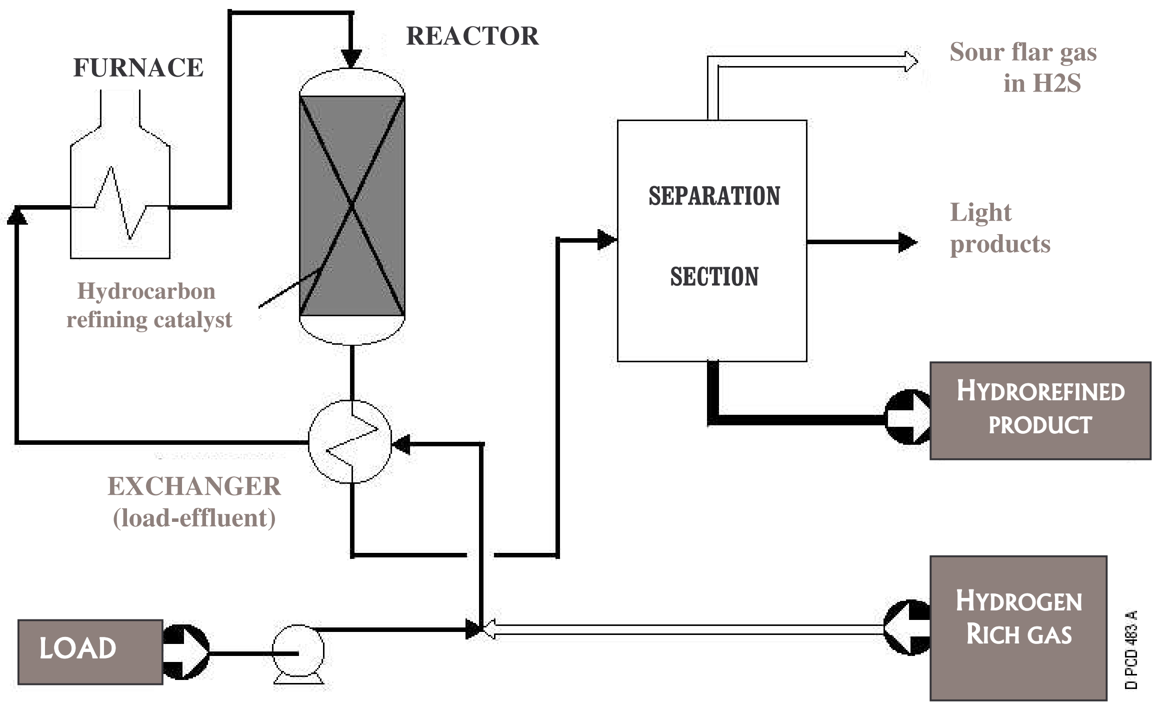


<u>Material assessment of the HDS unit in domestic fuel oil operation</u>

The HDS unit primarily processes fractions intended for the fabrication of diesel fuels and fuel oils. It is designed to reduce the sulphur concentration of intermediate products in order to produce combustibles and fuels that respect sulphur specifications required by environmental legislation.

Desulphuration takes place by hydrogenation in the presence of a catalyst, with the hydrogen being supplied by a gaseous mixture coming from the reformer and the steam cracker. The reaction produces hydrogen sulphide (H_2S) which the unit retransforms into sulphur (see the flow diagram below).

Sulphide loads + Hydrogen		>>>>>>>	Cleaned loads + Sulphur-containing gaseous effluent	
Sulphur-containing gaseous effluents		>>>>>>>	Fuel Gas + Hydrogen sulphide	
Hydrogen sulphide	>>>	Claus reaction	>>>	Liquid sulphur
Fuel Gas	>>>	Combustion	>>>	Refinery energy



HDS unit flow diagram

Characteristics of furnace 42F201:

The furnace was commissioned in 1974 and is used to desulphurize diesel fuel, distillates and domestic fuel oil.

Specifications:

- Nominal pressure: 56.9 bar,
- Maximum operating pressure: 42 bar,
- Nominal temperature: 425°C,
- Usual operating temperature around 410°C-420°C depending on the products to be desulphurize.

It is essentially made up of 6"-diameter tubes (ND 150) and elbows made of austenitic A 312 TP 347 stainless steel, selected for its resistance to the main type of corrosion in this type of furnace, which is sulphuration.

It consists of a lower radiation part where the vertical tubes are normally accessible, lapped by the flame, and an upper convention part where the horizontal tubes in superimposed and tight layers are thus not subjected to the action of the flame. Only the lower layer of convention tubes is visible, as well as the peripheral junction elbows between the layers.

On the convection part, the tubes in place were the originals while in the radiation part; several tube replacements had already taken place (1 tube was replaced in 2001 and 16 tubes were replaced during the last shut down of 2002, prior to the ten-year testing). The reasons for this were accidental overheating during a restarting operation for the tube replaced in 2001 and overheating zones due to the maladjustment of burners in 2001 for the 16 tubes.

View of furnace 42F201 (after the fire)

THE ACCIDENT, ITS BEHAVIOUR, EFFECTS AND CONSEQUENCES

The accident:

A fire broke out on furnace 42F201 on June 26, 2004 at 4.38 pm. Flames engulfed the furnace (the metal of the convection section was red hot) and black smoke was released.

The fire was not preceded by an explosion although witnesses noticed a suspicious noise, described as a whistling noise (like a valve) which became louder and louder, followed by a "mechanical" noise.

Personnel working at a neighbouring site were able to rapidly sound the alarm and manually opened part of the water curtains before the fire brigade arrived to the site. The operator stopped supplying the unit (load and hydrogen) and began decompressing via the flare stack, which rapidly reduced the combustion. The furnace's load-bearing structures, subjected to an intense thermal flux, were cooled down.

The external fire was brought under control in 30 minutes using the refinery's internal resources. The external firefighting means dispatched to the site did not have to intervene.

The ignition of the products coming from the reaction loop (reactor 42R202) continued intensely for a few hours in the furnace's convection chambers and flue exits.

Intermittent flames were observed for several minutes at the outlet of the common stack that collects the atmospheric releases from the HDS units, atmospheric distillation No. 2 (DA2) and removal of aromatics (hydrotreating section No. 2 - HDT2) and a significant plume of smoke.

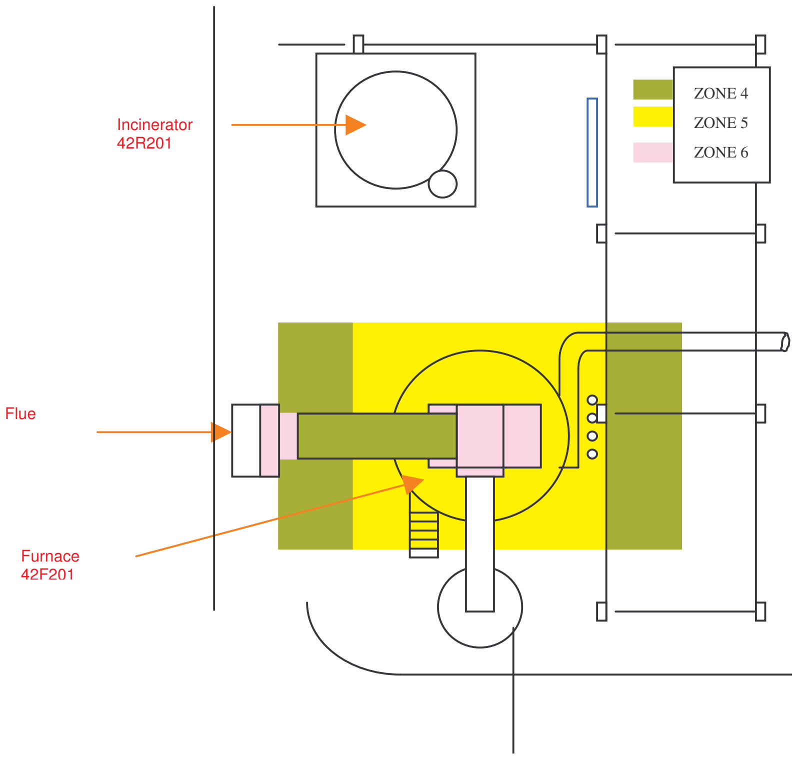
None of the H_2S detectors on the unit triggered the alarm. Most likely, however, a certain quantity of H_2S was released through the flare stack.

Among the pollutants continuously monitored by the sensors in the refinery's environment (including a network of air quality measurements in the Lyons community), the amount of sulphur dioxide and particles in suspension is likely to be high in the event of an incident of this type. The concentrations measured did not increase significantly (they remained below the information and recommendation threshold for sensitive individuals).

The consequences:

Property damage:

✓ The detailed evaluation of the damage to pressurised equipment involved in the accident was conducted according to API 579 methodology which consists in determining the temperatures reached during the fire, including spatial classification of the 6 corresponding zones and the definition of an acceptance or replacement criterion depending on the zone concerned.



Classification of zones	Description
1	Ambient temperature, no exposure to the fire
2	Temperature below 70 °C, smoke and fire protection water
3	Temperature below 200 °C, slight exposure to the heat
4	Temperature between 200 and 430 °C, moderate exposure to the heat
5	Temperature between 400 and 700 °C, high exposure to the heat
6	Temperature above 700 °C, very intense exposure to the heat

Classification of the temperature levels reached
(zones between elevations 8 m and 25 m)

Partial view of furnace 42F201 after the fire and dismantling for inspection

✓ Furnace 42F201 underwent the most extensive damage:

- × Total destruction of the convection array (fusion of the upper levels of the convection, only the lower layer had tubes that were not melted, including a burst tube) (see photo below),
- × Fusion and vitrification of the refractory material on the convection part (see photo below),
- × Overheating of the radiation array,
- × Damage or deformation of convection and radiation wall and structural elements,
- × Degradation of support columns,
- × Deformation of the first section of the flue.

View of the lower convection layer (after the fire)

✓ The support columns of incinerator 42F502, located near furnace 42F201, were damaged (lagging concrete damaged). According to the operator, this damage was the result of ageing of the heat lagging. Supporting documents were requested on this point.

✓ The following equipment was damaged by the accident:

- × Piping in zones 5 and 6, primarily the fuel supply lines and furnace utilities,
- × Electric wiring and measuring channels,
- × 3 water curtains for furnaces 42F201 and 42F501, and
- × Certain gas detectors.

✓ The furnace loading and transfer lines located in zone 5, as well as the set of pipes on the East rack and at ground level were not metallurgically affected by the accident owing to their heat lagging,

✓ The metal ladder on furnace 42F201 was twisted, and the wall (concrete) supporting the flue that connects the HDS unit to the stack common to the HDS, DA2 and HDT2 units was also damaged,

✓ Flames were observed for several minutes at the outlet of the chimney shared by the HDS, DA2 and HDT2 units, indicating that the structure may have been damaged (notably the refractory material),

✓ At the effluent monitoring platform of this chimney, a temperature peak of at least 500 °C (upper detection limit) was recorded, further recording was impossible as the sensor had been damaged.

Environmental consequences:

The resulting environmental consequences were described and evaluated:

- × Type, quantities, composition, and toxicity of atmospheric releases (H_2S, SO_2, dusts, …),
- × Type and quantities of the waste and polluted water, as well as the possible clean-up options.

The evaluations at this point were as follows:

- × The quantity of hydrocarbons involved in the fire was estimated at 45 tons, which represents approximately 1 ton of SO_2 released into the atmosphere.
- × While emissions of H_2S were noted in the site's environment, the fixed detectors of the HDS unit did not detect the presence of this pollutant.
- × The quantity of dust from unburnt particles was not determined,
- × In late September 2004, the overall quantity of waste was estimated at approximately 240 tons,
- × The internal treatment station treated approximately 3,000 m^3 of water from firefighting operations.

Economic consequences:

The economic consequences were estimated to be approximately 28 million €, notably with:

- × 250,000 €/day in operating losses (the facility being out of operation for 3 months),
- × 6 M€ dedicated to unit refurbishing operations, including 2 M€ required to rebuild the furnace.

Human consequences:

Two operators were slightly injured during the fire extinguishing operations (from falls resulting from irregularities in the slabs of the HDS unit covered by foam).

According to the public emergency services, 600 people were temporarily evacuated from a neighbourhood in Feyzin (including the swimming pool and stadium). As a precautionary measure and due to a lack of precise information from the refinery, the law enforcement agencies decided to temporarily block the A7 motorway.

Seveso II Directive – Appendix VI

The accident was considered “major” according to the following criteria of Appendix VI of the Directive:

- "property damage inside the establishment": approximately 6 million € for a threshold set at 2 million €,

- "evacuation or confinement of individuals for more than 2 hours" (people x hours): 600 people temporarily evacuated (for more than 2 hours) for a threshold set at 500.

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, which comprise these indices and the corresponding rating method, are indicated in the appendix hereto and are available at the following address: *http://www.aria.ecologie.gouv.fr*

Quantities of dangerous substances	■ ■ □ □ □ □
Human and social consequences	■ ■ ■ □ □ □
Environmental consequences	□ □ □ □ □ □
Economic consequences	■ ■ ■ ■ □ □

The index relative to the quantities of dangerous materials is equal to 3 owing to the release of 1 ton of SO_2 into the atmosphere. Level 3 for the human and social consequences is the result of the evacuation of 600 people. The index relative to the economic consequences is rated level 4 due to the production losses that were evaluated at 22 M€.

ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

Furnace 42F201 inspection plan:

The furnace inspection plan in force at the time of the accident offers the possibility to extend the periodic inspection intervals to 6 years and periodic requalifications to 12 years depending on a scheme approved by the DRIRE November 8, 2001, in terms of the regulations governing pressurised equipment.

With this goal in mind, the refinery's inspection department established inspection plans for the unit's pressurised equipment according to the RBI (Risk-Based Inspection) method, in compliance with the UFIP (Union Française des Industries Pétrolières) of February 2000, and recognized by the administration per DM-T/P No. 31 538 of October 20, 2000.

The implementation of the RBI method relies on "RBeye" software used within the Group, which automates the search of degradation modes according to fluid, equipment material, pressure and temperature data.

The furnace has undergone periodic inspections since its installation, with triennial verifications up to 1997, and ten-year testing. The last successful periodic requalification with performance testing took place in April 2002. It had thus been in service for 27 months at the time of the accident.

The HDS unit was inspected during the plant shutdown of 2002 ("metal" shutdown) and was shutdown in 2003 for a simple catalyst replacement operation.

The non-destructive testing conducted since the initial installation consisted in ultrasonic thickness measurements, and dimensional inspections to check for creep along the radiation portion of the furnace as the inspection department considered that it was the most exposed. Since 1993, metallographic replicas on the radiation tubes were taken and showed the initiation of stainless steel sensitisation (incipient corrosion which could modify the mechanical characteristics). The inspection department nevertheless determined it to be acceptable due to the lack of cleavage or microcracking.

On the convection part, only thickness measurements were conducted on the peripheral elbows (see photo below), and no anomaly was recorded.

View of a peripheral elbow on the convection chamber (after the fire)

The inspection report of the periodic requalification operations conducted in 2002 show that, for the convection part, the visual examination performed by the inspection department on the lower layer showed no signs of anomaly. Furthermore, the history of the thickness measurements on the radiation tubes and convection elbows since 1993 showed no abnormal decrease in thickness.

For obvious design reasons, verification operations cannot be conducted inside the tubes.

Periodic requalification is accompanied by hydraulic testing at 85.5 bar.

Condition of the HDS unit prior to the fire:

Since the day prior to the fire, the HDS unit had been in "domestic fuel oil" (FOD) operation. This operating mode is considered as moderate. It was fed by a mixture of light distillate coming from vacuum distillation unit No. 2 and LCO (light cycle oil) from the catalytic cracking unit. The load's sulphur content was estimated at 1.16%.

It should be noted that prior to introduction into furnace 42F201, the load is injected with hydrogen which contributes to the desulfuration reaction.

According to the recordings, the skin temperature of furnace 42F201 was stable at around approximately 373 °C, with a maximum allowable temperature of 392 °C (setpoint temperature).

Origin of the fire:

It appears that the tubes which make up the lower convection layer were not melted due to the fact that they were being supplied all the way to the end by the load and thus "cooled".

Among them, a tube that was found ruptured (a clean rupture 500 mm in length), was then determined to be the cause of the fire (see photo below).

Views of the ruptured tube

Expert assessments:

Two expert assessments were conducted; one by an external expert, and the other by the Group's research centre.

Assessment of the external expert:

The assessment was performed on 2 tubes (the ruptured tube and the tube next to it) based on a geometric, fractographic and metallurgical analysis of the ruptured tube as well as mechanical tests and X-ray diffraction analyses.

It appears that the rupture was the result of four types of damage which combined their effects and reduced the thickness of the tube to the point where it could no longer resist the operating pressure.

The damage:

✓ **presumed corrosion from polythionic acids:** these acids form when the load's sulphur compounds come in contact with oxygen. This situation cannot occur during normal operation, as the load does not contain oxygen. It is encountered during shutdown periods and hydraulic testing operations. To avoid this phenomenon, a passivation operation is performed during the shutdown period (the procedure was formalised in 1985). It appears that the attack may have happened some time ago as the passivation operation has been performed since 1980. It appears to be the result of localised formation of ruts on the inside of the furnace tubes.

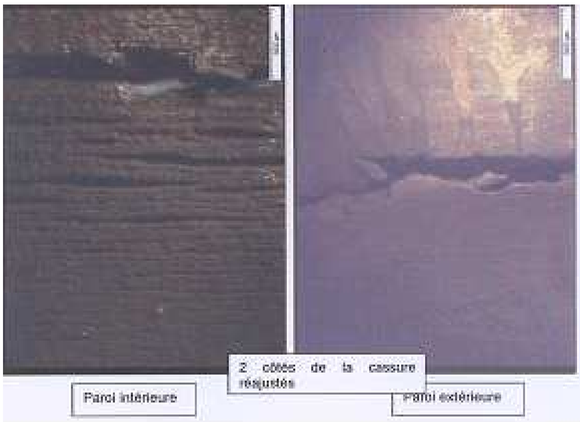
✓ **decreased thickness by oxidation/sulfuration**: in the ruts formed by the polythionic acid corrosion, the material (austenitic stainless steel) lost its corrosion-resisting properties, resulting in reduced thickness through corrosion.

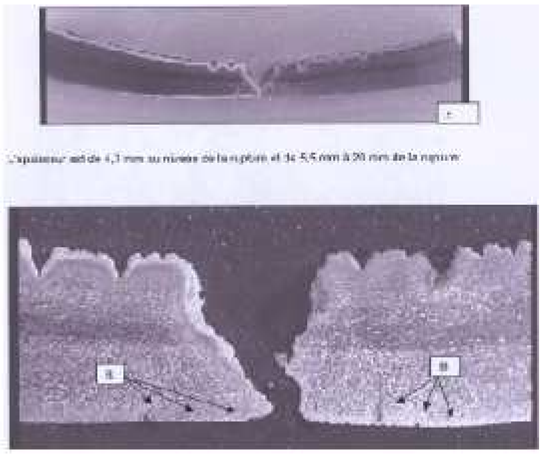
✓ **presence of sigma phase** (intermetallic compound causing highly marked brittleness of the metal) in small proportion which may have facilitated the development and penetration of the intergranular corrosion.

✓ **intergranular cleavage leading to slow creep** which eventually generates cracks on the outer skin of the tubes: this phenomenon could be explained by poor heat exchange due to a coke deposit inside the tube. This external tube damage was not visible with the naked eye.

Assessment by the Group's research centre:

This assessment, conducted on another tube, revealed none of the internal intergranular corrosion patterns found on the ruptured tube. However, cleavage due to creep on the outside and dense sigma phase on the inside were noted. The assessment concluded that the defects were localised.





Microscopic view of the break and its two edges readjusted (burst tube)

Decrease in thickness through oxidation/sulfuration (internal skin), presence of sigma phase (internal skin), intergranular cleavage (internal skin) and cracking (external skin).

ACTION TAKEN

DRIRE intervention:

The DRIRE began an administrative inquiry June 26, 2004. The main contacts with the operator were was follows:

✓ visit on June 26, 2004 by the Classified Installations Inspectorate in order to conduct the first reports and to collect the first testimonies,

✓ visit on June 28, 2004 by the Classified Installations Inspectorate,; this visit continued that of June 26, 2004,

✓ working meeting and visit of the furnace on July 8, 2004 by agents in charge of monitoring pressurised equipment and the inspection of classified installations. The goal of this meeting was to collect the first elements concerning the furnace and draw up an initial progress report concerning the prefectorial order outlining the emergency measures of June 30, 2004 (see infra),

✓ participation by the Classified Installation's Inspectorate in extraordinary meetings by the CHSCT (Comité d'Hygiène, de Sécurité et des Conditions de Travail), July 19 and August 26, 2004 relative to the fire which took place on June 26, 2004,

✓ working meeting of September 2, 2004 of agents in charge of monitoring pressure equipment and the Classified Installations Inspectorate; this meeting was a follow-up to the meeting held July 8, 2004,

✓ working meeting and visitation of the furnace and neighbouring equipment on September 23, 2004 by agents in charge of monitoring pressurised equipment and the Classified Installations Inspectorate following documents submitted by the operator September 8 and 14, 2004.

In order to identify the causes of this accident and to implement the provisions required for safe restart of the HDS unit, the operator was issued a prefectorial order on June 30, 2004, outlining emergency measures proposed by the DRIRE.

Analysis of failures and causes:

The examination of event chronology (recordings of alarms, sensors, valve movements, etc.), the description of possible precursors and the list of special operations performed during the day were presented.

The following points were determined:

✓ the analysis of the HDS unit's operating parameters showed no derivation of the process parameters prior to the accident and no pre-incident indicators,

✓ no malfunction of the control and safety PLCs (independent systems) was reported.

An internal multi-disciplinary task force conducted the failure and cause analysis. An individual skilled in the fault tree method, and not concerned by the management of the accident in question conducted the work session.

Equipment:

✓ Checks and inspections were conducted on the equipment of the reaction loop downline from the furnace (reactor 42R202, exchangers 42E201 and 42E202A/B) which underwent rapid decompression when the furnace tube ruptured although normal operation calls for the application of a very progressive depressurisation procedure. For this reason, the cladded internal lining (covered by an internal skin of welded strips) or stainless steel liner may have underwent a separation phenomenon (disbonding by hydrogen). No anomaly of this type was recorded.

✓ The chimney, from which flames were seen exiting for several minutes, was subjected to thermographic inspections, visual inspections of the chimney cap with a telescope and verticality checks. It appears that the condition of the concrete structure and its internal lining (refractory bricks) are satisfactory and in compliance with construction specifications.

✓ 34 lines were inspected:

- × the pipes in zones 5 and 6, mainly the furnace's combustible supply lines and utilities, were replaced or removed (to make room for a new furnace operating on gas fuel only),

- × The furnace loading and transfer lines located in zone 5, as well as the set of pipes on the East rack and at ground level were not metallurgically affected by the accident owing to their heat lagging, The refurbishing work consisted in replacing the threaded fasteners, seals, lagging and their protective sheeting, and the spring supports,

✓ All electrical wiring and measurement channels were refurbished, and damaged equipment was replaced,

✓ All valves and pumps were overhauled,

✓ The water curtains of furnaces 42F201 and 42F501 were completely rebuilt,

✓ The gas detectors were checked and replaced as required,

✓ Considering the extent of the damage to the furnace, the decision was made to completely rebuild it, including the associated civil works structures (concrete support posts, first section of the flue). The furnace was rebuilt nearly identically, although the following improvements were made:

- × 6 burners were installed instead of 4 for better distribution of the heat flux,

- × installation of a remote burning ignition device,

- × installation of temperature sensors on the skin of tubes on two heights in the radiation part, as well as on the lower layer of the convection part, in order to monitor any abnormal increase in temperature that may be due to coke deposits accumulating inside,

- × the installation of additional inspection ports.

Inspection plan:

The furnace inspection plan was reviewed in order to consider the first lessons learned form the expert assessment and includes additional inspections, made possible by a new design:

✓ On the convection part:

- replicas and X-ray inspection of convection tubes once per cycle,
- during the next major shutdown in 2007 (after 25,000 hours of operation): thickness measurements of lower level tubes and 20% of the peripheral tubes, geometric calibration of tubes (search for creep), X-ray inspection (search for internal corrosion and the presence of coke),
- continuous monitoring of tube skin temperature.

✓ On the radiation part:

- thickness inspection on 20% of tubes and elbows during each annual shutdown (reactor catalyst change),
- on the occasion of the next major shutdown in 2007: thickness measurements of tubes and elbows, geometric calibration of tubes (search for creep), metallographic replicas on tubes at two different heights (search for sensitisation of the stainless steel),
- continuous monitoring of tube skin temperature on two heights.

The inspections and periodic requalifications include the verification of safety accessories and the requalification of a hydraulic test.

Passivation procedure:

An internal task force was created to re-examine the passivation procedure and equipment likely to be concerned. The conclusions drawn at this point were as follows:

- A procedure was drawn up in compliance with recognised trade standards,
- A few modifications were made to this procedure (including the use of a surface agent in the preparation of the carbonate solution, the addition of the pH test of the water during passivation and a decrease in the carbonate concentration from 5 to 2%).

Feedback on other equipment or other units:

The Feyzin site does not have other desulfuration furnaces exhibiting this type of corrosion.

According to the operator, polythionic acid attacks can also occur on the catalytic reformer, as well as in the HDT2 (hydrotreatment) unit where passivation cannot take place considering the geometric stresses involved. The DRIRE nevertheless requested that the operator conduct more extensive investigations on these units in order to search for any evidence of this corrosion phenomenon.

The examination of the accidentology involving these refinery furnaces (in the ARIA database established by the BARPI) revealed no other similar accident.

LESSONS LEARNED

The accident reminds us of the importance of certain problems such as detection, intervention (Internal Contingency Plan), external communication and the limits of the installations' inspection plan.

Detection and intervention:

As there was no fire detection on the HDS unit, the presence of personnel working on a neighbouring unit allowed the alarm to be raised rapidly and to operate the unit's decompression and cooling systems in the next 5 minutes.

This favourable situation cannot obscure the crucial importance of rapid detection of an accident of this type, conditioning the intervention delays of the personnel and the time required to implement the Internal Contingency Plan.

Also, faced with the drop in personnel in the immediate proximity of the installations for obvious security reasons (an ongoing construction program for new control rooms away from the units), the detection of accidental events within production units (fire, gas detection, …) and the visual and audio monitoring of installations, without detriment to the monitoring of operating parameters.

A think tank was created in order to clarify Internal Contingency Plan implementation methods. The event of June 26, 2004 gave rise to questions concerning the formal implementation of the Internal Contingency Plan.

Questions could be raised concerning whether or not the number of people assigned to operate the production units is adequate with those required to intervene in case of an accidental situation. This aspect reveals particular importance for the periods where the workforce is reduced.

Considering the human consequences of the fire on June 26, 2004, the decision was made, at the request of the CHSCT, to finish off the slab floor of the HDS unit. It would be desirable to apply this measure to the rest of the platform.

Inspection plan:

The rupture on the tube that caused the fire was the result of certain degradation modes (coke deposit, polythionic acid corrosion) that were unidentified when the inspection plan was drawn up using the Group's RBeye software. An upgrade of this tool appears necessary as a result in order to integrate the aforementioned degradation modes and to consider the age of the equipment in the criticality calculation.

Furthermore, the degradations of the tubes can also be determined during a hydraulic resistance test provided that the equipment is pushed beyond its service loading. If the initial resistance testing meets this concern for the furnace rebuilt completely, according to the provisions of the Order of December 13, 1999, it must be proven that this condition is also fulfilled for similar older equipment.

In order to verify the pertinence of these measures, it may be of interest to compare the inspection plans of such units currently in operation in French refineries.

External communication:

In the crisis management phase, the assessments provided by the operator about the extent of the accident and its consequences were considered insufficient by external organisations (including the Feyzin Town Hall, Police, Public Emergency Services, Sport Infrastructure Superintendent, etc.).

The operator felt that the decisions taken by the Authorities regarding the nature of the accidental phenomenon were disproportionate. In terms of communication, a press conference was held June 26, 2004 by the site director, the day of the accident, at 6.30 pm, nearly 2 hours after the start of the fire.

These differences in appreciation ware studied a posteriori during a debriefing meeting at the Rhône Préfecture, in which the following points were made:

✓ the organisation of crisis management must be improved between the Feyzin Town Hall, law enforcement agencies and the refinery,

✓ for the operator, the notion of an "event visible from the outside" must be formalised in the site's alert procedures, including systematic and rapid information provided to the authorities, including the absence of the implementation of an Internal Contingency Plan.