Explosion in a sulphuric acid tank

26th November 2005

Pierre-Bénite [Rhône]

France

Chemistry
Hydrogen
Corrosion iron / acid
Corrosion by pitting
Heat exchanger
Anti legionellosis treatment
Organization / modifications

THE INSTALLATIONS CONCERNED

The site :

The plant, classified high level Seveso (AS), synthesises some forty substances principally derived from sulphuric, hydrochloric and hydrofluroric acids produced on the site.

The installation concerned

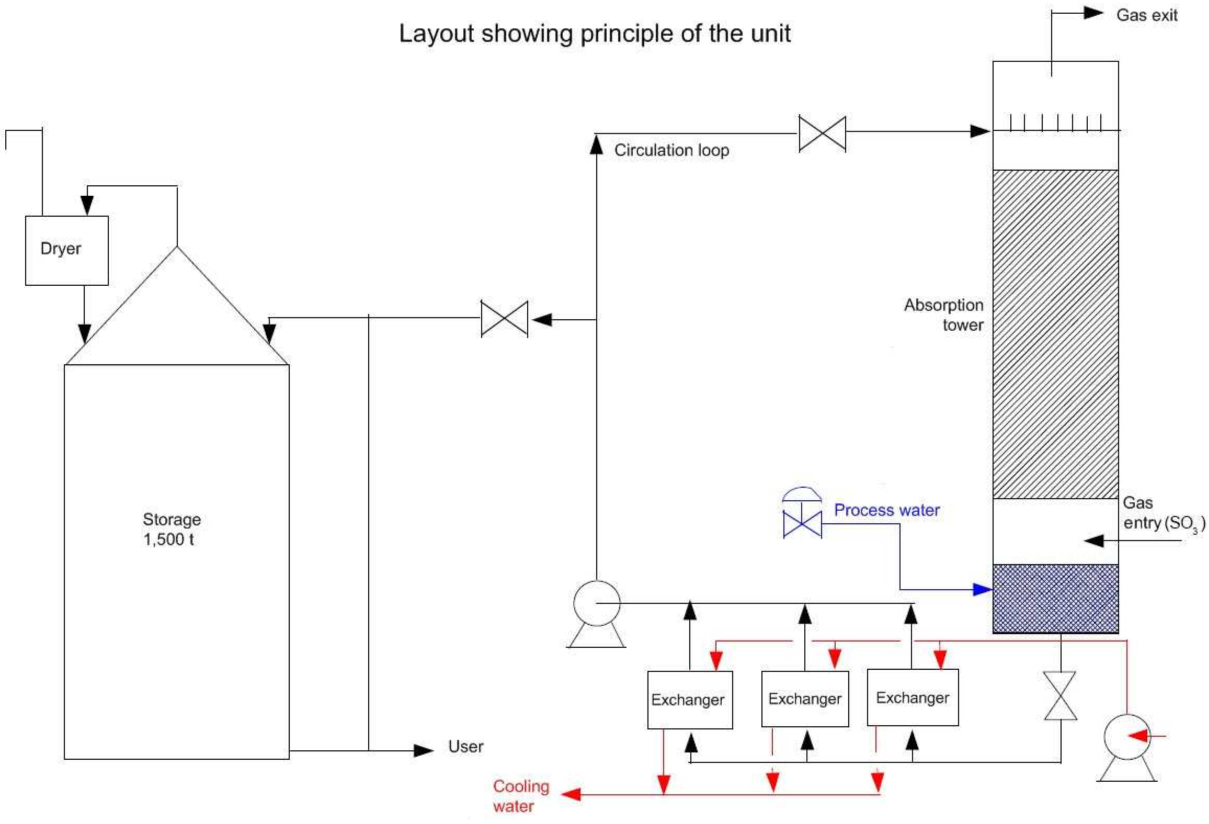
The “sulphuric acid” unit produces 99.2 % acid by absorption of SO_3 in two columns. The SO_3 itself is obtained by catalytic oxidation of SO_2 produced by the combustion of sulphur (contact process).

For each column, the heat generation from the absorption reaction is compensated by a cooling system known as the “circulating loop” using spiral heat exchangers fed by the cooling water circuit.

The sulphuric acid is evacuated by regulation of the level of the column towards storage tanks by pipes piercing the circulating loop.

Several tanks with a capacity of 1,500 t each allow for the storage of the 99.2 % acid produced. They are fed via access points on the conically shaped dome from the production lines. They also have, at the bottom of the tank, a decantation pipe and a recirculation pipe as well as a vent high up on the dome to allow ventilation of the gas phases via a collector and an acid dryer.

Layout showing principle of the unit



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

The accident

Since 21/10,the sulphuric acid unit had been halted, the acid stocks were at full capacity level.

On 22/11, the restarting of the installations was interrupted during the preparatory phase, following a leak in the water/acid heat exchanger of the 1st absorption column. This leak, detected by the rising temperature on the coil and on the acid exit pipes, required the replacement of the exchanger, which was completed on 24/11.

Replacement of the exchanger
Source : exploitant

On the morning of 25/11, the analysis of the acid strength on the 1st column showed an abnormally low level at the base of the column (84.3 %). Believing that this was a consequence of the previous incident, the operator corrected the anomaly by the addition of oleum to the column and decantation of acid to the storage tanks to maintain a constant level in the column. Progressive increases in strength were observed: 84.3 %, 88 % then 91.3 %.

On 26/11 at midnight, the strength of 55 % analysed on the coil of the 1st tower indicates an infiltration of water into the installation. The sample taken was of a greenish colour, indicating the corrosion of equipment. A second heat exchanger had already sprung a leak on the previous day without this having been detected on account of the addition of the oleum. The water/acid and oleum/acid were both in effect heat generating.

At 1 a.m., restrictions were applied to undertake further checks ; the water entry valves were closed as well as the return valve to the column of the circulating loop in order to favour the flow to the storage tank.

At 2, a leak appeared on the flange of the circulation pump.

At 4:30, the leak became more serious ; the viscosity of the product alerted the personnel who conducted tests with litmus paper, this indicated that the substance released was neutral. The pump for transmission to the storage tank was halted.

At 5:30, following the raise of the level in the 1st tower, this was emptied into the neutralisation trench. The halting of the cooling water pump caused the rise in level to cease.

At 10:30, the storage tank contents were stirred to allow for a measurement of the acid strength and a decision as to the measures to be taken.

At 11, the acid strength at the base of the tank was measured at 89 % with a temperature 27 ℃.

At 11:30,the strength reached 88 % with a temperature of 27℃.

At 11:43, an explosion was heard on the site : the dome of the storage tank was partly opened around the circumference (ring die-dome). Only a few fumeroles were observed on the right of the opening on the dome.

At 11:45, The POI (emergency plan) of the establishment was put into effect ; the security personnel marked out the zone. No release or leakage of product was observed. The units using the 99.2 % acid were halted to avoid movement of the tank (the open venting pipes could allow the entry of humidity), the bottom valves of the tank were closed. During the afternoon, plastic sheeting was used to cover the venting pipes and the tank was slowly emptied into the neutralisation trench.

The dome of the storage tank is partly opened around the circumference.
Source : exploitant

The consequences :

Deformed gangway
Source : exploitant

No consequences were observed for the personnel nor the environment.

Equipment above the tank was deformed or broken (acid entry piping from the factory, pipe towards the dryer from the other storage tanks, gangway, vapour pipe…).

European scale of industrial accidents

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

Parameters composing these indices and corresponding methods of calculation can be found at the following address:: http://www.aria.ecologie.gouv.fr

Following analyses of material damage to the installations, the operator estimated that a quantity of several dozen grams of hydrogen were at the origin of the explosion, which corresponds to less than 0.02 % of the Seveso threshold for substances describes as "highly inflammable" (50 t) ; the index "dangerous materials released" on the European scaleis therefore 1 (parameter Q1).

The absence of precise information on the economic consequences of the accident prevents us from knowing the level corresponding to the European scale.

ORIGIN, CAUSES AND CIRCONSTANCES OF THE ACCIDENT

Origin of the explosion :

Material damage observed correspond to those resulting from a low powered explosion, which could be due:

- to a hydrogen (H_2) explosion linked to corrosion of steel by diluted acid resulting from the mixture of sulphuric acid and water,
- to a massive generation of water vapour linked to the heat generation from the water/acid mixture when the agitation in the tank was initiated.

This latter hypothesis was rapidly set aside on account of the temperatures measured at the base of the tank (27°C) and on the surface of the liquid (66°C) a few minutes b efore the accident.

The formation of a small quantity of hydrogen (of the order of several dozen grams) - a gas which requires very little energy for ignition, was the probable cause of the explosion. In the absence of movement in the reservoir between 4:30 and 10:30, a zone of high concentration of H_2 (10 % at a minimum) could develop in the tank; its ignition (which requires very little energy, of the order of a few mJ) could result in an electrostatic phenomenon when the agitation process was initiated.

The primary cause of the accident was therefore the production of diluted acid which corroded the steel interior of the tank while forming hydrogen.

Origin of the dilution of the acid :

The water supply not being suspect, the analysis of the causes of the accident was directed at the internal water tightness of the heat exchangers which equipped the circulating loop of the 1st tower.

Observations on site and analyses conducted on the metallurgical slices of the exchangers provided evidence of a phenomenon of corrosion by pitting (observation of pits of 3mm in depth) initiated on the “water cooling” side, around welds and on the maintenance covers of the metallic envelope (zone where the material is heavily strain hardened).

The sudden rapid corrosion which caused the piercing of the exchangers followed a flow of water onto the acid side, the heat generation of the reaction accelerating considerably the phenomenon (speed of several dozen mm/year).

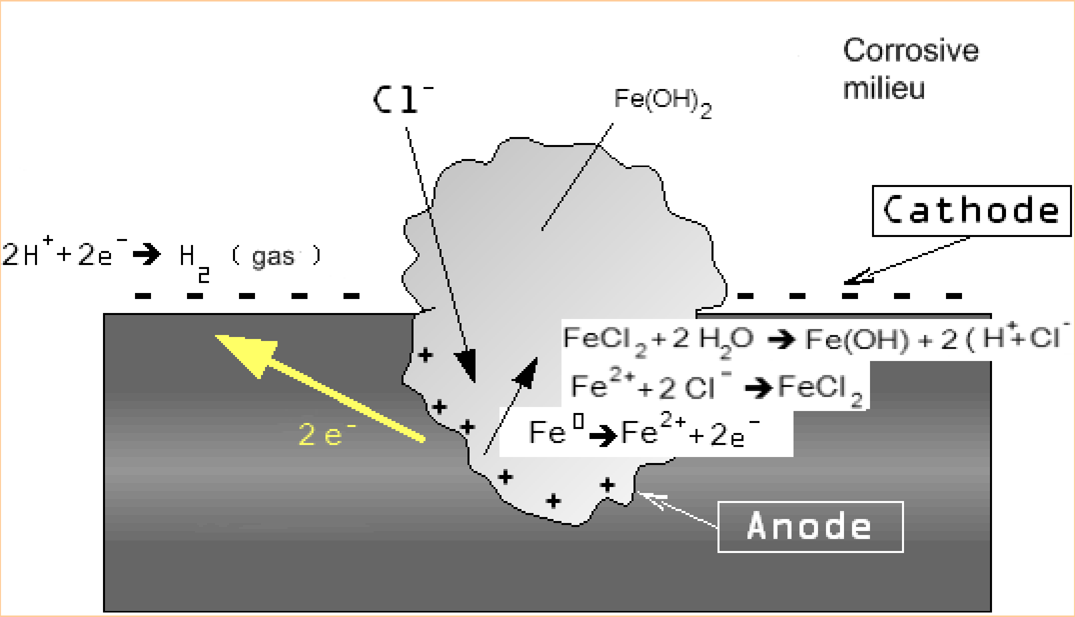
The dilute acid formed on the contact with the cooling water was highly corrosive on the 316L stainless steel of which the unit was constructed.

Origin of the pitting corrosion :

This corrosion having never been observed on this type of exchanger, in service for 25 years on the site, the accident can only be attributed to recent changes in the operating conditions.

In fact, the usual anti-legionellosis treatment (biocide following a bromide base) was replaced by a continuous treatment with sodium hypochlorite. This must be overdosed to ensure its effectiveness as a long-term biocide taking into account also the pH over 8 of cooling water, considerably increasing the oxidising power of the latter. Moreover, the lowering of the speed of the flow of water following the reining in of the exchangers associated with the operation at a low regime in the factory for a long period, caused an increase in the temperature of the water which amplified the phenomenon: increasing the oxidising potential of the milieu and lowering the temperature required for the pitting (between 15 and 30℃ for a chlorine content 500 mg/L for the most s ensitive zones such as those affected by strain hardening or those affected thermally at the level of the welds).

The pitting observed being almost exclusively on one side of the welds (the closest fo the passage of sulphuric acid and thus the warmest) this pitting began during normal operation of the exchangers.



Stainless steels are particularly sensitive to corrosion by pitting in the presence of aqueous solutions charged with chlorine, bromine or particularly hydrochloric ions.. At the level of germination, a link is established between unconnected zones which constitute small anodes where the metal is dissolved, and the rest of the surface where a cathode reaction is produced as shown (example with chlorine ions).

THE STEPS TAKEN

Several Measures were taken to avoid further incidents of this kind..

→ Modification of the anti-legionellosis treatment of the cooling water

The treatment of the water with Javel was replaced by a non-oxidising biocide treatment associated with an increase in the doses of a bio-dispersant until the entry into service of new heat exchangers.

A continuous treatment with a mixture of chlorine/bromine gave the advantage of being effective in a basic milieu and not therefore needing strong concentrations is under study.

→ Improvement of the detection of abnormalities in the water at arrival in the procedure

An alarm linked temperature sensor is placed on the acid exit from each exchanger..

Two titrimeters having a wide measurement range (55 % à 100 %) were installed in each absorption column.

→ Procedure for storage of acid

The flow of weak acid into the reservoirs was prevented by:

- installation of procedures and reflex actions on the handling of high temperature alarms and the handling of abnormally low concentrations.
- Information of the personnel concerning the new practices.

THE LESSONS LEARNED

The initial cause of the accident which occurred at Pierre-Bénite lies in the modification of the operating conditions of the unit (anti-legionellosis treatment) almost a year beforehand. All modifications of procedure, even minimal or on ancillary equipment or procedures can thus have an impact on the security of installations in the short or longer term. It is thus essential that all effects should be subject to profound study, that a follow up covering these modifications should be included in the documentation covering the unit (plans, operating, security and maintenance checking procedures…) and that the personnel be trained accordingly.

On a more technical plane, the accident reminds us that iron, like most common metals (zinc, aluminium) are attacked by dilute acids involving the emission of hydrogen, as shows the following reaction:

$$Fe + 2H^+ \leftrightarrow Fe^{2+} + H_2$$

Taking into account the extreme flammability of hydrogen on account of its very wide field of flammability (from 4% to 75% in air) and the very low amount of energy required for ignition (0.02 mJ as against 0.29 mJ for methane), the risk of a hydrogen explosion exists as soon as acid corrosion of metal of any scale is observed. In certain cases, the flow of liquid against a surface (friction) or a slight jolt can suffice to ignite the hydrogen

A locally high concentration of hydrogen (above 4 % in air), for example in a dead zone or at the upper level of a volume, can thus create a risk, as illustrated by the explosion of hydrogen during work undertaken on reservoirs in which no prior measurements of explosiveness had allowed for the detection of the presence of hydrogen (ARIA n°169).