VCE in a waste treatment tank of a pharmaceutical plant

10 June 2010

Brindisi (Apulia)

Italy

Explosive atmosphere
Modifications
Hot work
Fermentation
Risk analysis

THE FACILITIES INVOLVED

The site:

The plant, covering about 150.000 m², is located in Southern Italy in an industrial area situated in a natural port on the Adriatic coast (Figure 1).

It has been operating since 1966 and produces pharmaceutical intermediates and active principles for antibiotics through chemical and biological processes. It falls under Seveso II Directive (lower tier plant).

Fig. 1: Aerial view of the facility (source: Google maps)

The involved unit:

The waste treatment unit (Figure 2) is part of the principle O antibiotic production process, which is composed of the steps below:

- production of active principle B through inoculation of specific microorganisms into the fermentation broth;
- oxidation of principle B into principle O (end product) by reaction with sodium persulphate;
- stripping of principle O by solvent: the oxidized broth is mixed with chloroform and sodium lauryl sulphate, in order to separate the product (top layer) from the aqueous phase (bottom layer). The latter, which is the waste

from stripping, is called BES. The stripped product goes on with the process, whereas the BES is sent to the solvent recovery unit for further stripping to eliminate chloroform and residual solvent traces, and then to the TKX in the waste treatment unit;

- concentration and crystallization of principle O in alcoholic environment;
- centrifugation of principle O;
- drying and packaging of principle O powder products.

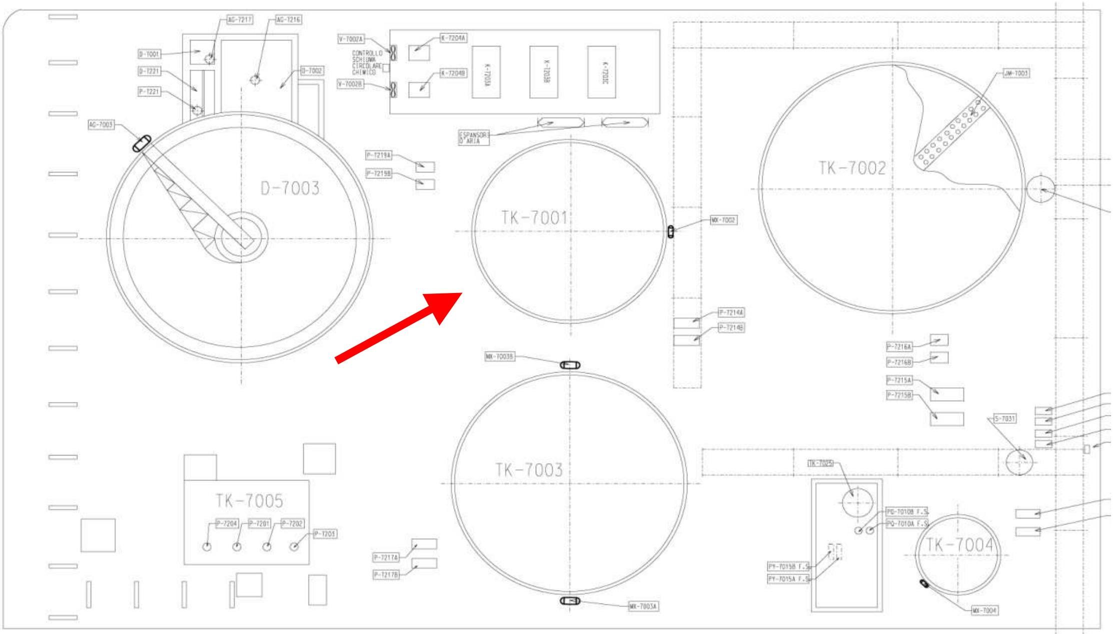

Fig. 2: Waste treatment unit layout (source: operator)

The equipment at the origin of the accident:

The accident occurred in a fixed-roof cylindrical atmospheric tank (TKX), with a capacity of 320 m³, 7.62 m of diameter and 7.9 m of height. It was equipped with an internal helical lateral mixer, in radial position, and with a 20 cm-diameter vent installed at the centre of on the roof of the tank.

The TKX, located in the waste treatment unit of the principle O production process, was used to homogenize the BES for its storage. The BES, with high organic amount and a COD (chemical oxygen demand) of 80 g/l, was sent to the TKX from the stripping unit at a flow-rate of about 2-3 m³/h. The maximum design-filling of the TKX was 50% of its capacity. During its 2 to 3-day stay inside the TKX, the BES was shaken by the internal helical lateral mixer and mixed with a caustic soda solution at 30% in order to maintain a fixed pH (around 8-8.5).

After homogenisation and equalization in the TKX, the BES was transferred to a bioreactor (TKY) for the stabilization treatment: a biological pre-treatment to reduce COD by almost 70% before sending the BES to a lagoon.

In its original design, the TKX was equipped with an internal system to insert and spread the air and an external system to suck air out. These systems, not operative at the moment of the accident, should have been active during normal TKX operation (Figure 3), planned as follows:

1. introduction of air into the internal liquid mass (BES) through the sparger system at the bottom of the tank;
2. extraction of air and gas formed through a sucking system, located on the roof and connected to the vent.

In March 2000, during revamping of the TKX, the air system was considered as “additional” with respect to the internal helical lateral mixer, and “responsible” for causing bad smell and foam. As a consequence, it was locked off.

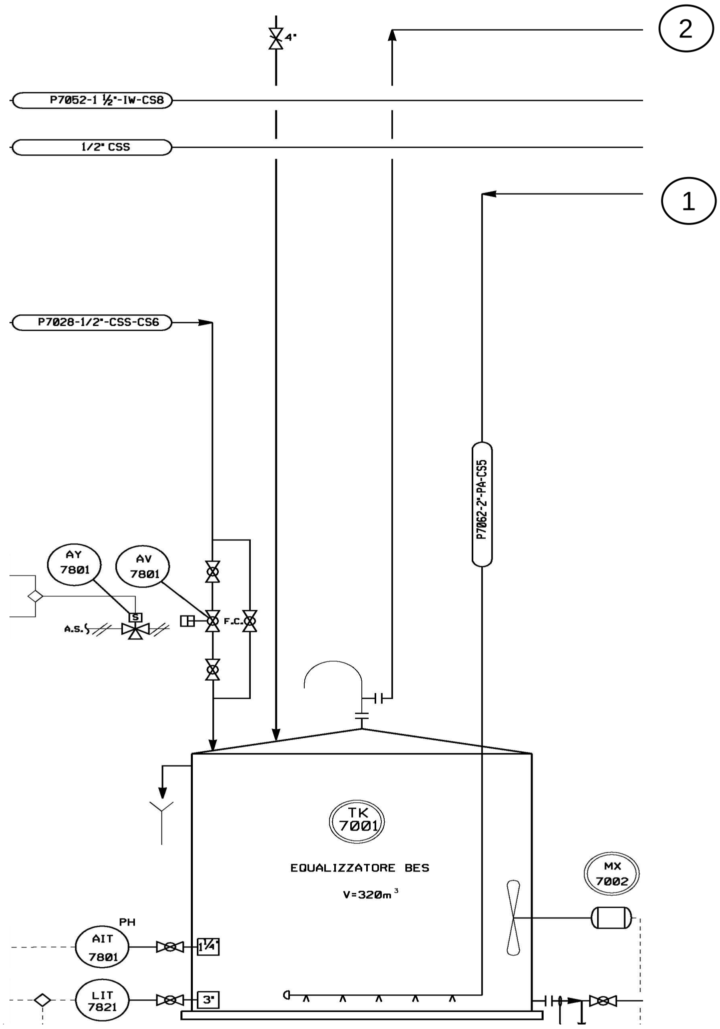

Fig. 3: Normal TKX operation principle (source: operator)

THE ACCIDENT, ITS CHRONOLOGY, EFFECTS AND CONSEQUENCES

The accident:

On 10 June 2010, a Vapour Cloud Explosion (VCE) occurred in the TKX containing BES during hot works on the tank feed line. The tank roof and debris were thrown far away.

The aim of the operation was to add a second feed line to the TKX (Figure 4). Coming from the fermentation unit, it should have allowed the delivery into the TKX of the waste broth from a new antibiotic production unit. The existing feed line had been cleared up and disconnected from the tank, without closing (blind flange) the tank or the line. The tank was half filled with BES.

The maintenance works were carried out by one employee of the operator and four contractors. One of the contractors started to cut the line with an electric disk cutter generating sparkles. These ignited the explosion of an explosive atmosphere inside the tank, probably due to a fermentation reaction still going on in the BES.

The facility was immediately put in emergency. Four wounded workers were transferred to the nearest hospital, the fifth was found dead by the firemen.

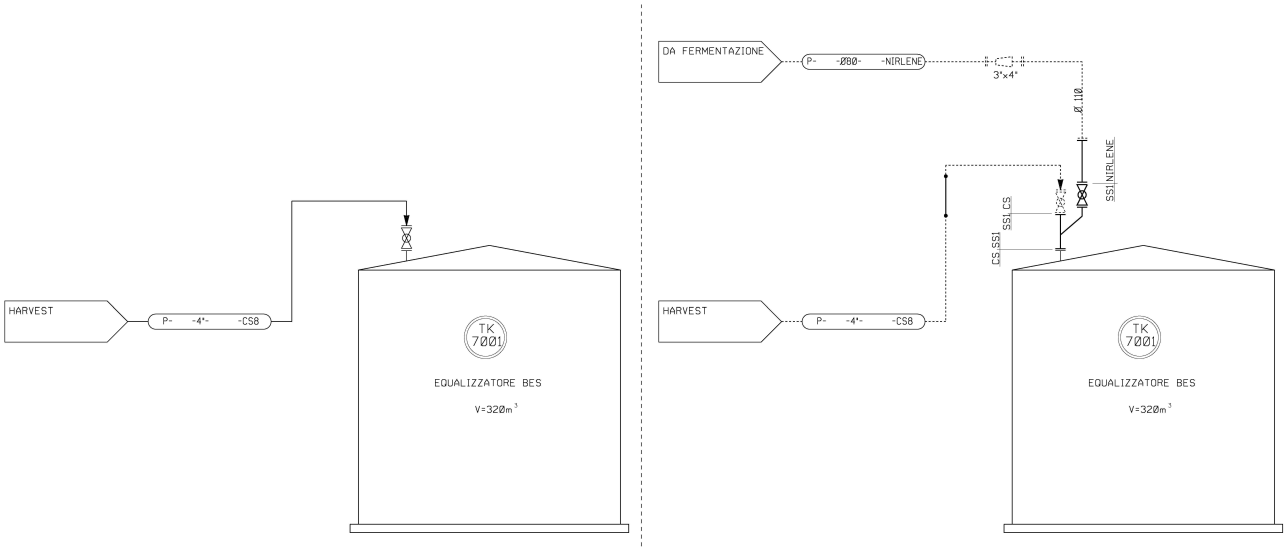

Fig. 4: (Left) Existing TKX; (Right) modification project at right (source: operator)

The consequences of the accident:

Human consequences

Five workers were present when the explosion occurred: four contractors and an employee of the operator. One contractor standing on the roof was holding the line to be cut, the others workers were on the walkway leading to the tank (Figure 5).

When the explosion occurred, the roof was torn out along the circular welding line (Figures 5 to 7) and thrown at a distance of 20 m, pulling up the air sparger line (Figures 8 and 9). The contractor on the roof was thrown on the roof of the TKY and died.

The four operators were injured by tank and roof debris, seriously burned by the explosion and thrown on the closest tank walls and to the ground by the wave pressure. Promptly helped by the internal assistance, the three contractors and the employee had respectively 40, 166, 198 and 120 days of sick leave.

Material consequences

According to a preliminary evaluation made by the operator, the accident generated a € 2.6 million loss:

- € 1.8 million of equipment, structure and production losses;
- € 0.8 millions for response and restoration of the establishment.

The accident can be called 'major' according to the Seveso II Directive as both human and material consequences exceed the threshold values indicated in Annex VI.

Fig. 5: Pulled-off sparger line on the TKX viewed from the walkway (source: ARPA Puglia)

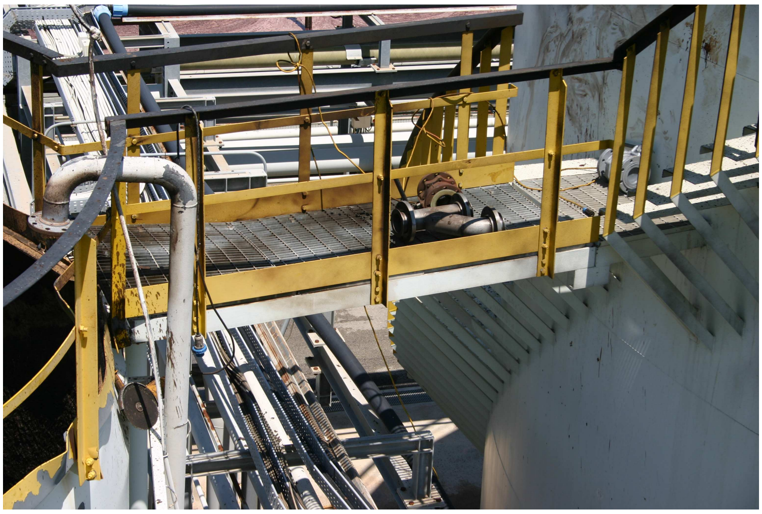

Fig. 6: Walkway between TKX and TKY (source: ARPA Puglia)

Fig. 7: Exploded TKX (source: ARPA Puglia)

Fig. 8: Projected roof at the foot of the TKX (source: ARPA Puglia)

Fig. 9: Exploded roof, note the absence of plain flange on the air line (source: ARPA Puglia)

The European scale of industrial accidents:

By applying the rating rules applicable to the 18 parameters of the scale officially adopted in February 1994 by the Member States' Competent authority Committee for implementing the '*SEVESO II*' directive on handling hazardous substances, and in light of the information available, this accident can be characterised by the four following indices:

Dangerous materials released	■	□	□	□	□	□
Human and social consequences	■	■	□	□	□	□
Environmental consequences	□	□	□	□	□	□
Economic consequences	■	■	□	□	□	□

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

The index on quantities of dangerous substances released is set to 1: some exploding gases were present even if the quantities could not be precisely estimated (parameter Q1 – quantity of substance released).

The death and injury toll of the accident led to a grade 2 for human and social consequences (parameters: H3 – number of deaths, H4 – number of severely wounded people).

The economic consequences set the index at 2 with €1.8 M property and production losses inside the site.

THE ORIGIN, CAUSES AND CIRCUMSTANCES SURROUNDING THE ACCIDENT

The main suspected direct causes of the accident are the presence of undesired explosive atmosphere inside the TKX (probably produced by anaerobic fermentation of BES) and the irrelevant maintenance works organization.

The substances involved:

The equipment at the origin of the accident (TKX) was not expected to contain dangerous substances. In order to understand the situation before the accident, the operator carried out a specific analysis on the components present inside the tank to ascertain what could have led to the production of an explosive atmosphere.

Liquid phase: the composition of BES before the accident (conform to normal operating condition) was determined through the analysis of samples collected in April and May 2010 and analysed by a specialized laboratory. It contained 93% of water and 7% of mycelium and organic remains of microorganisms (high COD 80g/l), traces of chemicals used during process (metals, chlorides, sulphates, sodium persulphate, ammonial nitrogen, flammable solvents) and solids. Some flammable solvents were found: isopropanol (500 – 1000 ppm), ethanol (about 500 ppm), acetone (< 100 ppm), tetrahydrofurane (1.5%), ethyl acetate (< 0.5 ppm), methanol (about 300 ppm). Chloroform was detected in the range of 500-600 ppm. The amount of all the solvents present in the liquid phase could not generate enough flammable vapour could in the TKX to reach the lower explosive limit (LEL).

During the investigation of the root causes of the accident conducted by the operator, additional tests have been carried out to analyse the BES composition at the moment of the accident. Samples collected immediately after the explosion showed a flammable solvent quantity below 700 ppm, and a chloroform concentration below 0.2% in the liquid phase. According to these results as well, not enough flammable vapour could have been generated from the liquid phase to reach the LEL. Same results were obtained from BES samples collected 10 days after the accident.

Gas-vapour phase: after the accident, BES samples were collected from the bottom of the tank. After an anaerobic fermentation in sealed ampoules, a gas-chromatography identification of gases formed was done. A high pressure had developed inside the ampoules, and some of them exploded due to overpressure after three weeks (Figure 10). The gas analysis confirmed the presence of traces of methane (CH_4), hydrogen (H_2), methanethiol (CH_3SH) and flammable sulphides compounds, probably formed from the solid phase accumulated at the bottom of the tank in the absence of aeration system.

Ion chromatography of liquid phase carried out by the operator the day of the accident showed the presence of sulphates, phosphates and thiosulphates with other anions. Persulphate is normally used in the oxidation process to transform principle B into principle O. Not all the product is converted in sulphates. The oxidation could have continued inside the TKX with organic harvest and possibly formed organic sulphates, carbonyl sulphide (COS), carbon disulphide (CS_2) and other organic sulphur derivatives responsible for the foul-smelling bubbles observed inside the water. The same was also detected on the liquid phase inside the tank after the accident.

Solid phase: the analysis carried out by the operator on gas produced by the solid phase or paste residues collected in December 2010 from several parts of the tank (bottom and lateral sides, Figures 11 and 12), revealed the presence of carbon disulphide, carbonyl sulphide, tetrahydrofurane (THF), dichloromethane (CH_2Cl_2), chloroform ($CHCl_3$) and other residual solvents present in the production processes.

In particular, different techniques showed that flammable solvents based on sulphides like CS_2 and COS were present in the solid phase. Both compounds show high flammability with a flash point (FP) below room temperature:

- CS_2 is a low boiling point (46℃) solvent, has a FP of - 30℃, wide explosive limits range of 1.3 – 50% v/v, and a very low auto ignition temperature (90℃). Moreover, this compound has very low water solubility (2.9 g/l) and its vapour is denser than air.
- Carbonyl sulphide (COS) is a nasty-smell gas with a FP below - 30℃. The boiling point is about -50℃ and the vapour density at room temperature is higher than air. It remains in the bottom part of the tank above the liquid phase. It is a stable compound in anaerobic ambient, and is oxidized in sulphide moieties in presence of air.

Both these two compounds can be obtained by anaerobic fermentation: e.g. methanococcus maripaludis, methanothermobacter marburgensis, thiobacillus thioparus strains. Several references in literature show the role of these strains in the degradation of volatile organic sulphur compounds (carbon disulphide, methanethiol, dimethyl sulphide, dimethyl disulphide). Unfortunately, the presence of these microorganisms could not be checked as most of them are degraded in aerobic environment.

As a conclusion, the main substances responsible of the TKX explosion were the whole mix of flammable compounds generated by anaerobic fermentation in the solid and liquid phases which moved to the gas-vapour phase and stratified according to their density: hydrogen and methane (lighter than air) in the upper part close to the roof, sulphide gas compounds remaining just above the liquid level.

The exact amount of the gas mix compounds involved is difficult to estimate. The only available data is the tank free volume, completely filled by the gas mix: about 170 m³.

The dangerous compounds of the flammable mix are listed below:

	CAS	Risk classification
Hydrogen	1333-74-0	R12
Methane	74-82-8	R12
Carbon Disulphide	75-15-0	R11, R-36/38-48/23-62-63
Methanethiol	74-93-1	R12, R20, R50/53
Carbonyl Sulphide	463-58-1	R12, R23

The presence of the dangerous substances above, not expected by the operator because not normally processed or present, was also made possible by the presence of identified dangerous substances (persulphates).

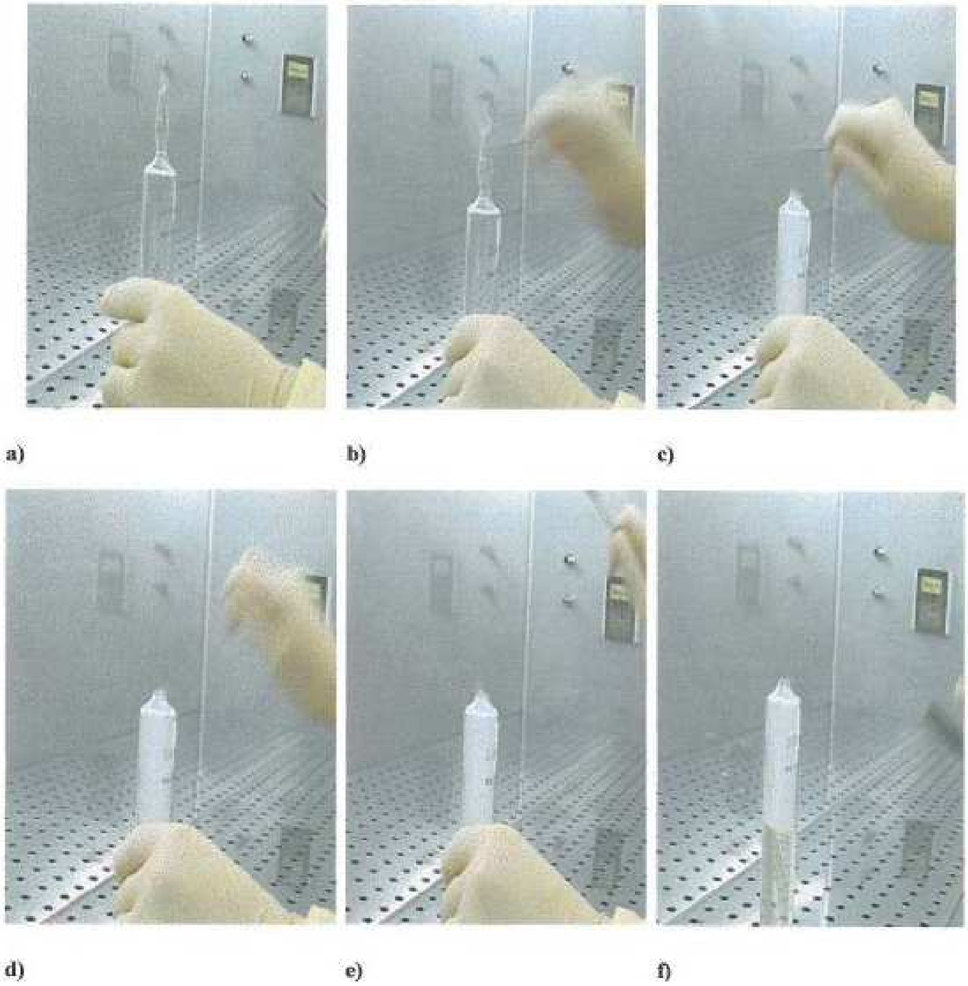

Fig. 10: Gas overpressure after anaerobic fermentation in sealed BES samples ampoules (source: ARPA Puglia)

Fig. 11: TKX after emptying in December 2000 - solid residues collected from the bottom (source: operator)

Fig. 12: Solid / paste residues collected from the exit nozzle (source: operator)

Direct causes:

Considering the analysis results mentioned above and the investigation results available in July 2012, the direct causes identified for the accident are:

A. An explosive atmosphere was present inside the TKX, which was ignited by the sparks generated while cutting the feed pipeline by the electrical cutter. The feed line had been cleaned up and disconnected from the tank without closing them with blind flanges, and leaving the nozzle on the tank opened (Figures 6 and 9).

B. The explosive atmosphere was produced by the fermentation of BES still going on inside the TKX in anaerobic condition. Different types of bacteria hard to identify are involved.

C. BES anaerobic fermentation was caused by the accumulation and permanence of mud and organic residual paste for a long time inside the tank (bottom, sides) due to:

a. high organic content in BES: COD 80 g/l;

b. temperature of TKX (40-50°C) favourable to bacteria fermentation according to analysis and research conducted by the Regional Environmental Agency ARPA Puglia (Agenzia Regionale per la Prevenzione e la Protezione dell'Ambiente) and data from scientific literature on the anaerobic fermentation process;

c. absence of oxygenation: the internal systems for air spreading and sucking should have been active during normal TKX operation according to the initial tank design. The air spreading system had been locked off after revamping of the tank (in 2000) because it was considered redundant with respect to the internal helical lateral mixer and “responsible” for causing bad smell and foam and for disturbing the stability condition of the BES (otherwise guaranteed by the basic pH, presence of residual chloroform and limited time of permanence inside the tank);

d. inadequate mixing and homogenisation of the BES: only the lateral helical mixer was active, without the strong support of the air system mentioned in point c. The helical mixer was too small to provide an adequate mixing for the whole liquid mass, which could have prevented the solid phase accumulation at the bottom and on the walls;

e. long stay (2-3 days) of the BES inside the tank, which facilitated the fermentation. The positioning of the exit nozzle 40 cm above the tank bottom allowed the accumulation of up to 40 cm of solid phase.

Chemical analysis of liquid and solid phases, carried out by the operator, confirmed the production of methane (CH_4), hydrogen (H_2), methanethiol (CH_3SH), carbonyl sulphide (COS), carbon disulphide (CS_2) and other flammable sulphide compounds generated by the anaerobic fermentation. These substances could have been some of the explosive mix compounds inside the tank.

Root causes:

Beyond the direct causes mentioned above, root causes (underlined in the text below) can be identified and analysed according to the issues addressed in the Seveso II Directive SMS (see in Annex the SMS check-list in use in Italy):

A. Explosive atmosphere inside the tank ignited during hot work[1]:

a. The contact between the sparks generated while cutting the feed pipeline and the explosive atmosphere was made possible by the absence of mechanical closing of the tank with blind flanges. This should have been done before the maintenance operation, according to the work permit procedure of the operator that required indicating:

i. on a general permit, the type of work, the possible hazardous situations and the risks they generate;

ii. on a specific permit, all the safety measures to implement for the type of work to be done, in relation with the risks identified on the general permit.

Both operator and contractor signed the work permit without filling the parts related to risks and safety measures to be adopted for the hot work. In particular, the use of an electrical cutter, the absence of explosiveness test and closing of the tank showed that the zone was not considered as an ATEX area: risk assessment fault; personnel training fault.

b. An interview of the chief of contractor-workers by the firemen showed a confuse understanding of the work permit procedure by the contractors and the employee involved, as well as insufficient know-how of the mechanical closing of equipment. Moreover, a SMS inspection by the Regional Environmental Agency pointed out that the process of maintenance works authorization, delivered by the Direction/SMS responsible to the contractor, was not clearly described: personnel training fault; maintenance procedure fault.

It should be underlined that the application of a proper work permit procedure alone could have avoided the accident, regardless of all other SMS faults.

B. Explosive atmosphere was produced by the anaerobic fermentation process of BES inside the TKX:

a. BES, supposed to be an exhausted waste from the microorganism fermentation process (only containing water and dead organic mycelium), was not considered dangerous by the operator: dangerous substances identification fault.

b. The possibility of anaerobic fermentation during BES treatment inside the TKX was not identified in the risk assessment phase. No detailed analysis (like HAZOP) of the tank was performed: dangerous process identification fault.

c. The waste treatment unit was not classified as ATEX area during risk assessment, due to the reasons mentioned above. In addition, risk assessment was not correctly updated after the revamping of the plant in 2000, during which the internal air system was wrongly locked off: risk assessment fault and management of change fault.

C. The accumulation and permanence of mud and organic residual paste for a long time inside the tank (bottom, sides) made the BES anaerobic fermentation possible:

The locking (during 10 years after revamping of the tank) of the internal system for air spreading and aspiration resulted in the absence of internal oxygenation and inadequate mixing and homogenizing of the BES (essential to avoid undesired anaerobic fermentation). This was an infringement of the plant safety requirements from the original tank design: fault in following the safety requirements and management of change fault.

ACTIONS TAKEN

Emergency measures:

The internal emergency plan was immediately activated; the internal team provided first aid for the four injured operators, and transferred them to the nearest hospital. The plant was shut down and put in safe condition.

External fire brigades arrived 15 minutes after the accident, found the dead worker on the roof of the TKY and checked the safety of the area using an ATEX detector. The fire brigades were not called by the operator, but by people from outside the plant who heard the explosion.

The emergency situation was cleared within 4 hours. Local authorities arrived together with the judicial authority, which closed and sealed the whole area.

[1] Hot work is any work that can create a source of ignition of flammable material, or a direct fire hazard even if no flammable material is present: welding, soldering, metal cutting, brazing, grinding, drilling, etc.

Other actions taken in the aftermath:

A detailed investigation was carried out by the judicial authority, supported by the Regional Environmental Agency and technical experts. In July 2012, 15 persons were charged (among which the supervisor and the safety responsible of the plant).

The SMS inspection by the Regional Environmental Agency pointed out enough serious SMS faults to order the interruption of operations on part of the plant for 15 days.

The operator assisted by a consultant produced a detailed accident analysis, which provided the conclusions mentioned above. The operator then drew up a safety plan containing all the internal management and technical additional safety measures to implement in order to seriously improve their implementation of the SMS.

LESSONS LEARNT

The analysis puts in evidence several SMS faults in:

- **Identification of possible accidental events, safety analysis and residual risk**: the risk assessment did not identify all ATEX areas inside the establishment, as expected from the operator. The classification, size and location of a particular zone depend on the probability of an explosive atmosphere to appear and its persistence if so. The classification needs to take into account not only the present hazardous substances, but also the possible unwanted formation of other dangerous substances.
- **Personnel training**: the work permit procedure was not adequately applied during the maintenance operation and work permits forms were not correctly filled by both contractor and operator. In particular, the safety measures required for 'hot' maintenance operations, such as the closing of openings, were not adopted.
- **Operational control and maintenance procedures:** the written procedure was unclear and not easily understandable by the staff, particularly as concerns the delivery of authorization to the contractor by the Direction/SMS responsible, as noted above.

Biotechnology is a field in fast expansion where processes similar to that involved in this accident are used to obtain different products. A proper risk assessment should be conducted to take into account all substances that can be produced.

ANNEX: ELEMENTS OF SMS SEVESO INSPECTORS CHECK-LIST

1. The document on prevention policy

1.i Definition of prevention policy

1.ii Verification of the SMS structure and its integration with the establishment organization

1.iii Policy Document Contents

2. Organization and personnel

2.i Definition of responsibilities, resources and planning of activities

2.ii Information activity

2.iii Training and formation activities

2.iv Human factors, operator/plant interfaces

3. Evaluation and identification of major hazards

3.i Identification of substances and processes hazards; definition of safety requirements and criteria.

3.ii Identification of possible accidental events, safety analysis and residual risk

3.iii Planning and updating of technical and/or managerial solutions for the reduction of risks

4. Operational control
4.i Identification of plants and equipment to be subject to inspection plans
4.ii Process documentation
4.iii Operating procedures and instructions in normal, abnormal and emergency conditions
4.iv Maintenance procedures
4.v Materials and services procurement

5. Management of change
5.i Technical and organizational plant modifications
5.ii Documentation updating

6. Emergency planning
6.i Accident analysis, planning and documentation
6.ii Roles and responsibilities
6.iii Controls and verifications of the management of emergency situations
6.iv Alarm and communication systems and support to the external intervention

7. Monitoring performance
7.ii Performance evaluation
7.ii Accident and near-accident analysis

8. Audit and review
8.i Safety audits
8.ii Review of safety policy and of Safety Management System.

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