Explosions in a pharmaceutical plant

13/08/2003 and 09/08/2004

Linz

Austria

Explosion
Glyoxylic acid
Peroxide
Ozone
Design / conception
Heat insulators
Domino effect

THE FACILITIES INVOLVED

The site:

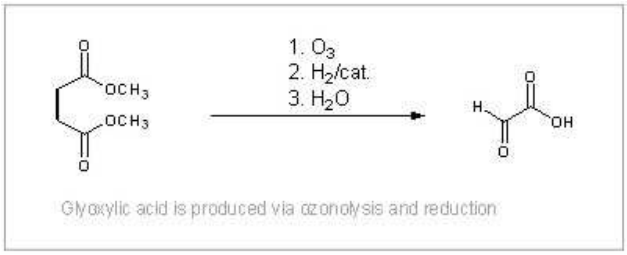
The plant is located in a chemical park in the city of Linz, where about 30 chemical companies are concentrated in order to develop synergy effects in their exploitations, such as easing the exchanges of products, energy etc.

The plant produces chemicals and intermediate products for the pharmaceutical industry ; it is classified as top tier Seveso.

The involved unit:

The unit where the accident took place includes two ozonolysis columns that produce glyoxylic acid from dimethyl maleate, methanol and ozone/oxygen in various steps.

The process involved in the accident uses ozone at –20°C and 1,7 bars. According to the operator, this process allows producing a higher quality product, thus making it a top-selling product for the company.



Source : operator's website

13/08/2003 : THE ACCIDENT, ITS CHRONOLOGY, EFFECTS AND CONSEQUENCES

The accident:

At 10h44, 2 columns and 2 tanks exploded in the glyoxylic acid unit during a ozonolysis reaction.

This unit contains 2 tanks and 2 columns through which the reaction mix is pumped and put in contact with an O2/O3 mixture.

The upper part of the columns are blasted, one column is ripped on 2/3rd of its height. The 2 tanks are completely destroyed and their filling (mainly methanol) caught fire. A fireball with a diameter of 80 m is formed over the installations.

Firemen from the industrial park and the city arrived on site within a few minutes. The intervention allows the fire not spread to other installations.

Consequences of the accident:

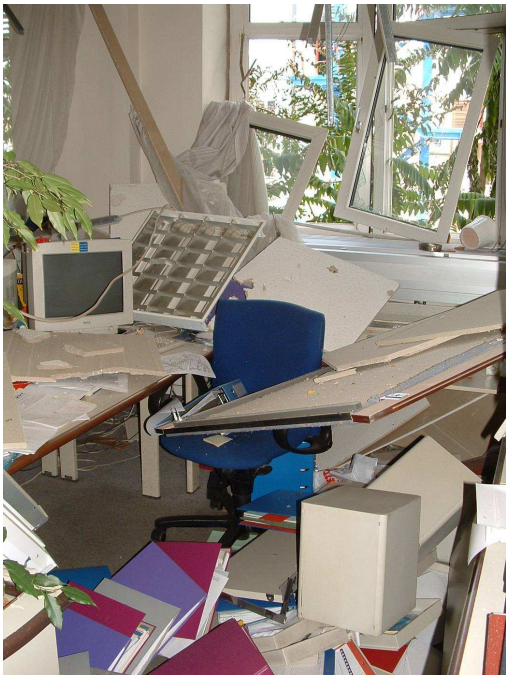
20 workers from the industrial park got injured ; they suffered from burns, bone fractures or bruises due to broken glass.

The part of the installation where the ozonolysis reaction took place (1/4 of the installation) is destroyed. Material damage are significant within a 150 m radius perimeter, mostly due to projections and broken glass. Offices are destroyed in buildings closed to the explosion.

All reactions involving ozone are stopped on the industrial park until the causes of the accident are known.

No environmental damage has been observed outside the chemical site. Most of the chemicals (mainly methanol) burned.

Experts from the company and from the municipality (?) are sent to the site to look for explanations on the causes of the accident.



Office at 40 m from the explosion

Workshop at 60 m from the explosion

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:

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

The "dangerous materials released" parameter equals 1, the released quantity being unknown and the distance at which windows have been broken being less than 300 m.

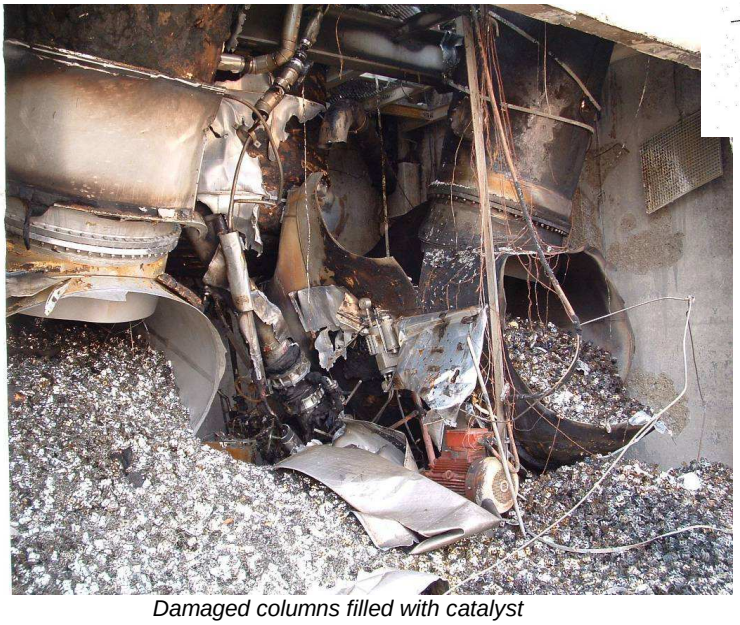
20 people got injured, among which 2 stayed over 24h in hospital: the global Human and social consequences parameter equals 3.

No environmental damages have been observed (level 0).

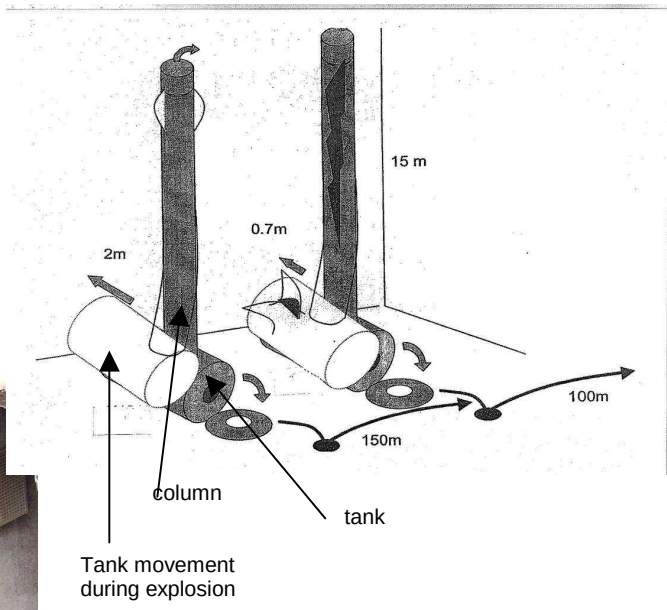
The economic consequences parameter reaches 4 : the company suffered one-year production losses of about 20 million euros.

THE ORIGIN, CAUSES AND CIRCUMSTANCES SURROUNDING THE ACCIDENT

The analysis concluded that a leakage (most probably leak on a flange) in a pipe released methanol / peroxide into the insulation material of the column, made of polyurethane.
Due to long-lasting high summer temperatures, the methanol (solvent) evaporated, concentrating the peroxide, which then self-ignited and decomposed.
The rise in temperature was strengthened upon contact with the rusty grid that maintained the insulation material on the column (accelerating the decomposition reaction because of metallic ions of the grid?).
The decomposition of the peroxide started the fire, which then spread and caused the explosion of the first column followed by the explosion of the second column (domino effect).



Damaged columns filled with catalyst



Tank movement during explosion

ACTIONS TAKEN

Following the accident, the company kept the process unchanged but installed the ozonolysis columns in a separate cold box at -20°C in a separate building with video control. The columns are not isolated anymore, but a leakage indicator system is installed. The reactors are built to resist an explosion and a pressure relief valve is added, as well as additional safety measures such as pressure and temperature measurements.

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09/08/2004 : THE ACCIDENT, ITS CHRONOLOGY, EFFECTS AND CONSEQUENCES

The accident:

Despite the improvements in the process following the above-described accident, two explosions occurred on the same installation at 03:30 a.m. almost one year after, during the re-start of the process.

Consequences of the accident:

The explosions destroyed the devices in the cold box entirely. There was a big crack in the wall. No one got injured and no building got damaged, but a few broken glasses in the surroundings.

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:

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

The "dangerous materials released" parameter equals 1, the quantity of the dangerous materials being unknown and the effects of the explosion being less than 300 m.

No one got injured : the global Human and social consequences parameter equals 0.

No environmental damage have been observed (level 0).

The economic consequences parameter reaches 5 : the company had to re-design the plant and suffered production losses of about 50 million euros.

THE ORIGIN, CAUSES AND CIRCUMSTANCES SURROUNDING THE ACCIDENT

The analysis showed that the safety concept was implemented correctly (design, planning, construction). No explosion trigger was found.

Two hypothesis of the explosions are either the creation and accumulation of foam that ignited upon local heating or hot spots (hot or catalytic particles) or the synthesis of unusual peroxides with following decomposition and ignition.

Other root causes are possible. Any future design would have to be challenged against all the possible scenarios. As a comparison, other ozonolysis users operate their systems at a lower oxygen concentration and mostly with air. Some of them use less or no flammable solvents in addition.

ACTIONS TAKEN

The company involved more than 50 experts from different countries and spend about € 400.000 for the analysis. The company modified the process to implement a reaction with air and inert gas instead of ozone.
The local government closed all ozonolysis plants with flammable dilution except for laboratories, until the causes of the accident are clarified.

The destroyed "cold box"

LESSONS LEARNT

The process was neither safe enough nor well controlled. Did the process go through a full safety analysis with identification of physico-chemical and toxicological characteristics of the substances, study of the reaction's criticity, possible secondary reactions, safe operational conditions etc. ?

One positive point is that the safety concept which was implemented after the first explosion was correct. The redesign of the reactor (cold box, leakage indicator system and advanced explosion proof reactor) allowed avoiding any injury during the 2004 explosion.

These accidents also raise the concern of chemical reactions involving (huge) quantities of flammable solvents. The risk of leakage and consequent ignition with important consequences is indeed relatively high and needs to be carefully

studied. The question of domino effects should also be mentioned: were they effectively taken into account during the design of facilities?

This accident raises more generally the question of re-starting units after an accident, while root causes are not clearly identified. The re-start has been decided with additional prevention and protection means (“cold box”, pressure-proof reactor and safety devices). These measures allowed avoiding any injury but were yet insufficient to prevent the second accident from occurring.