Explosion in a carboxymethyl cellulose production plant 11th July 2009 NIJMEGEN – [Gelderland] The Netherlands

Explosion Ethanol ATEX Directive 1999/92/EC Degraded mode of operation Human factor / operating procedures Risk analysis Management of change

THE FACILITIES INVOLVED

The site:

The company was part of a worldwide organisation with several plants in Finland and China. The site concerning in this case was located in the city of Nijmegen at the bank of the river Waal. This site was licensed to have 50 tons Monochloracetic acid (MCA), a toxic component which makes it a lower tier SEVESO site.



Carboxymethyl cellulose (CMC) is a cellulose derivative with carboxymethyl groups (-CH₂-COOH) bound to some of the hydroxyl groups of the glucopyranose monomers that make up the cellulose backbone. It is often used as a sodium salt, sodium carboxymethyl cellulose.

CMC (food additive E466) is used in food science as a viscosity modifier or thickener, and to stabilize emulsions in various products including ice cream.

CMC has a high viscosity and is non-toxic and non-allergenic. These properties made it widely-used in many non-food products, such as lubricant, toothpaste, laxatives, diet pills, water-based paints, detergents, textile sizing and paper products. In Nijmegen this company produced carboxymethyl cellulose (CMC) in two separated production lines. The production was housed in a building which was founded in 1928 for the production of synthetic yarns.

After the production of synthetic yarns was delocalised to low-wage countries in 1969, the production of carboxymethyl cellulose for various applications started in this building in 1970.

The demand for CMC increased and in 1998 the old building was modified to house two separated production lines, one for the production of technical CMC and one for pharmaceutical CMC. Each line consisted of a reactor followed by two in line slurry tanks, a vacuum belt filter a grinding mill, a dryer and CMC powder storage tanks.

The production section is marked in red on the picture; the other buildings were used for the office labour and storage.

The production units have walls with a 60 minutes fire protection, sprinklers and LEL detection.

65 emloyees are working on site in several different shifts, with 25 employees in the factory during daytime. The involved unit operates in a continuous flow mode (24 hours a day and 7 days a week) and is permanetly controlled by a team of 2 persons also during weekends.



After one synthesis in the reactor, the CMC slurry is stored in a 15m³ tank. This slurry, so-called "Technical CMC", is a mixture of approximately 60% CMC and 40% salts (sodium chloride and sodium glycolate) and can be directly used, e.g. in detergents. A further purification process is necessary to remove the salts to produce pure CMC which is used for food, pharmaceutical and toothpaste applications. This purification process is carried out on a vacuum belt filter using a 65 %vol ethanol solution.



The involved unit:

The involved unit is a vacuum belt filter type RT (Reciprocating Tray). A continuously moving filter cloth is supported inside a rigid, profiled movable vacuum tray, providing the vacuum area of the filter. The bottom of the tray is an open grid structure. The cloth is driven via a head pulley.

The slurry is distributed on the cloth at one end and the liquid from the slurry is removed via the vacuum tray in a first vacuum step.



Slurry Ethanol solution Moving filter Head pulley Vacuum tray

Counter current cake washing (Picture Larox Pannevis R.R.)

In a second step called "counter current washing", the CMC cake is wet with a 65 % ethanol solution which is then sucked through the CMC cake in the vacuum step.

After three steps of counter-current washing, the cake is dried by a steam injection that removes the ethanol solution from the CMC-cake.



Generic illustration of a RT vacuum belt filter (Picture Larox Pannevis R.R.)



View of the filter inside the enclosure



Outside view of the steel plated enclosure

In 1999, the CMC demand was high and the production capacity needed to be doubled. Two new vacuum belt filters were installed in the old factory. No safety facilities such as Explosion Release Control (ERC) equipments were present or installed in the old building.

Good practice is to use a GT (Gas Tight) type vacuum belt filter when a solvent is used during the purifying process. However, due to the experience of this company (difficulty for maintenance, adjusting the belt) and the costs involved (GT Type 3 times more expensive than RT type)) the company decided to buy two RT Types vacuum belt filters and build the enclosure on their own behalf.

Since possible ignition sources were present in the enclosure, the prevention of an explosion entirely rested on upon the prevention of an explosive atmosphere. A nitrogen purge unit was used to prevent an explosive atmosphere in the enclosure.



GT type (Picture Larox Pannevis R.R.)

Around 2003, a chemical expert from this company stated that the nitrogen purge was not necessary. He claimed that the ethanol vapour was presumed to be at its saturation point and therefore above the upper explosion limit (UEL). The drops on inside of the window screen of the enclosure were supposed to indicate the presence of saturated vapour of ethanol inside the enclosure. From this point on, continuously nitrogen purge was no longer applied.

In 2005, the operator wrote a new procedure for operating the vacuum belt filter. In this procedure the nitrogen purge was only applied after opening and closing the doors of the enclosure. Furthermore, the nitrogen purge should not excess 2 hours.

To comply with the ATEX regulation, an explosion protection document was prepared by an external expert. This document showed that the maximum oxygen concentration in the enclosure should not excess 10 %vol O_2 . The inerting system inside the enclosure of the vacuum belt filter should be maintained with a continuously purge of nitrogen. In

practice however, no nitrogen purge was applied other than two hours during start-up after an open enclosure as described in the procedure.

No other measures like overpressure, minimum flow supply or automatic shut-down, for preventing explosion of an explosive atmosphere (according to NPR-CEN/TR 15281) were implemented. Although an oxygen meter in the control room showed an oxygen percentage between 18 %vol and 20 %vol during process, the management of the company did not react.

Finally, because of a rise in prices and taxes on ethanol, the company implemented a close follow-up of the quantities of ethanol used (to avoid spills and ethanol vapour losses...). To reduce the loss of ethanol vapour, a cooling system was installed in the enclosure, which cooled the vapour to 24 °C. At this temperature, the potential losses of ethanol were reduced and well monitored, but the volumetric concentration of ethanol consequently came closer to the stoichiometric volumetric concentration at which the vapour explosion force is the greatest).

THE ACCIDENT, ITS CHRONOLOGY, EFFECTS AND CONSEQUENCES

The accident:

At 6.45 am on that Saturday morning, the vacuum belt filter was automatically stopped because of an emergency shutdown in the CMC dryer installation. It seemed that a large peace of CMC-cake blocked a cell-lock.

This shutdown lasted for 9 hours, as maintenance had to be called in to the factory. The cell-lock had to be dismantled and repaired before installing back into the dryer line.

The remaining CMC-cake on the filter belt was unusable and had to be removed from the filter. In order to do so, a trap door was opened in the closed transport screw that conveyed the CMC cake to the mill and dryer unit. By slowly running the filter belt, the cake was removed from the belt and the cake-breaker and put into waste bags. The opening was then closed and the vacuum belt filter was re-started at 4.00 pm. No nitrogen purge was applied because the door of the enclosure itself, containing the filter and the cake breaker, was never directly opened.

At about 4.15 pm, the supervisor opened the slurry valve in order to continue the production process. Immediately after opening the valve an explosion occurred and destroyed the enclosure and surrounding compartments of the factory and set fire to the building. The stored CMC in the expedition part of the factory smouldered for 38 hours.

Consequences of the accident:

The explosion heavily injured one employee who was working in a compartment just beside the enclosure; he deceased later that evening.

Despite important fire-fighting efforts, the fire of the building lasted for 38 hours, producing a thick dark cloud of smoke over the city of Nijmegen. The authorities decided to recommend residents within 3 km of the plant to close doors and windows.

The installation and building where destroyed and the insurance calculated a damage of € 50 millions.

The company closed its facility in Nijmegen and transferred its CMC production to China, 65 employees were laid off.

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: <u>http://www.aria.developpement-durable.gouv.fr</u>



The quantity of ethanol in the enclosure was about 300 liters ; the amount of ethanol vapor in the enclosure was about 100 m³. The energy of the explosion caused by 100 m³ ethanol is about 350 Mj, that is \approx 70 Kg TNT equivalent. Thus, the dangerous materials released parameter reaches 1.

The human and social consequences index reaches 2 since one employee died.

Property damage and production losses was estimated to 50 million Euros. Cleaning and dismantling the building for investigation cost 1.5 million Euros, thus amounting to level 4 on the scale of economic consequences.

Despite atmospheric pollution by the fire, no harmful environmental consequences were reported; the environmental consequences index is not rated.

THE ORIGIN, CAUSES AND CIRCUMSTANCES SURROUNDING THE ACCIDENT

The explosion was the result of an ignition source associated with an explosive atmosphere in the enclosure of the vacuum belt filter:

- The ignition source is not precisely known, as the explosion completely destroyed the vacuum belt filter and surrounding enclosure, but several plausible sources were present: moving items, electrical components and a mechanical cake-breaker inside the enclosure as well as electric lights, pumps and engines outside the enclosure.
- The explosive atmosphere was present due to the presence of ethanol and air. Indeed, fresh air was brought into the enclosure via the opening of the trap door of the transport screw, which leaded to an oxygen (O₂) concentration of 20 %vol.

300 litres of liquid ethanol were present in the enclosure for washing the CMC-cake. The volume of the enclosure was about 100 m^3 , filled with air and ethanol vapour. The concentration of ethanol vapour depends on the temperature in the enclosure. The temperature was not monitored but estimated between 24 degrees (temperature of the cooling system) and 35 degrees Celsius (temperature of the ethanol liquid).

Depending on the temperature, the volumetric concentration of ethanol had to be between 5 vol% and 15 vol%.

The stoichiometric volumetric concentration of ethanol is 5.8 vol%. At this concentration, the lowest ignition energy can cause a vapour explosion which is at its maximum force.

Ethanol: C₂H₅OH

Flash Point: 16.6 ℃ Auto ignition temp: 363 ℃ Explosion Limit: 3.3 - 19.0 vol% Vapor Pressure: 59.3 mmHg Boiling point: 78 ℃ Molecular Weight: 46.04 g/mol

Considering the operating procedures and other circumstances described page 3, it was just a matter of time before an accident happened: the company had worked years along with a time bomb...

ACTIONS TAKEN

Short after the accident, a security perimeter of 500 m was set up and significant human and equipment resources were put in action including one hundred firemen, twenty-five vehicles and a fireboat to attack the fire from the river. The fire lasted 38 hours.



Fire fighting operations (picture: De Gelderlander R.R)

Administrative and penal actions:

The investigation resulted in a legal procedure to determine the responsibility of the players involved in the accident. The date for court sessions are planned mid-2012.

Technical actions:

Because the plant and production was not rebuilt, no technical actions were taken. However the Labour inspectorate stopped the same type of CMC production using a vacuum belt filter at a plant 25 km from Nijmegen. This company was forced to take several actions before starting up their vacuum belt filter, which included:

- a new explosion prevention document
- a study of all possible ignition sources,
- measurements to prevent ignition, for instance installing a spring lockwasher under every nut.
- establishing several LEL meters.

This company also made a study of new ways of purifying CMC cake and will replace in 2012 their vacuum belt filters by Rotary Pressure Filters (RPF). A RPF is a compact installation with less space (smaller risk of explosion hazards) and with all moving equipment (possible ignition sources) outside the installation.



LESSONS LEARNT

- Changes in production conditions or operating procedures can generate dangerous situations in the long run. Such changes must be reviewed and a risk analysis should be carried out to ensure the process is safely run.
- Identification and evaluation of explosive atmospheres and associated potential ignition sources are very important to be able to implement safety measures to prevent explosions.
- One has to be careful with data provided by experts in safety reports.
- The force of a solvent vapour explosion is often insufficient recognised.

For controlling the risk of an explosive atmosphere by inerting, the Guidance on inerting for the prevention of explosions NPR-CEN/TR 15281 must be fully applied. This means more than one oxygen analyser divided over the enclosure, awareness of temperature pressure and humidity and monitoring and controlling system to shutdown immediately when Oxygen rises up to MAOC (Maximum allowable oxygen concentration).

TECHNICAL REPORT RAPPORT TECHNIQUE TECHNISCHER BERICHT

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Atmosphères explosibles - Guide de l'inertage pour la prévention des explosions

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