Seveso accident: release of dioxins into the atmosphere in a chemical plant

10 July 1976

Meda – [Lombardy]

Italy

Trichlorophenol
Thermal runaway
Rupture disc
Chloracne
Crisis
Fear
Decontamination

FACILITIES INVOLVED

Site

The plant, located in Meda at 20 km north of Milan (Lombardy, Italy), is owned by an international chemical group that manufactures perfumes and pharmaceutical products.

The B department of the plant manufactures 2,4,5-trichlorophenol (TCP) which is subsequently transported to another site of the group to produce herbicides and antiseptics.

The TCP production unit includes three 10,000 litre reactors and various platforms, columns, condensers, pumps, etc. spread out over an area of 230 m².

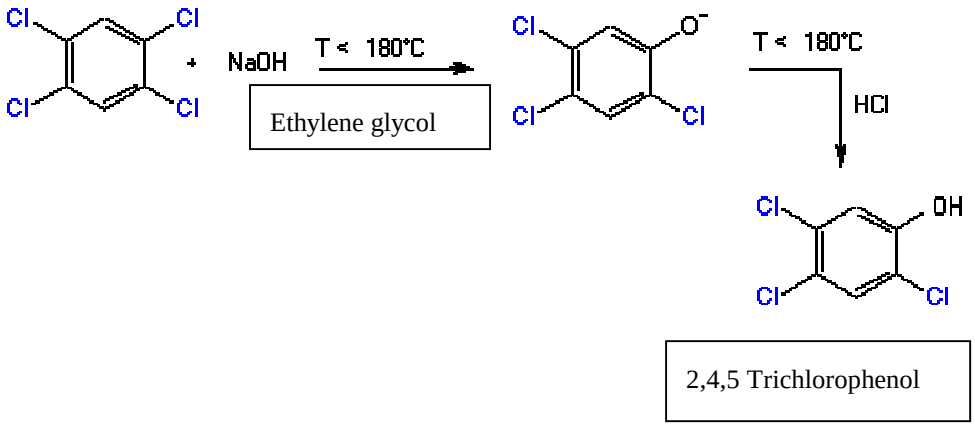
Manufacturing process:

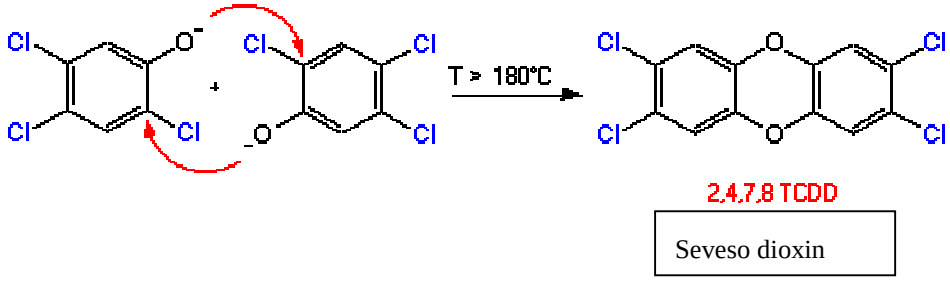
TCP is obtained from the hydrolysis of 1,2,4,5-tetrachlorobenzene (1,2,4,5 TCB) at atmospheric pressure and at temperatures between 140 to 170°C. Ethylene glycol is used as a solvent while xylene forms the azeotropic mixture with the water produced during the reaction.

After hydrolysis, the solvent is distilled and the mixture is diluted with water and acidified using hydrochloric acid.

The end product is then washed with water purified by vacuum distillation.

The by-product of the reaction, 2,3,7,8-tetrachlorodibenzodioxin (TCDD), can be produced in significant quantities under high temperature conditions.





The Meda plant uses a discontinuous total batch process where 10 m^3 reactors are fed with the following products at the start of the operation:

- solid sodium hydroxide: 1,050 kg
- 1,2,4,5 TCB: 2,000 kg
- ethylene glycol: 3,300 kg
- xylene: 600 kg

Step 1:

The reagents and solvents are fed into the reactor that is agitated and equipped with a condenser to eliminate the water in the condensate and feed back xylene into the reactor. In the quantities fed in, the NaOH / 1,2,4,5 TCB molar ratio is 2.7, i.e. an excess of 0.7 sodium hydroxide equivalent than 1,2,4,5 TCB.

The choice of solvent seemed appropriate. Sodium hydroxide is in fact soluble in glycol, while the reagent and the product are soluble in xylene. Moreover, xylene eliminates water by azeotropic distillation. This promotes the alkaline hydrolysis reaction of 1,2,4,5 TCB and help achieving nearly a 100% conversion rate.

The initial reaction mixture was heated at 170 °C using steam at 12 bar whose saturation temperature is 180 °C. This mixture was maintained at 170 °C for 6 to 8 hours where as the water + xylene azeotrope was distilled to eliminate water as and when it was produced during the reaction. The entire xylene and 1,650 kg of glycol were then vacuum distilled to recover clean solvents that can be used during the subsequent synthesis. At the end of this stage, 3,000 l of water was added to the reaction medium to bring the temperature down to 50 - 60 °C.

The production stage 1 lasted 11 to 14 hours:

- feeding: 1 h
- reaction : 6 to 8 h
- distillation of mixture: 3 to 4 h
- addition of water: 15 min

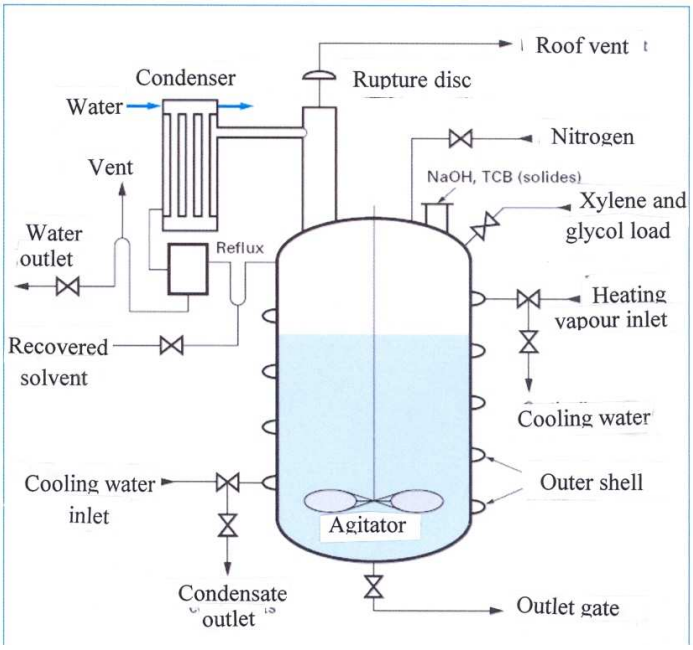
Step 2:

The contents of the reactor were hydrolysed with an aqueous solution of hydrochloric acid to release the trichlorophenol from sodium trichlorophenate.

The reactors, made of the Cr-Mo-Ni alloy, can either be heated using steam or cooled with water. There are various safety systems in place:

- The reactors were heated using steam at 12 bar (saturation temperature at 180°C). The reactors are thus never heated beyond 180 °C. Secondly, a quick switch over to the cooling mode promptly compensates for any possible temperature rise.
- An oversized cooler ensure efficient cooling.
- A 3,000 litre reserve of water is available to flood the contents of the reactor if necessary.
- A rupture disc whose tare pressure is set at 3.8 bar protects the reactor during the first phase of the operation, and during the last phase when the mixture is transferred under compressed air.

However, the reactor is not equipped with a temperature alarm and cooling can only be started manually.



Seveso process. Reactor diagram (d'après Gustin, 2002 ; Marshall, 1987)

THE ACCIDENT, ITS CHRONOLOGY AND CONSEQUENCES

The accident:

On Friday 9 July 1976, the 1,2,4,5 TCP production cycle started at 4.00 pm, i.e. ten hours late than usually.

On Saturday morning at 5.00 am, the reactor heater was stopped when only 15% of the solvent was distilled. The stirring process was stopped 15 min later and the reactor was brought to atmospheric pressure The technicians signed off at 6.00 am leaving the reactor unsupervised during the weekend. At 12.30, i.e. six and a half hours later, the safety disc of the reactor whose tare pressure is set 3.8 bar ruptured following in increase in temperature and pressure in the reactor. A reddish cloud was released into the atmosphere through the chimney of the building and rose several meters above ground.

The gas emissions containing dioxin (2,3,7,8 tetrachlorodibenzodioxine (TCDD)) lasted about 1 h. The prompt action taken by the workshop supervisor who happened to be close to the plant during the accident helped reduce the duration of emission.

According to various studies, 0.2 to 40 kg of dioxin was estimated to have been released into the atmosphere.

The consequences:

The height of the cloud and the direction of the blowing wind (4 m/s) steered the toxic cloud to the southwest of the plant impacting a chiefly farming area.

The initial effects of the accident were observed on the following day: some children showing symptoms of intestinal problems and high fever, burnt vegetation, and small animals affected. The plant managers informed the authorities that "a herbicide cloud of likely to damage crops" was released into the atmosphere.

The inhabitants of the neighbouring areas of the plant were warned two days after the accident to not consume anything from their garden.

Four days after the accident, the first symptoms of burns appeared on the skins children and small animals died.

Six days after, 15 children were hospitalised including four in serious condition. The doctors were unaware of the course of treatment to be followed. A general strike was called by the distressed inhabitants who pressurised the authorities for increased transparency with regard to the accident.

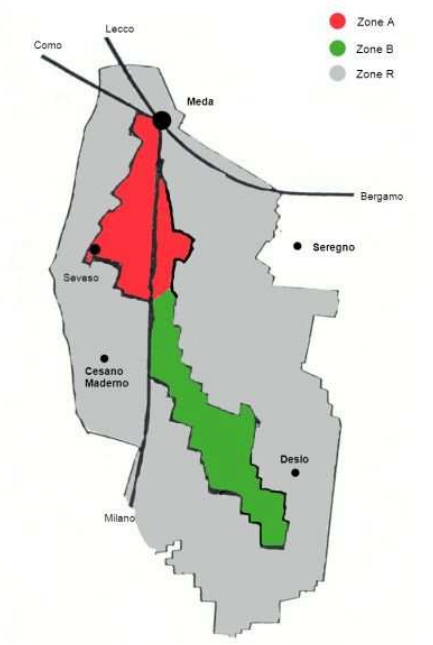
It was only ten days after the accident that the chemical group publicly declared the presence of dioxin in the toxic cloud.

14 days after, it was decided to evacuate certain areas and the prohibition on the consumption of products in the impacted zones was extended. However, people had been consuming there products for the past two weeks due to lack of clear information. The public was genuinely disgusted.

Gradually the psychological impacts of the accident spread to areas at several kilometres from the plant. Even in these zones, small animals had started to die. The symptoms and danger of dioxin poisoning were not well known in 1976.

Finally, 11 towns were impacted and the authorities defined three contamination zones:

- "Zone A" covering 110 hectares including the towns of Meda and Seveso with dioxin concentrations greater than 50 µg/m². The 736 inhabitants of this zone were evacuated at the end of July.
- "Zone B " covering 270 hectares including the towns of Cesano, Maderno and Desio with dioxin concentrations between 5 and 50 µg/m². It was decided in the beginning of August that children below 12 and pregnant women must leave the area during daytime. Farming, animal husbandry and other agricultural activities were prohibited.
- "Zone R" (“compliance” or caution zone) that included 1,430 hectares where dioxin was detected in trace quantities. Farming was prohibited and constructions were restricted.



There were serious environmental consequences:

- About 2,000 hectares of soil was contaminated
- 3,300 animals (rabbits, chicken, and birds) died. Several other animals were put down. In all, 81,000 animals were killed.

The health effects chiefly include chemical burns on the skin. 250 cases of diagnosed chloracne largely concern children and teenagers.

Despite strong opposition from moral and religious authorities, abortion was exceptionally authorised out of lack of information and fear of any possible malformations.

An abnormally high number of deaths from cardiovascular problems undoubtedly due to the prevailing anxiety have been reported in the impacted population.

The public, faced with a problem beyond the authority’s understanding to which science was unable to provide a cleat solution, was in deep distress. For this population the future as of then rhymed with several apprehensions such as malformations, cancers, etc.

The economic consequences were also significant: all activities were prohibited in "zone A", a decision effecting 2 industrial companies and 37 cottage industries. 61 farms and 4,000 kitchen gardens had to be abandoned.

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 that comprise these indices and the corresponding rating method are available at the following address: http://www.aria.ecologie.gouv.fr

According to the various studies, 0,2 to 40 kg of dioxin was estimated to have been released into the atmosphere. These estimates respectively correspond to 20% and 4,000% of the Seveso threshold (1 kg): the "dangerous materials released" index is at least equal to 4 according to the Q1 parameter.

Level 6 attributed to the "human and social consequences" index is justified by the number of inhabitants evacuated and the duration of evacuation (over 700 people for several months – H7 parameter), and the number of people injured (H4 and H3 parameters).

The "environmental consequences" index is also rated at 6 due to the number of wild animals killed or injured (Env10 parameter) and the soil surface requiring decontamination (Env13 parameter).

The pharmaceutical group spent over 240 M$ to compensate residents, companies, the concerned towns, the Lombardy region and the Italian government, explaining level 6 attributed to the "economic consequences" index (€17 and €18 parameters).

THE ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

In 1976, scientific literature mentioned the decomposition of the reaction mixture as of 230°C. Several TCP production accidents with dioxin formation have however been described in scientific literature between 1971 and 1974.

With regard to the Meda process, the Italian parliamentary commission underlined several points:

- *"The Icmesa plant technical manager and the production coordinator have confirmed that they were familiar with the works of Milnes before 10 July. In 1971, the author stated that an exothermic chemical reaction could take place in a mixture of caustic soda and ethylene glycol (…), with an uncontrolled and sudden increase in temperature to 410 °C releasing huge quantities of gaseous products.*
- *According to the "Givaudan" patent, distillation must be carried out after the acidification of trichlorophenol. This process was reversed in the Icmesa plant. This led to a longer period of contact of the ethylene glycol and caustic soda mixture with heat (contact being a risk factor), and the distillation of the solvent in a basic instead of an acidic medium. Moreover, the gradual decrease of solvent in the Icmesa process necessarily resulted in a constant decrease in the thermal wheel, creating the dangerous conditions described by Milnes. Lastly, the change in the molar ratio of the initial concentrations between tetrachlorobenzene, caustic soda and ethylene glycol from 1/2/11.5 in the Givaudan patent to 1/3/5.5 in the Icmesa process must be noted.*
- *These changes strongly influence production costs but increase the risks of an exothermic reaction and formation of T.C.D.D."*

Ever since, works have show that in presence of ethylene glycol and sodium hydroxide, a weak exothermic reaction may be triggered at 180 °C before a violent decomposition at around 200 °C.

The 2,3,7,8 TCDD is formed by the condensation of 2 molecules of 2,4,5-trichlorophenate. This secondary reaction is triggered by an increase in temperature in the reactor, resulting in the decomposition of the reactive mixture and dioxin formation: when the reactor's heating and stirring mechanism were stopped and the vacuum broken, after distillation of only 15% of the solvent, no water was added. The last temperature reading was 158 °C when the technici an signed off leaving the reactor unsupervised during the weekend.

Since the reactor was only half full, the coil heated the air above the reaction mixture leading to an increase in temperature of at least 31 °C at the surface of the still liquid. The temperature reached 190 °C and t riggered an exothermic reaction.

The temperature reading after the accident revealed that the reactor was heated over 200 °C. A plant t echnician also stated during his testimony that the reactor temperature that was uncontrolled ranged between 450 and 500 °C.

The safety disc ruptured releasing the toxic cloud.

ACTION TAKEN

Decontamination

Site clean-up operations started six months after the accident and lasted nearly five years.

The top soil of contaminated zones, destroyed constructions, and the carcasses of animals effected were buried in "zone A" in two airtight containers with a total capacity of 200,000 m^3. A relief well was used to extract water that was analysed before release into the natural environment. An inspection was carried out to check the reliability of the two concrete containers.

In July 1977, 511 people in "zone A" could return home and "zone R" was declared suitable for farming.

The plant was destroyed in 1982. The waste and material destroyed were place in barrels to be incinerated in Switzerland. The equipment was removed and decontaminated. The premises were subsequently cleaned and the ground repainted to fix any contaminated dust particles. Bulldozers were then used to demolish the plant with water continuously being sprayed to prevent a dust cloud from forming. The rubble and soil at 1m below the plant was buried in the second container.

In 1984, "zone A" was cleaned up and "zone B" was declared suitable for construction.

Meda has now built a sports complex on the site of the former plant and a natural park sprawls over Seveso in the area contaminated by the plant where the contaminated waste were buried as well.

The medical follow-up of patients exposed to dioxin

In all, around 220,000 people were exposed to dioxins including 37,000 inhabitants of any of the 3 zones A, B or R.

An epidemiological study was started in 1977 and focused on the following points:

- abortion (duration: 5 years),
- malformations (duration: 5 years)
- tumours (duration: 10 years),
- mortality (duration: 10 years),
- monitoring factory workers and cases of chloracne (duration: 7 years).

The lasting health effects seemed less severe than what was feared during the accident. However, there are divergent opinions according to the studies conducted: 10 years after the accident, no cancer or congenital malformation was diagnosed in the population exposed. Other studies conducted provide different results today:

- a study conducted by Warner et al. on 981 women under 40 years in 1976 and living in zones A and B during the accident showed that the risk of developing breast cancer increased significantly with the dioxin levels in the blood.
- 17 years after the accident, Professor Pesatori from Milan University published the results of a study started in 1983 on induced cancers. The study involved a target population between 0 and 19 years living in the three zones and included 600,000 people. Statistically, it was found that the rate of cancer in the contaminated areas is not higher than normal except for 2 thyroid cancers.
- A significant disturbance was also reported in the sex-ratio for births between April 1977 and December 1984 in the most contaminated region: 48 girls for 26 boys. This is surely linked to the oestrogen action of TCDD. This ratio gradually returned to normal after 1984. The relation between exposure to dioxin and the sex-ratio was studies by Paolo Mocarelli from the University of Milan.

Financial and legal action taken

The international chemical group spent over 240 M$ to indemnify inhabitants, companies, the concerned towns, the region of Lombardy and the Italian government.

During the Monza trial held in 1983, the senior management of the company operating the plant in Meda was given a suspended sentence of two and a half to five years. The court of appeal upheld the sentence in 1985.

LESSONS LEARNT

In Seveso, neither the residents nor the authorities suspected the Meda chemical plant to be a source of risk. They were even unaware of the nature of the end product and the chemical substances used. Moreover, changes in the procedure jeopardising the safety of facilities was carried out without informing the safety and public health authorities.

Moreover, after the accident, all concerned parties (operator, public authorities and residents) were incapable of taking appropriate action to curtail the impacts and manage the crisis that resulted in confusion, helplessness and fear.

The EU Member States thus became aware that it was necessary to make public authorities inspection procedure more stringent on industrial activities with major technological risk for their optimum management.

On 24 June 1982, the European Council adopted the “Seveso directive”, whose principles are as follows:

- the protection of the public and the environment calls for particular attention to be given to certain industrial activities capable of causing major accidents and the manufacturer taking all necessary measures to prevent such accident.
- In addition, in the case of the particularly dangerous industrial activities, it is necessary for the manufacturer to provide the Competent Authorities with information including details of the substances in question and high-risk installations and situations, with a view to reducing the hazards of major accidents and enabling the necessary steps to be taken to reduce their consequences. These are the installations that are commonly called “Seveso installations”.
- The public and workers must be appropriately informed of the safety measures to be taken and of the correct behaviour to be adopted in the event of an accident.
- The Member States are committed to exchanging information especially in the event of a problem in the national borders
- National legislations must be standardised to avoid unequal conditions of competition for Member States.

REFERENCES:

- Code Permanent Environnement et Nuisances, " La Directive Seveso I".
- Corliss M., "Dioxin : Seveso Disaster Testament to Effects of Dioxin", may 1999.
- De Marchi B, Funtowicz S, et Ravetz J. "Seveso : A Paradoxical Classic Disaster " .
- Fortunati G.U., “The Seveso Accident”, *Special Office for Seveso – Lombardi Regional Government.*
- Fortunati G.U., ” The Seveso Lessons : Advances in Reclamation and Disposal Techniques”, *Regione Lombardia, Ufficio Speciale per I Programmi della L.R*., 17.1.1977
- Gustin J.L., “Leçons des accidents majeurs dans l’industrie chimique”, Technique de l’Ingénieur, SE1050, Octobre 2002.
- Lagadec P., “Le Risque Technologique Majeur”, Pergamon Press, 1981, pp. 46-92.
- Le Monde, "La Dioxine Innocentée", 11 novembre 1987.
- Le Progrès, "Seveso : 10 Juillet 76", 10 juillet 1996.
- Marshall V.C., “Major Chemical Hazards”, ed. John and Sons, 1987.
- Mocarelli P., “Dioxin and Human Sex ratio : The Seveso Case”
- Warner M, Eskenazi B, Mocarelli P., Gerthoux PM, Samuels S, Needham L, Patterson D, et Brambilla P., “Serum Dioxin Concentrations and Breast Cancer Risl in the Seveso Women’s health Study”. *Environmental Health Perspectives*. 10 (7), july 2002.