Incident

Seveso – 40 years on

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Saturday 10 July 1976 was a day that changed the face of chemical process safety in Europe and linked a small northern Italian town with a European Directive and with a particular chemical molecule.

Introduction

The ICMESA factory in Meda, near Milan was founded in 1946 as a part subsidiary of the Swiss Givaudan SA of Geneva for the production of synthetic fragrances. In 1963, F.Hoffmann-La Roche AG bought Givaudan SA and two years later Givaudan became the majority shareholder of ICMESA, going on to buy up the remaining shares. By this time, in 1969, the production of trichlorophenol had begun at the ICMESA factory. Trichlorophenol was an intermediate in the production of hexachlorophene, a disinfectant used in the medicinal soaps of the Roche group.

1,2,4,5-tetrachlorobenzene was reacted with sodium hydroxide to give 2,4,5-trichlorophenol (TCP). This was a two stage process yielding 2,4,5 sodium trichlorophenate and NaCl after the first stage, which was then acidulated with HCl to obtain the final product. A side reaction, which occurs in particular at elevated temperature is the condensation to 2,3,7,8-tetrachlorodioxine (TCDD) (*see Figure 1*).

Two modifications were made by ICMESA to the original Givaudan process. Firstly the concentration of NaOH was increased from 17.5% to 31.6%, and secondly the xylene was distilled off before acidification. The results of these modifications increased the contact time between NaOH and the ethylene glycol.

The chemical process

A 10,000 litre reactor with a steam heating coil system, which could also be used to circulate emergency cooling water, was used for the batch process. The reactants were heated using ethylene glycol as the solvent and the addition of xylene to facilitate the removal of water through an azeotropic distillation. The ingredients were heated at ca.150 °C until no further water was formed. The temperature was then slowly increased to ca.170 °C to remove xylene, and ethylene glycol was subsequently removed under vacuum. Following the removal of ethylene glycol the reaction was quenched by the addition of a large excess of cold water. A schematic representation is shown in Figure 2.

The safety philosophy followed by the operator was careful control of temperature with the goal of preventing the formation of TCDD. The main protection device for the reactor was a bursting disc set at 3.8 bar, which was designed to provide protection during the initial stages of the reaction. The ethylene glycol removal could be protected through the addition of excess water which would cool the reaction.

The accident

On the day of the accident, the reaction was shut down with only 15 percent of the solvent removed. This was a direct violation of the operating procedures, which stipulated that either no solvent should be removed or that the removal should be completed and the reaction quenched before the reactor was shut down. The shutdown occurred at the end of the shift on the Saturday morning at 6.a.m., which was the end of work as the ICMESA plant was not operating over the weekend.

With the shutdown, the reactor was no longer stirred or heated (or actively cooled) and it was left to its own devices with its temperature at 158°C. Some six and a half hours later the bursting disc ruptured, releasing the contents of the reactor to the atmosphere. The aerosol cloud that escaped contaminated an area of about 1800 ha., encompassing four municipalities of the Lombardy region namely the townships of Seveso, Meda, Cesano Maderno and Desio.

At around 1 pm the deputy head of production was informed of the incident through a telephone call by a foreman. The deputy head of production then arrived ten minutes later, and having inspected the area immediately surrounding the plant noticed nothing out of the ordinary. At 7 pm he instructed the factory porter to contact the local public health officer for Seveso and Meda. The public health officer was however absent and it was not possible to identify his deputy. The incident was then reported to the carabineri at 8 pm. It was not until after 4 pm on the Sunday that representatives of ICMESA met the mayor of Seveso and an hour later the mayor of Meda to warn the population not to touch or eat the local fruit and vegetables. Only on the evening of 15 July, five days later, the
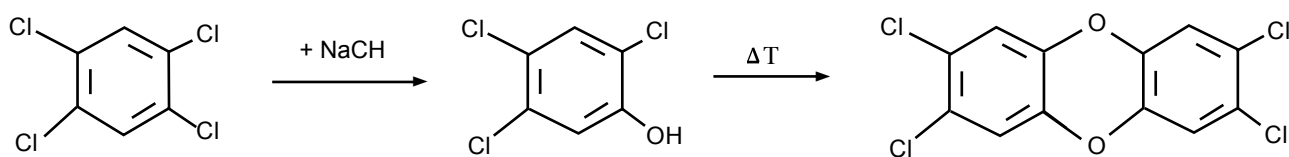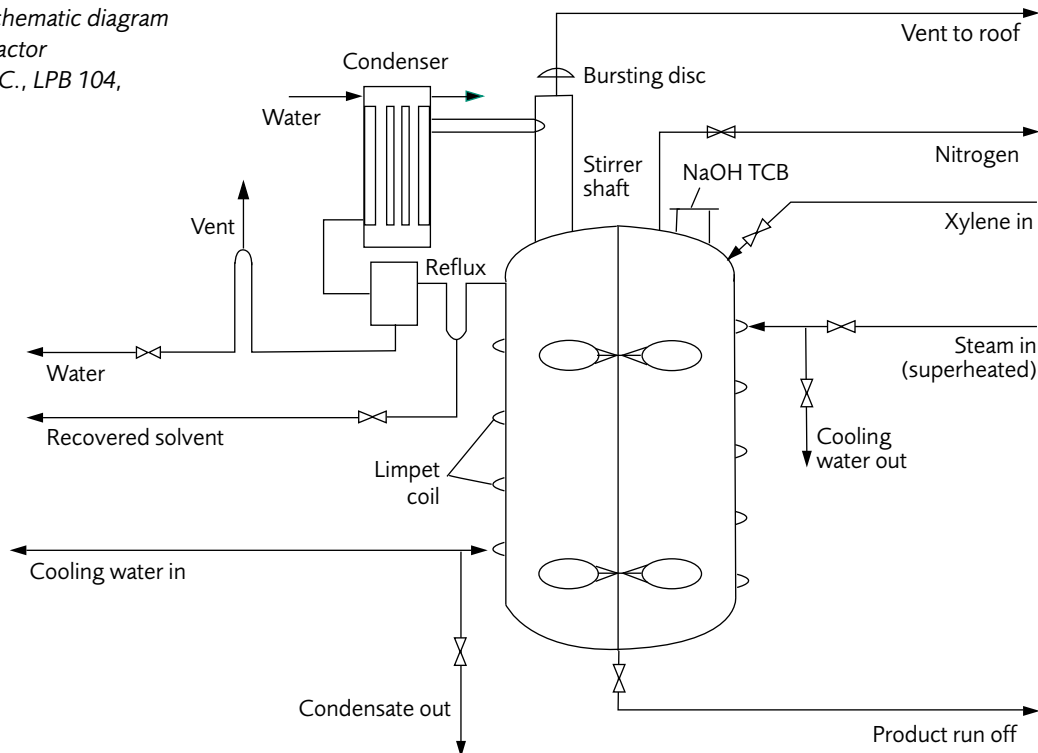

Figure 1 – Reaction of tetrachlorobenzine to produce TCP with side reaction leading to TCDD

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Figure 2 – Schematic diagram of Seveso reactor (Marshall, V.C., LPB 104, April 1992)

mayors of Meda and of Seveso designated a danger zone and prohibited the consumption of fruit and vegetables from this zone. By Wednesday 21 July it had become clear that parts of the neighbouring communities of Cesano Maderno and Desio were also contaminated and that the levels of TCDD detected were relatively high.

Experts from the companies Coalite (GB), BASF (DE), Philips-Duphar (NL), Chemie-Linz (A) and Dow Chemicals (USA), which had all had dioxin accidents, all recommended evacuation of the population. The first evacuation started on Monday 26 July and involved 208 people from 37 houses (Zone A) (*Figure 3*). Eventually Zone A (Concentrations > 50μg TCDD /m²) was extended and affected 736 people who were all evacuated. Zone B (5-50 μg/m²) included 4,700 people and Zone R (0-5 μg/m²) 31,800 people. Zone B was not evacuated. Over a period of several years buildings were demolished or decontaminated and as far as possible the land returned to agricultural and horticultural use. The most heavily contaminated area, Zone A, was decontaminated in April 1984 and a park laid out by the Region of Lombardy.

Causes of the accident

One of the significant causes of the accident, the initiation of the exothermic reaction, was for some time a puzzle. Initiation of the exotherm occurs at 220ºC; however, the last known temperature of the reactor before the operations were shut down was 185ºC, which is sufficiently below the onset temperature. In 1981 Theofanous published a paper in which the radiated heat from the reactor walls and its effect on a thin top layer of the reaction mixture was considered. From the technical detail available the reactor was only charged to just over a third (1.25 m height) and the heating was with superheated and not saturated steam. That meant that the upper two-thirds of the reactor initially had a temperature

of ca.300ºC. Experimental evidence indicated that, without stirring, the radiation from the vessel walls was able to elevate the temperature of a thin surface layer to 220–230ºC. This would provide sufficient energy to initiate the exothermic reaction. This mechanism was not understood at the time of the accident. The production instructions did however stipulate that the reaction should be left in a form which would not have been as sensitive to this radiated heat.

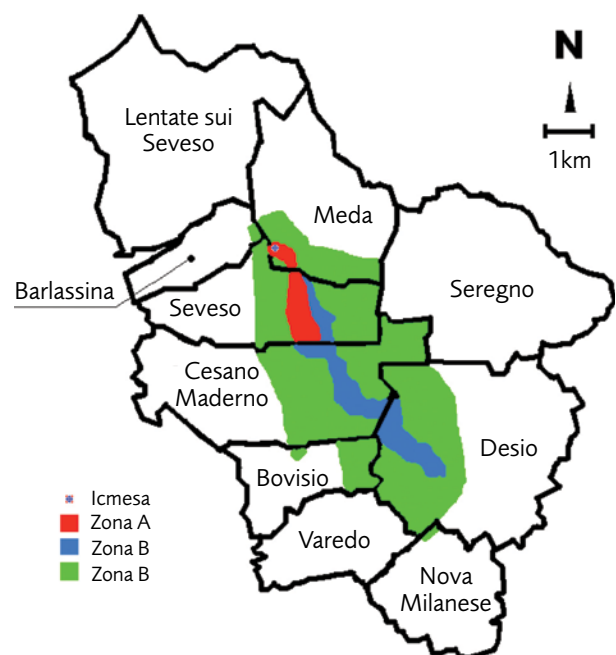Within the Italian prosecution documents it was claimed that

Figure 3 – Contamination zones (it.wikipedia.org, public domain)

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the reactor had never before been left in this unusual state. The claim was undisputed. However had appropriate consideration been given to the knowledge and understanding of the workforce (including the management and supervisors) and possible deviations from normal operation, then the possibility that the process was stopped part way was realistic.

Readers need to be aware that in 1976 concepts of "safety culture" and "human factors" were not well developed in the chemical process industries — in fact, in numerous industrial operations today, these issues present a considerable challenge.

Lessons learned from the Seveso accident

1) It is important that operators of facilities handling hazardous chemicals understand the thermodynamics of the reactions carried out. This includes side reactions and decompositions which may take place under plausible deviations from the intended reaction procedure.

2) Operating personnel must adhere to standard operating procedures. Production planning should be designed so that operations can be concluded safely within the available time-frame. Supervisors and management personnel should make themselves aware of the real operating practices and take appropriate action to ensure that training is carried out and expectations are communicated effectively. The safety management system should be devised to provide an appropriate structure to ensure that safe operation is a reality.

3) Batch reactors should as far as possible be provided with pressure relief systems that exhaust to containment systems to prevent either a release to the working environment or to the external environment. Modern blow-down systems exist which use tanks, bags or other forms of suppression.

4) In the event of a loss of containment event the alarm and emergency plan should be activated immediately and the internal and external communication channels provided with all of the relevant data and information to enable the correct response decisions to be taken. The operating company should draw up such plans well in advance and communicate them to the local authorities and coordinate them with external emergency responders. Regular exercises should be conducted. These should also cover the transmission of information through the various communication channels so as to ensure that information is provided, and that it is understood and acted upon appropriately. Operating companies cannot assume that they will be communicating with experts in the field of chemistry or toxicology; therefore the messages must be timely, clear in their interpretation as well as in the necessary measures to be adopted.

5) External emergency responders need to develop emergency response plans in advance and to train their implementation, including the communication channels. Should an emergency occur, then coordination and liaison with the law enforcement agency should take place to ensure that access to vital information and expertise is not inhibited through legal proceedings. As far as possible information on the appropriate measures to be taken in an emergency should be made available to the public in the area which could possibly be affected by a major accident. This information should be designed so that it can be readily understood and is likely to be read and implemented in an emergency.

Many of these lessons have become parts of the requirements of the so called Seveso Directives which are implemented within the Member States of the European Union and the European Economic Area. Other countries such as Australia and New Zealand have also adopted similar regulations. However regulations alone do not guarantee that accidents will not occur. It is necessary that the industrial operators are conscious of their responsibilities and that the public authorities carry out effective enforcement. For jurisdictions without effective chemical accident prevention, preparedness and response programmes there is a need to consider the risks posed in carrying out chemical operations without a robust framework. Guidance for establishing such programmes has been developed by the United Nations Environment Programme as well as the OECD and the EU.

Further events with loss of control of exothermic chemical reactions

Unfortunately, history has shown that the loss of control of exothermic chemical reactions still leads to major accidents. Within this selection it is clear that the lessons listed above have not been learned throughout the chemical processing community. Particularly vulnerable are toll manufacturers, which manufacture but do not always have the background in the chemistry, reaction kinetics or chemical engineering. Indeed some of this information might not be supplied by the customer under claims of commercial secrecy. Toll manufacturers often produce a range of chemicals for a number of different customers utilising a variety of reactions and processes, but with a limited set of equipment. Typically these are batch or semi-batch reactions together with mixing, blending, solvation, distillation, filtering and drying. Small-scale operations usually do not have access to process safety specialists in the same way as larger operations. Thus the available resources for carrying out risk assessments or executing management of changes processes, if at all available, may be so thinly spread that they are ineffective.

The following section documents briefly a few examples of exothermic runaway reactions.

22 February 1993 Hoechst, Frankfurt-Griesheim, Germany

A release occurred of almost 10 tonnes of ortho-nitroanisol from the pressure relief valve of a reactor, leading to a sticky, yellow precipitation (of ca. 1 t) over an area of 1.2 km length and 300m width. A residential area for 1000 people and allotments were affected. About 40 individuals received medical treatment for breathing difficulties and, skin and eye irritation. Initially the company's communication referred to a safety data sheet with a classification as "harmful" – in German "mindergiftig", which translates as "not really toxic". The company did however have data available which suggested that o-nitroanisol should be classified as a possible carcinogen. The public health authorities stated on the day of the incident that due to the low concentration, no acute health risks arose from the chemicals released. This did little to calm public fears, particularly as the workers carrying out the extensive decontamination work were

wearing protective suits and face masks. An epidemiological study over 30 years is still on-going, however the public health authorities have come to the opinion that no instances of chronic, asthmatic or neuro-dermatitis cases can be attributed to the incident.

The cause of the exothermic release was that the reactor was charged with two reactants. However in violation of the instructions, stirring did not take place during the addition and therefore the expected exothermic reaction (for which cooling was foreseen) did not start. Because the reaction was not initiated the operator had heated the reactant being added. Some two hours after charging the reactor and not having achieved the reaction, the stirrer was started and a spontaneous exothermic reaction occurred.

19 December 2007, T2 Laboratories Inc., Florida, USA

On 19 December 2007, four people were killed and 13 others were transported to the hospital when an explosion occurred at T2 Laboratories Inc. during the production of a gasoline additive called methylcyclopentadienyl manganese tricarbonyl.

The CSB determined insufficient cooling to be the only credible cause for this incident, which is consistent with witness statements that the process operator reported a cooling problem shortly before the explosion. The T2 cooling water system lacked design redundancy, making it susceptible to single-point failures. Interviews with employees indicated that T2 ran cooling system components to failure and did not perform preventive maintenance.

22 April 2012, Mitsui Chemical, Iwakuni-Ohtake Works, Japan

An explosion and fire at the resorcinol production facility led to one death and 21 injured, two of which seriously.

Due to problems with the steam supply system during the night before the accident, all plants using steam were ordered to be shut down. This "emergency shut down" triggered the interlock system switching the air supply to nitrogen and cooling water to emergency cooling water; agitation continued. About 70 minutes later it was determined that the temperature in the resorcinol oxidation reactor had not dropped, therefore the interlock was released and cooling returned to circulating water. With the release of the interlock the nitrogen supply was stopped and agitation ceased. The upper liquid phase of the reactor did not have a cooling coil and decomposition heat from the organic peroxide could not be removed, resulting in a gradual rise in temperature. In the lower liquid phase the temperature continued to fall. One and a half hours after the interlock had been deactivated the decomposition of the organic peroxide accelerated, the temperature rose and gas was generated. The pressure relief valve was activated, however pressure continued to rise. Five minutes later the reactor burst leading to the fire and explosion.

01 December 2014, Pirna, Germany

A serious explosion in a chemical factory caused the death of one person and seriously injured four others. Debris was strewn over the surrounding area. The reactor which exploded was producing the first, larger scale batch of a flame retardant for textiles. The investigations are still ongoing. However, there are indications that modifications to the originally intended production process may have been made.

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