Explosion of Chemical Plant in Seveso, Italy

【July 10, 1976 Seveso, Italy】

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At about 12:37 on Saturday July 10th, 1976, a runaway reaction occurred at a chemical plant manufacturing 2,4,5-trichlorophenol sodium salt by alkaline hydrolysis of tetrachlorobenzene in the suburbs of Milan in the northern part of Italy.

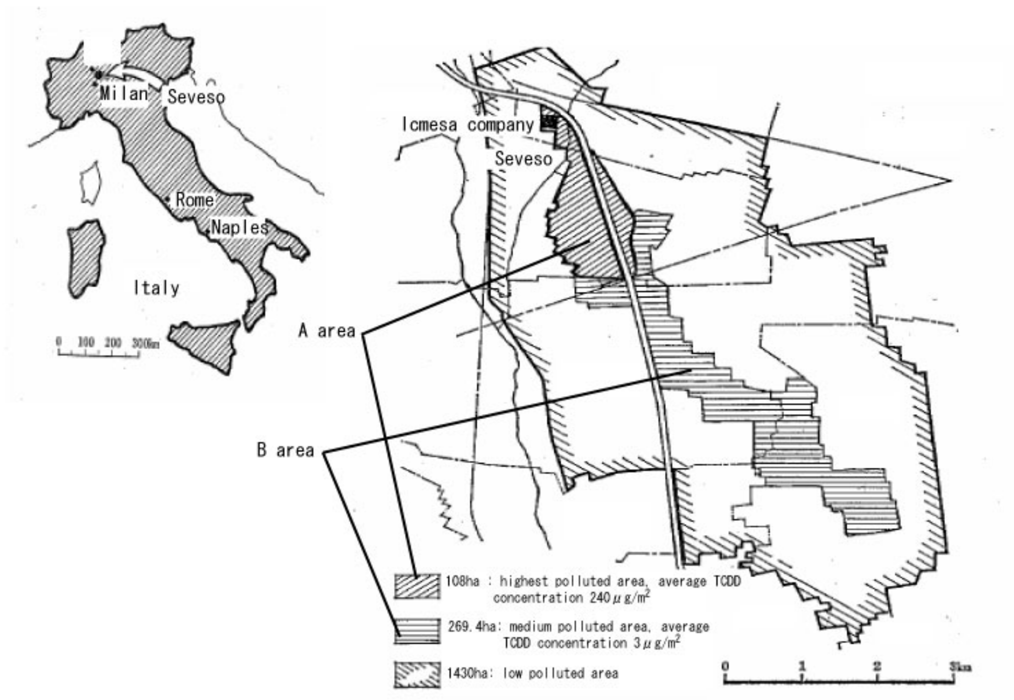

Fig. 1 damaged area

The pressure rise caused by the runaway reaction destroyed the rupture disk, and the contents were discharged into the atmosphere, forming a mushroom-like cloud. The mushroom cloud diffused to the south by the north wind that was blowing at the time, and it contaminated a vast area of about 1800 hectares. It is thought that 30 to 40kg of 2,3,7,8-tetrachlorodibenzo para dioxin (TCDD), a deadly poison, was contained in this mushroom cloud. The toxicity of TCDD is about 100000 times that of sodium cyanide.

For several days, no countermeasures were taken towards the leaked material, which fell down to the ground as a white crystal and was left as it was. As a result, in addition to the contamination of the 1800 hectares of land, victims of diseases such as cancer, chronic dermatitis, neuropathy, and deformed babies were estimated to be over 220,000, and over 80,000 domestic animals were killed. The abortion rate of pregnant women in the Seveso district from April to June in the following year reached 34%. The contaminated soil was buried underground in two large newly dug holes. The volume of one of them was 150,000m^3 and that of the other was a half. The holes were then enclosed by polyethylene sheet and covered with non-contaminated soil. Finally, the hole was covered with a 1 m thick layer of concrete, thus it was sealed completely.

The accident was caused by just a small violation of operation instruction. The existence of a runaway reaction at a lower temperature than the expected temperature was a major cause of the accident. It was not known at that time that a runaway reaction could occur at such a low temperature. There had been over 14 explosion accidents related to TCDD caused by TCP (2,4,5-trichlorophenol) manufacturing plants of the same product, and each accident caused enormous damage to human health. It was already known at the time that usually slight amounts of TCDD were formed in the reaction.

The damage of the accident was extensive, and there appear to be three points that led to the terrible disaster. The first point is that the operators did not observe the standard operation method. The second point is that the reactor was constructed without any knowledge of the possibility of a runaway reaction, so no countermeasures for preventing an abnormal temperature rise were taken. Furthermore, in the design of the safety equipment, no consideration was given to the protection of the environment. The third point is that the recommendation and later the order for evacuation of the local inhabitants were delayed. The identification of the leakage material was carried out by Givaudan Co., the parent company. It took the company five days to recognize the existence of dioxin, and furthermore, as the company spent more time on reconfirmation, they did not inform the local government of the existence of dioxin until 10 days after the accident. As a result, the damage greatly increased.

As a result of this accident, the EC established the EC Governing Board Directive (called the Seveso Directive) in 1982, which is intended to prevent major accidents in industrial activities from occurring as well as to minimize the damages to human health and to the environment.

Rupture disk: a board shaped pressure relief device that is mounted on the vessel directly or through the piping.

1. Event

The leakage accident occurred just before noon on July 10th, 1976. The rupture disk of the reactor is designed to rupture when the pressure increases due to uncontrolled reaction and so on, so that the leakage was a planned phenomenon. However, a large amount of dioxin TCDD, a deadly poison, was contained in the leaked material, which caused large-scale health damage and environmental pollution, because the material was spread widely by the wind. The plant managers were not aware of the existence of TCDD in the material, so the countermeasures were delayed and the health damages were increased.

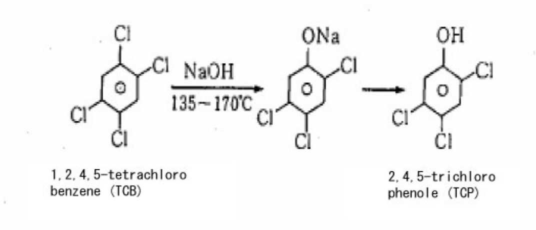

Fig2. reaction formula of TCP manufacture

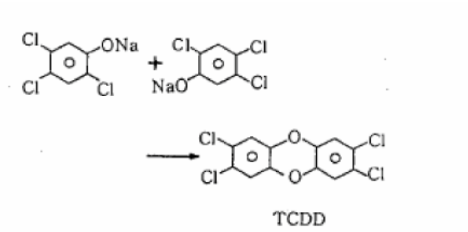

Fig.3 Reaction formula of TCDD generation

The accident occurred at a plant of a small chemical factory, Icmesa Co., in the Seveso district, the suburbs of Milan, Italy. This company is a subsidiary of the Swiss company Givaudan Co., and Givaudan Co. is a subsidiary of the well-known chemical manufacturing enterprise Hoffmann-La Roche & Co. A.G.. The plant of Icmesa Co. produced 2,4,5-trichloro phenol (TCP). TCP is then processed for producing products such as medicated soap, cosmetics, and shampoos. The main reaction formula of the process of production method that was developed by Givaudan is shown in Fig. 2. At the time, it was thought that the reaction did not generate any problems at temperatures of 200 ℃ or less; however, the poisonous dioxin TCDD was formed at a temperature of 230℃ by the reaction shown in Fig.3. A maximum of 10 ppm of TCDD is generated in the reaction process, but it is not clear whether the factory members were aware of this fact.

Removal of a solvent after the reaction was performed successively in a reactor with a thermal jacket and an agitator. According to the operation instructions, tetrachlorobenzene is generally heated to between 135 and 160℃. A hydrolysis reaction of the tetrachlorobenzene with a sodium hydroxide solution is carried out. Then xylene is added, and the generated water is separated by azeotropic distillation at 160℃. The remaining xylene is separated by distillation, and finally, the solvent ethylene glycol is recovered to 50% by reduced-pressure distillation. In addition, the operation is terminated by cooling the product down to between 50 and 60 ℃ by adding water. The processing operation after these steps is not clear. In a certain report, it is described that the remains were cooled with jacket water feeding and agitation if the remains were left in the bottom of the reactor.

In the operation of the batch that was involved in the accident, the final ethylene glycol separation of the distillation process did not reach the designated recovery rate of 50%; instead the operator stopped the process after the recovery of only about 15%. Furthermore, the addition of water for cooling the product was not carried out. Therefore, the final temperature of the product was 158℃, which is much higher than the normal range of 50 to 60℃. However, this temperature is still considerably lower than the dangerous temperature of 230 ℃. After the operator finished the series of reactions, he stopped the agitation and cooling process, turned off the power supply of the temperature recorder, and left the site. After that, the plant was no longer in the condition of being monitored.

The rupture disk of the reactor operated at 12:37, and the contents of the reactor became a foggy mushroom cloud, which was spread out and diffused to the south by the wind, resulting in the pollution of an area of about 1800 hectares.

2. Course

2.1. Operation course leading to the leakage

At 16:00 on Friday July 9th, the batch reaction which caused the accident started. At 04:45 in the early morning of the next day, the reaction and distillation processes for the batch finished, and heating of the batch was terminated by stopping the flow of steam. Next, the agitation of the reactor was stopped, the pressure was returned to atmospheric pressure, and then the operator went home. After that, there was nobody at the plant.

The rupture disk of the reactor suddenly operated at 12:37, and the reactor contents began to leak.

2.2. Course after the leakage

On July 10th, the technical manager of the factory warned the local residents that "TCP has leaked from the plant. The leaked material has a strong odor, but it does not cause any actual harm. However, it would be better not to eat any produce from your garden until the results of an accurate analysis are obtained".

On Monday July 12th, the first signs of health hazard appeared, and by July 14th, the local hospitals were flooded with patients. However, because the cause of the health problems was unknown, the doctors were unable to treat the patients.

On Thursday July 15th, the laboratory in the parent company, Givaudan Co., found a high concentration of TCDD in the leaked material, but they did not announce their findings to anyone outside the company, including the local government until the laboratory reconfirmed the existence of TCDD on Tuesday July 20th.

On Saturday July 24th, a local government officer ordered a compulsory evacuation from the A area where the pollution was most severe (Fig.1). On Tuesday July 29th, the local government expanded the evacuation area (the A area).

3. Cause

Violation of instruction became a trigger of the accident, the rupture disk operated, and the content fluid leaked from the reactor. It was not known what was in the material that had leaked, so after the leakage, nothing was done to improve the situation. Furthermore, even after the laboratory of Givaudan Co. found the TCDD in the leaked material, they did not notify the local government of the existence of TCDD until they reconfirmed it. Therefore, the initial countermeasures were greatly delayed, resulting in a large expansion of the damage.

3.1. Cause of operation of the rupture disk and leakage of contents

a) The trigger of the accident was the occurrence of a runaway reaction. It was thought that the runaway reaction would not occur at a temperature less than 230℃ and so the conditions of the reactor were believed to be safe, because the operator stopped the operation at 158 ℃. However, it was found in research conducted later that an exothermic reaction actually occurred at temperatures as low as 180℃. What could have caused the reactor to rise to 180℃? One possibility is the following. The operator stopped the agitation when he stopped the operation at 158℃. The reactor heating jacket was heated by superheated steam of 1.2MPaG, 190℃. The supply valve of the steam was closed when the operation was stopped. However, the superheated steam remaining in the jacket would have continued to heat the liquid near the jacket surface and could have caused the temperature to rise to over 180℃ locally. The stopping of the agitation also made to the local temperature rise. An exothermic reaction began in the liquid that was heated to over 180 ℃ and expanded throughout the reactor. However, the volume of the jacket was very small, so it was questionable if there was enough steam remaining in the jacket to heat the liquid material to 180 ℃. According to the "Loss

Prevention in the Process Industries (2nd Edition) Appendix 3 Seveso", turbine exhaust was used for the jacket stream. When the turbine load drops, the steam temperature can reach 300℃. Therefore, the temperature of the turbine exhaust fluctuates with the turbine load, and it is necessary to take measures to maintain the temperature at a constant value when turbine exhaust is used in a process application. Judged from the description of Loss Prevention, the design of the steam was mistaken. In addition, because the agitation was stopped, the liquid material close to the wall surface was easily heated. No one noticed the heating, because the thermometer was turned off. The operator operated the process without sufficient care, resulting in a deviation from the standard operation method. It is thought that the combination of this deviation from the standard operation method with the process design error of the steam supply led to the accident.

b) The safety device was inadequate. The rupture disk was mounted as a pressure rise countermeasure of the reactor. Also, the pressure of the rupture disk had been set by factors for other operations, and the pressure setting was too high for the runaway reaction that caused this accident. Therefore, the process temperature rose, and the formation of dioxin increased. To make matters worse, the leaked material was discharged into the atmosphere from the rapture disk. On general principles, the outlet of a pressure relief device, such as a rupture disk or other safety valves, should be directed to a safe place. If possible, it is desirable that discharge is discharged only after the combustion treatment or detoxification treatment.

c) The related companies did not refer to the other accidents that had occurred before this accident. There were at least fourteen similar accidents at TCP manufacturing plants. The damage to the company's employee from the deadly poison TCDD was extensive, and it is thought that the contravention of instructions might not happen either, if study and education had been conducted more seriously. Another cause is considered to be overlooked the possibility that an exothermic reaction could occur at a temperature of less than 230 ℃. Even though the possibility was only confirmed in research conducted later, it is still a problem.

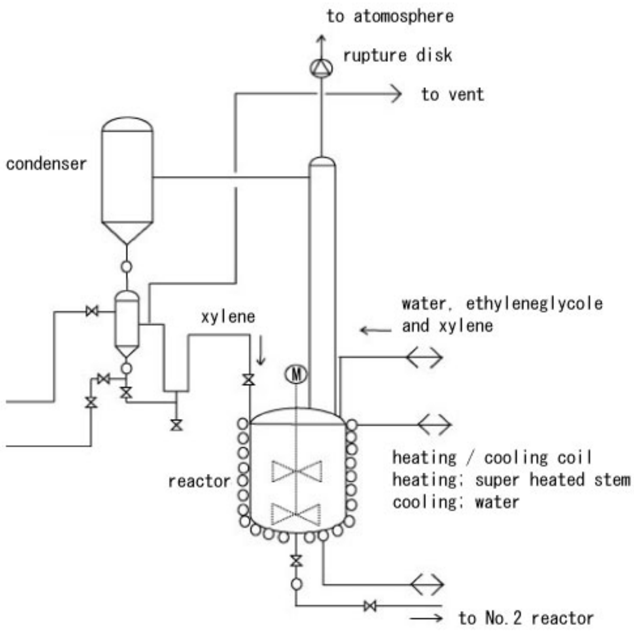

Fig.4 Outline around the reactor

3.2. Cause of expansion of damage

Icmesa Co., which caused the accident, did not have the facilities required for the identification of the leakage material, so it was identified in the laboratory of Givaudan with the help of Hoffmann-La Roche & Co. A.G. Co., which was the parent company of the parent company of Icmesa. The existence of a large amount of dioxin in the leakage material was confirmed by the first sample from the Icmesa plant, but they did not notify the local government of the findings, because they wanted to confirm the polluted range and quantity of TCDD. The quantity of dioxin in the samples which were sent successively did not decrease 10 days after the accident. Furthermore, the presence of TCDD was proven by other experiments. At last they notified the local government, resulting in the evacuation. Although the reason for the information delay was concern for an unnecessary panic, the delay caused a great expansion of damage. From the beginning, the company causing the accident was not aware of the existence of the TCDD; it recognized only the leakage of TCP. As the accident happened at the weekend, the company could not establish an effective system for dealing with the accident.

4. Process of cause elucidation

It had already been proven at the time that a runaway reaction occurs over 230 ℃, and that one molecule of TCDD is formed from two molecules of TCP sodium by the removal of two molecules of sodium chloride when the reaction temperature exceeds 200℃. It had also been proven that there is TCP sodium salt that is an intermediate of the TCP manufacturing process in the liquid when the distillation stops. Therefore, the key to the elucidation of the cause was to show why the temperature increased over 230℃.

After the accident, two Italian chemists prepared sodium of TCP. They analyzed the chemical system by thermogravimetric analysis (TG) and differential scanning calorimetry (DSC), and they found that a weak exothermic reaction might be caused at temperatures of 180 to 200 ℃. Furthermore, they found that an exothermic reaction could occur even at 180℃ by isothermal thermal analysis. In addition, they measured the time required to generate an explosion by ARC (Accelerating Rate Calorimeter) analysis. The results were as follows: a little longer than eight hours at 180 ℃, a little shorter than eight hours at 190 ℃ and about five hours at 200 ℃. In short, it was proven that a runaway reaction can be cause at the temperature of 180℃, though it had been thought before the accident that a runaway reaction cannot be caused at the temperatures lower than 230℃.

Note; TG, DSC and isothermal thermal analysis are methods for measuring what kind of exothermic behavior occurs in the chemicals. ARC is a method for measuring whether or not the chemical causes a runaway reaction by measuring the rate of temperature change. They are generally called “thermal analysis”, which include the methods and devices for analyzing the temperature dependency of dangerous reactions of chemicals.

The reason that the reactor reached 180℃ is described in the “ Causes” section.

5. Immediate Action

Since the accident itself was only that "the rupture disk operated and leaked", and since there was not an operator at the site, any immediate action was not taken. Some maintenance staff who heard the sound of the rupture disk operation ran to the site and injected the cooling water into the jacket, but they could not stop the rupture disk operation. The only action was that the technical manager of the factory warned the local residents that “TCP has leaked from the plant. It would be better not to eat any produce from your garden”.

6. Countermeasure

There are many reports and articles that refer to the Seveso Directive and the Basel Convention entitled "Convention on the Control of Transboundary Movement of Hazardous Waste and Their Disposal". But here, instead of the famous two declarations, countermeasures to prevent a recurrence of the accident will be discussed below.

a) The understanding of the process should be deepened. In particular, through improved investigation and research on a reaction, knowledge of the abnormal reaction mechanisms will be satisfactory. Besides, it is necessary that not only "in-house" information but also information from other companies and from experts of other fields related to similar reactions will be used.

b) The material that is formed as a by-product or as a product of an abnormal reaction may be a highly toxic chemical compound including elements such as nitrogen, sulfur, or phosphorus, even if the main product of the process is not toxic. It is necessary to be careful about all of the materials that may be formed in the process including the products of abnormal reactions.

c) The direction of the emitted gas from pressure release devices such as a safety valve and a capacity of processing devices should be carefully considered. Safety devices such as safety valves or rupture disks are the devices for discharging the contents of a vessel so that the vessel and piping will not be destroyed when the pressure rises over a particular design value. However, if the discharged gas causes harmful effects on humans and the surrounding environment, then the safety device has no meaning. Sufficient processing methods and a processing capacity for ensuring that the discharged material does not cause bad effects on humans and the environment are necessary. At least, a flare stack, absorber, and other basic devices should be equipped with a suitable capacity.

d) Operations that deviate from the standard operation method should not be done. Accidents often occur when some changes are made to the operation method. The operation method instructions are often made under the principle of "safety first", even if all of the possibilities which might occur could not be considered. It is dangerous to change the operation procedure without careful consideration, and sufficiently prudent investigations and study will be necessary if a change is made.

e) The related companies should establish a cooperative system with the local government and neighborhood inhabitants for the notification of potential danger and the recommended countermeasures.

7. Knowledge

a) Ideally, a chemical plant should be designed and the operation manual should be prepared after all of the reactions that occur in the reactor and vessels are clarified. However, in reality the knowledge may not be perfect, and some unknown parts may remain. Investigation and study for collecting information should be made during designing and operating, the results should be reflected in the operation and equipment. Besides, instructed technical details must not be changed thoughtlessly.

b) The enterprise that sold the technology may be responsible to some extent for the safety of the plant which is constructed and operated depending on the technology. In particular, if the plant owner is a subsidiary or affiliated company that has less capital and a lower technical level, it is the responsibility of the parent enterprise to carry out sufficient information services and guidance required to avoid an accident.

c) The local administration must recognize the potential area of contamination on the assumption that a catastrophe happens, make a plan for the evacuation of the local inhabitants, and prepare facilities for medical treatment beforehand, when there are facilities that handle toxic substances in the region. The enterprise must act positively to furnish information to public and cooperate with the local administration.

d) There is a large possibility that a mistake in the temperature control of the steam can occur. Although the importance of the process design is apt to be neglected, neglect of the process design can result in a large catastrophe.

8. Influence of Failure

Although there were no immediate deaths, many people were affected by the leaked material for a long time after the leakage accident. The victims of diseases such as cancer, chronic dermatitis, neuropathy, and the birth of deformed babies have been estimated as over 220,000 people. An abortion rate of pregnant women between April and June of the next year reached 34%. The results of investigation that was continued over ten years after the accident showed the higher mortality and morbidity rate than that in another area.

The soil-polluted area was about 1800 hectare. Contaminated soil was removed, then soil dressing was done with new topsoil. The contaminated soil was buried in a

150000m3 large newly dug hole and a half-sized hole, the holes were enclosed by polyethylene sheet, and the holes were covered with non-contaminated soil and a 1 m layer of concrete. Over 80,000 domestic animals were killed.

Considering the enormity of the damage, in June 1982 the EC issued an EC governing board order, what is called "Seveso Directive". The directive was revised in 1987 and 1988. The EC put this order out in order to prevent major accidents by manufacturing activities as well as to reduce the bad effects on the environment. Later, the United Nations proposed the Basel Convention, which forbids the transfer of hazardous wastes between countries and the disposal of wastes in South Pole. The Basel Convention was adopted by all 116 nations that participated in the conference in 1989.

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