Blaze at an ethylene pipeline and a nearby acrylonitrile tank

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Köln (North-Rhine-Westphalia) Germany

Ethylene
Acrylonitrile
Pipeline
Tank
Insulating flange
Gate valve
Fire
Maintenance work
Organisation / procedure

THE FACILITIES INVOLVED

The site:

The accident happened in the northern part of Cologne on the site of a petrochemical plant of the company. The plot of the company is situated in an industrial area for mainly chemical companies. The company is the third largest chemical enterprise in the world. It's a leading manufacturer of petrochemical, special chemical and oil products with 70 production sites in 14 countries. The site, with its 2200 employees, a production volume of 5 million tons and a turnover of 2.6 billion euros, is the biggest chemical site in Cologne and one of the most import locations of the group. The plant is connected to an international ethylene pipeline net - owned by another company - that is used by the plant for consumption as well as injection of ethylene. At the day of the accident ethylene was injected into the net. The shortest distance from the location of the accident to the next inhabited area is about 600 meters.

The involved unit:

The accident happened at the blocking station of the international ethylene pipeline owned by a company which is a joint venture of six international chemical companies including the company of the plant. The blocking station is situated at the transition from subsurface to surface course of the pipeline. It is equipped with a remote controlled hydraulic gate valve, an insulating flange and a bypass with manual gate valves (Figure 1). The diameter of the pipeline is 250 mm and of the bypass 80 mm. Ethylene is produced by the company form LDF - light distillate feedstock (light petroleum) - and used for the production of polyethylene. At the time of the accident about 27t/h of ethylene were injected into the pipeline under a pressure of 83 bars. The pipeline is assigned to the German pipeline regulation, the so called "Gashochdrucksleitungsverordnung". Pipelines are excluded from the Seveso directive.

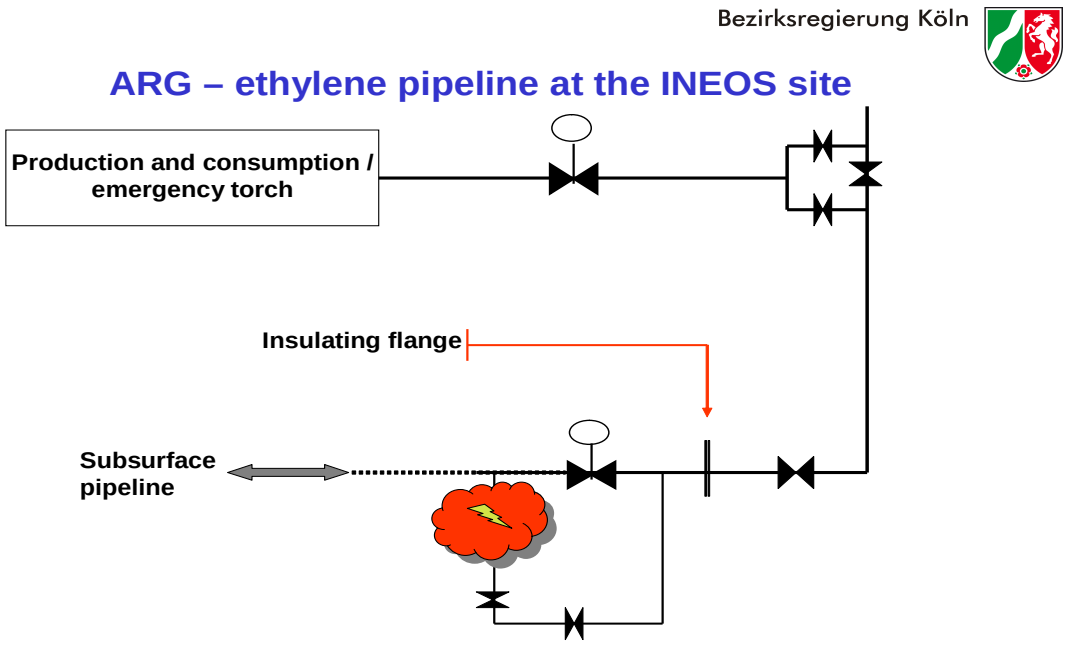


Figure 1: Scheme of the ARG ethylene pipeline at the site.

A tank field for the storage of acrylonitrile - an upper tier Seveso installation - is situated in the direct vicinity of the blocking station (Figure 2). The nearest of the three tanks with a distance of about 10 meters to the pipeline was filled with 3517 cubic metres of acrylonitrile. The height of the tank with attached ceiling is 16 metres and its diameter is 18 metres. The wall and the ceiling of this tank are made of aluminium. It is surrounded by a concrete wall of identical height with a distance of 1.2 meters from the aluminium wall. This concrete wall also serves as retention basin. At the time of the accident about 14m^3/h were taken from this tank. The site mainly uses acrylonitrile for sale to the plastics producing industry.

THE ACCIDENT, ITS CHRONOLOGY, EFFECTS AND CONSEQUENCES

The accident:

At 2:26 pm a leakage at the insulating flange of the ethylene pipeline blocking station was induced and/or detected during the execution of maintenance work. At 2:28 pm the leakage was announced to the operator of the ethylene pipeline by the plant. Two minutes later the remote controlled hydraulic gate valve was locked.

From the moment of the announcement on there is a video recording of a surveillance camera that was directed to the transfer station and the near by tank field. On this recording the exhausting gas is detectable. 7 minutes after the beginning of the leakage the ethylene ignited as can be seen on the video recording (Figure 2). At 2:32 pm the plant fire brigade arrived at the scene and - after the ignition of the ethylene – began with cooling of the nearby acrylonitrile tanks.

Figure 2: Ethylene flame from the leakage at the insulating flange (arrow) and cooling of the acrylonitrile tanks by the fire brigade

Immediately after the announcement, the injection of ethylene from the plant was stopped, the injection valve was blocked and the remaining gas in the transect was directed to an excess gas burner(Figure 1). In consequence of the leakage and these measures the gas pressure dropped from 83 bars to a few mbars within 12 minutes. Simultaneously the gas temperature dropped from 16℃ to -30℃. Sho rtly after the ignition the height of the flame was about 3 to 4 meters with decreasing tendency. At 2:36 it had nearly gone out in consequence of the decreasing gas pressure. But from 2:38 pm on it increased again and after a short time it set the hydraulic valve under fire which was only two meters away from the insulating flange. A reason for this was probably the destruction of the hydraulic oil tank at the valve in consequence of the high flame temperature. Short time before the fire brigade had begun with cooling the acrylonitrile tanks to guard them against ignition. Maybe some of the cooling water drifted to the burning pipeline because of the small distance to the neighbouring tank. A few seconds later the hydraulic valve and the bypass were completely under fire (Figure 3).

Figure 3: Increasing of the flame in direction of the hydraulic valve and the bypass. Support of the flame by the hot and inflammable hydraulic oil from the broken holding tank of the valve is most likely.

As a consequence the ethylene in the bypass and pipeline on the other side of the gate valve, which was still under pressure of 83 bars, was dramatically heated by the flames. This eventually caused the decomposition of the ethylene in the pipeline with an enormous increase in temperature and pressure. Due to these events the bypass was destroyed and the pipeline opened up again. Now all of the ethylene in the pipeline under a pressure of 83 bars was released into the burning surrounding. The next gate valve was situated at a distance of about 11 km. It was closed two minutes before the bypass gave way. But there were still 200 tons of ethylene in this transect of the pipeline.

Immediately after the destruction of the bypass at 2:43 pm a jet flame with a height of about 30 to 40 meters formed in the direct vicinity of the acrylonitrile tank (Figure 4). This flame burnt with the same height until 5:30 pm, then began to decrease until it extinguished at 7:26 pm. From 3:00 pm on the Cologne fire brigade a lot of other auxiliary fire brigades supported the fight against the fire.

Figure 4: Ethylene jet flame from the broken bypass of the gate valve; gas pressure: 83 bars. Half an hour later the nearest acrylonitrile tank caught fire.

The neighbouring acrylonitrile aluminium tank was surrounded by a protecting concrete wall but without concrete on top of the tank. Because of the enormous heat radiation of the jet flame (about 2000 °C) plastic components of the fire engine at a distance of 50 meters began to melt as well as parts of the aluminium tank ceiling. First flames formed at the top of tank at 3:12 pm. From 4:30 pm on the whole roof area of the tank was burning (Figure 5). The flames reached a height of about 16 to 20 meters. At this time about 35,000 litres per minute of quenching water were used for extinction of the fire as well as for cooling of the surrounding tanks.

The inhabitants of the nearby districts of Cologne were warned and requested to close the doors and windows. But at this time the cloud of smoke rose straight to an altitude of about 700 meters in consequence of the thermal lift. Due to a considerable deployment of measuring units the dissemination of the polluted cloud was well tracked. For that purpose the fire brigade also was supported by the well equipped measuring unit of the State Environment Protection Agency. At some measuring points positive results were found for nitric oxides and hydrogen cyanide, but with 2–5 ppm for NOx and 2 ppm for HCN they were in the range of the detection limits.

Figure 5: Whole roof area of the acrylonitrile tank is burning at 4:30 pm.

Not only the ceiling but also the aluminium tank wall burnt down to the acrylonitrile liquid level which was about six metres below the ceiling. From this time on a mixture of water and acrylonitrile poured into the gap between the tank wall and the surrounding concrete wall. Due to the extreme circumstance cracks formed in the concrete wall. Now the stability of the whole tank was in question. A break down of the burning tank would have had grave consequences to the surrounding tank field, the fire fighters and the environment. So the fire brigade started an enormous foam attack on the tank and eventually succeeded in extinguishing the flames at 11:50 pm. Since the Second World War there was no fire in Cologne that demanded the deployment of 1180 fire fighters within five hours.

After extinction of the flames the temperature of the acrylonitrile was 75 °C, two centigrade below the boiling point. In succession of the strong wind and the associated holes in the foam layer some of the acrylonitrile evaporated batch-wise. As a consequence, acrylonitrile was found in the ambient air in the near by Cologne district Worringen in concentrations of up to 20 ppm.

Consequences of the accident:

There were no serious injuries as a consequence of the accident. Altogether 600 persons from the fire brigades, police and aid organisations participated in an investigation of acrylonitrile in blood samples. No result indicated abnormalities due to the operation. For the estimation of the seriousness of the found pollutant concentrations in the inhabited districts Emergency Response Planning Guidelines (ERPG) and Acute Exposure Guideline Levels (AEGL) were used (Table 1). Found concentrations of nitric oxides (2-5 ppm) and hydrogen cyanide (2 ppm) were well below the ERPG-2 limits of 15 respectively 10 ppm, which are one hour mean values!

Table 1: ERPG and AEGL

1. Emergency Response Planning Guidelines (ERPG)

ERPG-1: The maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing other than mild, transient adverse health effects or perceiving a clearly defined objectionable odour.

ERPG-2: The maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing or developing irreversible or other serious health effects or symptoms which could impair an individual's ability to take protective action.

ERPG-3: The maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing or developing life-threatening health effects.

Acrylonitrile:

ERPG-1: 10 ppm (22 mg/m^3)

ERPG-2: 35 ppm (76 mg/m^3)

ERPG-3: 75 ppm (63 mg/m^3)

Source: AIHA - Emergency Response Planning Committee

2. Acute Exposure Guideline Levels (AEGL)

AEGL-1: is the airborne concentration (expressed as ppm (parts per million) or mg/m3 (milligrams per cubic meter)) of a substance above which it is predicted that the general population, including susceptible individuals, could experience notable discomfort, irritation, or certain asymptomatic no sensory effects. However, the effects are not disabling and are transient and reversible upon cessation of exposure.

AEGL-2: is the airborne concentration (expressed as ppm or mg/m3) of a substance above which it is predicted that the general population, including susceptible individuals, could experience irreversible or other serious, long–lasting adverse health effects or an impaired ability to escape.

AEGL-3: is the airborne concentration (expressed as ppm or mg/m3) of a substance above which it is predicted that the general population, including susceptible individuals, could experience life-threatening effects or death.

AEGL values are developed for 10 minutes, 30 minutes, 1 hour, 4 hours and 8 hours

Acrylonitrile (ppm), status: proposed

	10 minutes	30 minutes	60 minutes	4 hours	8 hours
AEGL-1	4,6	4.6	4.6	4.6	4.6
AEGL-2	290	110	57	16	8.6
AEGL-3	480	180	100	35	19

Source: http://www.epa.gov/oppt/aegl/

For the estimation of the acrylonitrile exposure in the Cologne district of Worringen a distinction was made between a main exposure area nearest to the incident with highest individual acrylonitrile values and the rest of the district (Figure 7). From March, 18th, until March, 23rd, altogether 506 single measurements were taken, 175 thereof in the main exposure area. The highest one hour mean value in this area was 10 ppm which is identical with the ERPG-1 value (Table 1). This value covers the time of 4:00 am until 5:00 am (March, 18th) while most of the inhabitants were in their houses. The highest eight hours mean value was 5.1 ppm which is 10% above the proposed AEGL-1 value (Table 1).

For the estimation of the acrylonitrile cancer risk a short study was established by the State Environmental Protection Agency of North-Rhine Westphalia. For this assessment the mean concentration over the whole exposure time is important. In the study a mean value of 1.7 ppm over a time period of 5 days was found in the main exposure area, outside this area the value was 0.3 ppm. From the 1.7 ppm value an additional cancer risk of 1:50,000 was calculated. An individual risk can not be deduced from this calculation. One also has to bear in mind that the found mean concentration over this time period is only valuable outdoors and that most inhabitants were in their houses during occurrence of the highest concentrations.

Immediately after the exposure 15 soil samples and 10 grass samples were taken from sensitive areas - like children's playing grounds, schools, kindergartens and so on - and were analyzed for acrylonitrile. In addition 5 soil samples and 5 plant samples from nearby acres were also investigated. All results lay below the detection limits in the range of <5 to <20µg/kg.

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 amount of ethylene burned is 300 t. The ethylene SEVESO threshold being equal to 50 t, the amount released corresponds to 600 % of the threshold. The amount of acrylonitrile burned is 1 200 t. The SEVESO threshold being equal to 200 t, the amount released corresponds also to 600 % of the threshold. The indice related to the amounts of dangerous materials released for these percents is 5 (see parameter Q1). The property damage resulting fromf the accident in the establishment amounted to 19 M€, the establishment's production losses to 32 M€ while the costs of cleaning and decontamination are estimated to 2 M€. The indice related to the economic consequences is therefore equal to 4 (see parameters €15, €16 and €18).

THE ORIGIN, CAUSES AND CIRCUMSTANCES SURROUNDING THE ACCIDENT

For clarification of the facts leading to the accident two expert survey reports were commissioned. The first one dealt with the origin, causes and circumstances of the blaze of the ethylene pipeline and the acrylonitrile tank. The second one which was independent of the first one focused on the pipeline. The surveys confirmed that the pipeline and the tank were constructed and operated in accordance with the technical rules and the permissions before the commencement of the incident. Also the requirements of fire and explosion prevention were fulfilled and the necessary distance between pipeline and tank was kept. The accident could not have been predicted or restricted by any systematic risk assessment. The provisions in the alarm and hazard defence plan of the tank field were sufficiently accurate to initiate the necessary measures.

The influence of the maintenance work could not be clarified by the surveys because of an ongoing investigation of the department of public prosecution. But the expert figured out that a leakage at the insulating flange could evolve during the maintenance work when the sequence of the tightening of the screws is not followed correctly or when the wrong torque is applied.

Concerning the cause of the ignition of the exhausting gas both surveys came to identical results. The most probable mechanism of ignition was electrostatic charging because all other ignition sources could be excluded. According to both surveys the cause of the expansion of the fire and the following exposure of the gate valve and the bypass to the fire could not be clarified definitely. The most probable cause is the destruction of the hydraulic oil tank with subsequent leakage of the hot and inflammable hydraulic oil. The influence of the cooling water that came into contact with the hot hydraulic oil is discussed controversially. An insertion of drifting water droplets could not be avoided during cooling of the nearby acrylonitrile tank (Figure 4). As it is technical accepted to let a gas flame burn until the gas is consumed the fire brigade did not use the water for quenching of the gas flame.

The cause for the bypass breakdown was with high probability a thermal decomposition of the ethylene. Under certain pressure and temperature conditions the property of ethylene is to decompose explosively. Temperatures of up to 1500°C could occur during this process. According t o the surveyors the conditions for decomposition were given. Due to the spontaneous rise in pressure and the softening of the bypass caused by the flame heat the breakdown of the bypass was inevitable. The chain reaction - first burning of the exhausting ethylene and then destruction of the hydraulic oil tank with subsequent under firing of the bypass and eventually destruction of the bypass - could have been avoid, if there was a bigger distance between the insulating flange and the other fittings.

During the first phase of the fire the acrylonitrile tank was only marginally affected by the heat. Only from 2:43 pm on as the bypass was destroyed and the jet flame with a height of 30 to 50 meters appeared the tank was affected by relevant heat radiation. The survey comes to the conclusion that due to the long time of heat radiation and the direct flame exposure of the tank roof part of the aluminium roof melted and gave way to acrylonitrile vapour that ignited. The

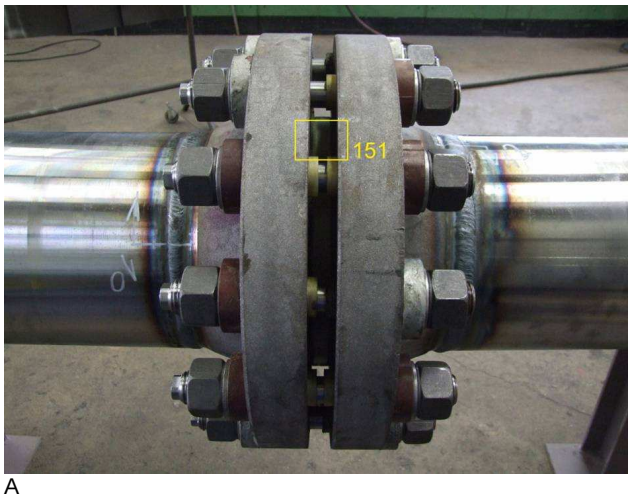
additional heat formation of these secondary fires had a supportive effect on the meltdown of the aluminium roof. At 4:30 pm the roof had completely melted down so that the complete tank square was free to burn.

ACTIONS TAKEN

The low contaminated water used for cooling of the acrylonitrile tanks was given to Currenta´s own waste water treatment plant and after purification discharged into the river Rhine without exceeding of emission limit values. The mixture of fire water and acrylonitrile from the tank was given to an incineration facility. The tank remains were removed to give place for a new construction. The ethylene pipeline was displaced and the blocking station reconstructed at a distance of 62 meters from the tank field. The insulating flange with inserted nuts was removed by a maintenance-free welded insulating connector (Figure 8).

The Cologne District Government as competent authority developed a concept of measures related to Seveso sites that are operated in close vicinity to pipelines with inflammable gases. As a first step the operators of such sites were requested to register the pipelines in the vicinity of Seveso sites. Priorities for registration were pipelines with highly inflammable and inflammable gases. In this survey the operators were also asked to describe the technical construction of the pipelines with emphasis on removable connections and fittings and the distance between the pipeline and safety relevant installations of the Seveso site. During this survey it will also be evaluated if the pipelines are considered as a source of environmental danger in the risk assessment of the site. Finally there has to be a documentation of the risk assessment in the safety report. Depending on the answers of the operators there will be a specification and enforcement of the necessary measures. This Cologne concept for increasing the safety standards of Seveso sites in close vicinity to pipelines with inflammable gases has been adopted for the whole State of North Rhine Westphalia.

In addition to these measures a state wide extra inspection program on Seveso sites with special emphasize to the above mentioned constellations was launched. During this survey a further focal point was the human factor as it played an important role at the beginning of the ethylene leakage.



A

B

Figure 8: Insulating flange with inserted nuts (A), maintenance-free welded insulating connector (B)

The State Environment Ministry of North-Rhine Westphalia has tasked the State Environment Protection Agency to advance the pipeline land register of the Cologne region to the whole area of the state. This register is based on a geographical information system and will be developed to a web application. So every civil protection authority and the ministries will be informed very quickly in case of catastrophes.

LESSONS LEARNT

We learned from the expert surveys that a leakage at the insulating flange of a high pressure gas pipeline could evolve during the maintenance work when the sequence of the tightening of the screws is not followed correctly or when the wrong torque is applied. In the case of pipelines with inflammable gases it is very important to prepare very detailed standard operation procedures and employ very skilled technicians to performance the maintenance work when the pipeline is under full pressure. A similar situation appeared a year before this accident as during maintenance work a leakage was detected. At that time the gas didn't ignite and the flange was renewed and used again after tests by an independent surveillance organisation. The best way to reduce the risk of leakages and subsequent fires is to use maintenance-free welded insulating connectors as shown in Figure 8(B).

Pipeline leakages with inflammable gases under high pressure tend to ignite even in the absence of external ignition sources. Removable constructions and fittings can be destroyed if they are arranged in the direct vicinity of potential leakage points. Fire supporting liquids like hydraulic oil can have dramatic effects on the development of the incident. So it is very important to arrange the valves, flanges and other fittings of the pipeline at a distance as long as possible from one another. If this is not possible it is highly recommended to use fire proof constructions of the fittings. Especially remote controlled hydraulic gate valves have to be considered under this perspective. These measures will be most important if a near distance to a high risk installation with inflammable substances is not avoidable.

Concerning Seveso sites pipelines have to be considered as a source of environmental danger. If a high risk pipeline is not taken into account in a proper way the risk assessment has to be adapted and documented in the safety report. Such an investigation may have subsequent impact on the requirements on removable connections, valves and other fittings of the pipeline in the direct vicinity of the Seveso site. A reduction of flange connections and fittings, fire proof constructions and a replacement of flange connections with inserted nuts by welded insulating connectors could be necessary. If possible, the distance between the pipeline and the Seveso site should be increased, as it is realized here.

Operators of Seveso sites and operators of nearby pipelines should exchange safety relevant information especially in the case of a change of the arrangement or the building of new pipelines. The same is valid for competent authorities who are responsible for the surveillance of Seveso sites and pipelines. Article 8 of the Seveso II directive (see below) should be applied in a similar way.

Article 8: Domino effect *(Seveso II directive)*

1. Member States shall ensure that the competent authority, using the information received from the operators in compliance with Articles 6 and 9, identifies establishments or groups of establishments where the likelihood and the possibility or consequences of a major accident may be increased because of the location and the proximity of such establishments, and their inventories of dangerous substances.

2. Member States must ensure that in the case of the establishments thus identified:

a. suitable information is exchanged in an appropriate manner to enable these establishments to take account of the nature and extent of the overall hazard of a major accident in their major accident prevention policies, safety management systems, safety reports and internal emergency plans;

b. provision is made for cooperation in informing the public and in supplying information to the competent authority for the preparation of external emergency plans.

Gas pipelines are not included in the Seveso II directive and there are no other European laws for this kind of installations. In Germany different directives for gas pipelines are in force (amongst others: Rohrfernleitungsverordnung, Gashochdrucksleitungsverordnung) with different requirements on construction and operation of these installations. There are also different competent authorities in charge of surveillance of the different kinds of pipelines. The maximum requirements concerning permission and inspections are demanded by the Rohrfernleitungsverordnung (pipeline directive). But ethylene pipelines lie in the jurisdiction of the Gashochdruckleitungsverordnung (directive for gas pipelines under high pressure) which only requires an announcement of new pipelines to the competent authority and inspections by approved private surveillance organisations. A change of these kinds of pipelines to the regime of the pipeline directive is highly recommended, as under this regime requirements similar to the Seveso directive are applied. Because of the threats of a leakage and the potential domino effect in combination with a near by Seveso site it is also recommended to incorporate gas pipelines in the next amendment of the Seveso II directive.