Leaks of hydrogen cyanide in a unit producing acrylonitril.

October 1999, the 14th, December 2000, the 6th and April 2001 .

Sittard-Geleen-Born

The Netherlands

Chemistry
Pipeline
Carbon steel / Stainless steel
Corrosion
Maintenance / repair
Weld

THE INSTALLATIONS IN QUESTION

The company involved is one of the largest Dutch multi-national chemical companies. One of its production locations is situated in the city of Sittard-Geleen-Born, a town near Maastricht. This large chemical complex contains 57 plants and its surface is approximately 800 ha. The naphta crackers and the polymer plants of this large complex have been sold recently to another company. The company in question still produces fertilizer, industrial chemicals and pharmaceutical intermediates. It operates 2 acrylonitril plants, called ACN-1 and ACN-2 plants. Acrylonitril is used as a raw material for synthetic fibres in garment. It is also used in plastics like ABS and other chemicals that the company produces. In the production of acrylonitril, a number of side-products is formed. Hydrogen cyanide or HCN is one of the most important side products. It is a lethal chemical substance that is converted into other products. Both ACN plants were built in the 1970's and have been used for now 30 years.

The ACN-plants were ISO-14000 certified. The local authorities issued the environmental permits for these plants. The distance between the plants and the urban population is only 500 m.

In the last 3 years, the following incidents happened at the ACN-plants :

- ✓ On October 1999, the 14th, loss of containment and leak of HCN due to a pipe rupture,
- ✓ On December 2000, the 6th, a storage tank leaked during the investigations searching for the cause of the previous one. Fortunately, the tank was located in a liquid-tight tray.
- ✓ On April 2001, a leak occurred during the start-up of the ACN-plants.

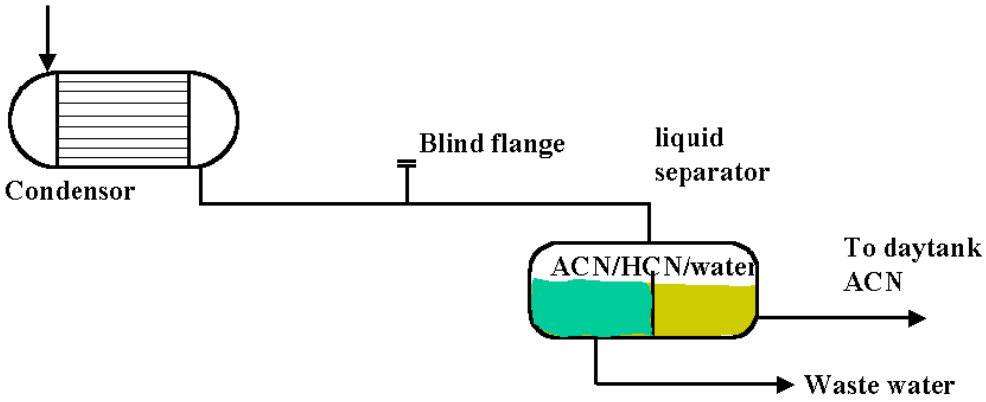
The accident which will be most developed in this sheet is the 1st one. The other ones will be described as consequences and actions taken (they occurred whereas the 1st incident was investigated and during the start-up of the units involved).

THE ACCIDENT, ITS BEHAVIOUR AND CONSEQUENCES

The accident of October 1999, the 14th (n°ARIA 24856):

A leak occurred in the part of the process whose normal operating conditions are 30 – 40°C and nearly atmospheric pressure. It took place in a pipe between a condensor and a liquid separator, as mentioned on the diagram here-under. About 4 000 l of liquid were emitted containing about 200 kg of hydrogen cyanide. At one point, the pipe involved contained stump, which should be closed with a blind-flange. However, it appeared that the blind-flange was not present and that the stump was ruptured.

In hindsight, it is expected that this situation was present during at least 1 week before the accident. Moreover, probably the stump was plugged due to polymerised product. However, due to a high level in the crude product storage tank and the omission of opening a proper release valve, an overpressure took place. This caused the loss of process fluid.



Immediately, the operator applied a water screen to prevent loss of the HCN outside the battery limits. Frequent monitoring of the atmospheric HCN concentration was applied, because of the short distance to the nearest urban population about 500 m. The operator immediately shut down the ACN-plant.

The ruptured pipe was replaced and the same pipe in the other ACN-plant was inspected. At that time, no deviations were detected in the other plants so the ACN-plants were restarted.

The consequences :

Only one employee of the company was injured due to a mild cyanide intoxication.

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 indicated in the appendix hereto and are available at the following address: http://www.aria.ecologie.gouv.fr

200 kg of hydrogen cyanide were released, representing 1 % of the Seveso threshold which is 20 t. The index relative to the amount of 'dangerous materials released' is thus 3 (parameter Q1).

As an employee was slightly injured (hospitalisation less than 24 hours), the "human and social consequences" index is rated 1 (parameter H5).

ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

Immediately after the leak, the Labor Inspection, the operator and the local authority started an inquiry to investigate the cause of this accident.

The first conclusion was that the probable cause was cyanide stress corrosion.

What stress corrosion is?

Cyanide stress corrosion frequently occurs in carbon steel. Due to welding, such material contains residual stress unless the welds are annealed to release the welding stress. Annealing of welds means slowly heating to 650℃ and subsequently cooling of the welded material to environment temperature. Welds that not have been annealed are very sensitive for stress corrosion. Especially in an aqueous hydrocyanide environment. A cyanide concentration of as low as 1% is expected to be harmful. Annealing is not necessary for welded stainless steel constructions. In the early seventies,

stainless steel was too expensive. That was the reason why this type of plants all over the world was made of carbon steel.

The effect of cyanide stress corrosion was studied. It was generally expected that cyanide stress corrosion leads to failure within 6 years of exposure to aqueous cyanide. The ruptured weld at the point of the missing flange was constructed in 1984.

Although, during the initial plant construction, the licensor ordered that all the welds had to be annealed when the medium contained more than 1% thus 10 000 ppm cyanide.

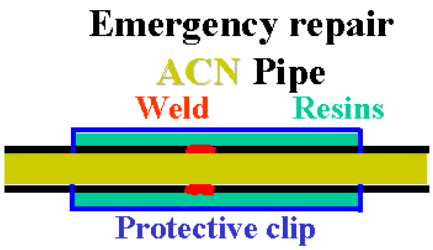
According to its experience, the company estimated that no cyanide stress corrosion occurs at a concentration of less than 200 ppm. This is a factor 50 lower than the licensor stated. It was reasonable to expect that the operator instructed its personnel that all modification welds, when the medium contains more than 200 ppm cyanide, should be annealed. However, the operator could not show the authorities the heat diagrams of the welds.

Moreover, at that moment, its personnel did not know how many modification welds were applied. Therefore, the 2 plants were completely inspected with the result that probably 15 modification welds were made.

Using an experimental method, it was proved that all these welds showed stress corrosion. The welds made during the initial period showed no stress corrosion.

For the control, an emergency repair as shown on the drawing was found. Normally, such repair is a temporary measure but this one was carried in 1994.

It was reasonable to expect that during the next maintenance stop (1996), the pipe would be properly repaired.



ACTIONS TAKEN

These findings resulted in severe doubt about the integrity of the installation. The Public Prosecutor was informed and decided that this incident should be investigated with respect to violation of the environmental and criminal law.

When the newspapers published that the Public Prosecutor started an inquiry, a lot of discussions took place in the surrounding villages. People did not feel safe anymore. Because the operator wanted to delay the maintenance stop within 3 months, the local authority hired an independent institute to investigate the integrity of the plant.

TNO reviewed the measures immediately after the incident, evaluated the number of gas detectors and concluded that there should be a back-up detector system available. TNO concluded that there was no problem to delay the maintenance stop for 3 months. So, the local authority approved the delay and ordered that all modification welds had to be replaced at the maintenance stop.

However, the Public Prosecutor still had serious doubts about the plant integrity. This was based on investigations carried out by an expert from the United States. This institute had the opinion that stress corrosion also occurs at a concentration less than 200 ppm cyanide.

In April 2001, during the maintenance stop, the results of the Public Prosecutor were challenged by TNO.

After the 1st incident, the replacement of all modification welds by stainless steel during the stop was planned. Because of the results of the Public Prosecutor, the local authority ordered additionally that not only the part were the modification

welds were present had to be replaced by stainless steel pipes but that all the carbon steel pipes, containing medium with more than 200 ppm hydrogen cyanide, had to be replaced before January, the 1st, 2002.

Indeed, while the investigation following the 1st incident was still going on, a 2nd incident occurred in the ACN-units. This situation constituted a part of the file in connection with the 1st one so, as a consequence, it is shortly presented in the following paragraph.

Another aspect of the question was the outside corrosion. The operator stated that a reduction to 10% of the initial wall thickness was still acceptable due to over design in the initial construction. This was not accepted by the local authority : it ordered that in the future, all the pipes and installations need to be replaced in the case where wall thickness is reduced to less than 50%.

The Public Prosecutor still kept doubts about the integrity of the plants. However, the operator had already replaced the most critical spots by stainless steel constructions; After lengthy discussions between all the parties involved, it was decided that the plants were safe enough to be operated again.

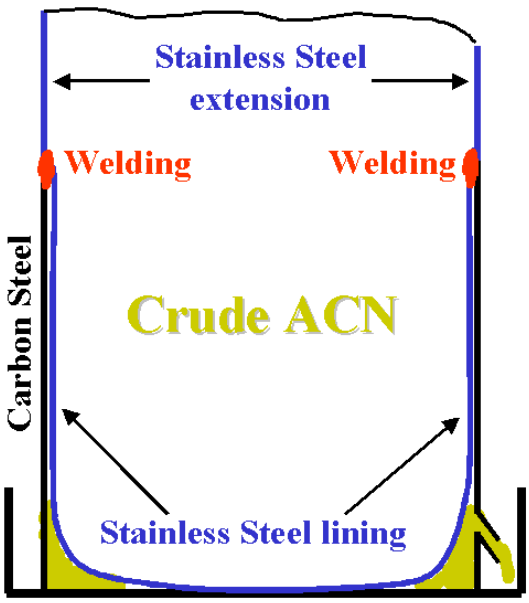
Reminding of the accident dated December 2000, the 6th (n°ARIA 24853)

From a carbon steel storage tank with a stainless steel lining, a leakage of about 600 l of crude product took place. Fortunately, the tank was located in a liquid tight tray.

The product contained 10% hydrogen cyanide. The leakage from the tank was caused by a ruptured weld in the stainless steel inner tank lining. This lining had been constructed in 1974, after a leakage due to cyanide stress corrosion. On the drawing, it is possible to see that the upper side extension of the tank was made of stainless steel.

The lining was 2 meter high.

Due to the rupture, the crude product was able to attack the carbon steel material of the tank. Because there was an opening to the environment at the bottom of the tank, the incident was immediately observed.



The direct measures were a foam layer to prevent evaporation of hydrogen cyanide. The content of the storage tank was immediately pumped into another tank and the damaged tank was blocked for normal operation. The spilled crude ACN was transported to the waste-water treatment plant of the operator.

After investigations, I seems that also in this case, stress corrosion was the probably cause. The operator explained that this lining was made as a low-cost investment.

After this incident, the operator exchanged this tank with a tank completely made of stainless steel. A comparable other storage tank will be replaced in due time..

Incident in April 2001 : (N°ARIA : 24854)

During the start-up after the maintenance stop, a regular water run was carried out for about 2 h. This means that the equipment is filled with water to test the tightness of the equipment. A stainless steel pipe showed an unwanted leakage. Since no toxic process fluid was present, this incident needed not to be reported to the authorities. Nevertheless, the company informed the local authority and the Mayors of the surrounding villages. This incident was also investigated.

Because stainless steel is susceptible for chloride stress corrosion, and chloride is present in the isolation material around the pipes, initially the occurrence of this kind of corrosion was investigated. A large number of spots in various stainless steel pipes were analysed. These results excluded chloride stress corrosion as a possible cause. Further investigations showed that the stress corrosion occurred at the place were frequently the installations are cleaned with caustic soda solution. Because of the polymerised product, the installation must be cleaned frequently. Again, the Public Prosecutor doubted the integrity. Because of the safety risks in this case, the local authority asked again a new assessment to TNO: It agreed that the most probable cause was caustic stress corrosion. Thus, the stainless pipe was replaced.

As an extra safety precaution, the operator was forced to test the equipment tightness by filling the system with water and nitrogen, applying the maximum process pressure for 24h. These tests were carried out under supervision of the local authority and TNO. Since no leakage was detected, the operator received permission to restart the production of ACN again.

As needed measures, the replacement of all carbon steel pipes was ordered before January, the 1st, 2002. Also, the enhancement of the gas detection system should be carried out in this period. Total repair of the outside corrosion should be ready before 2004.

LESSONS LEARNED

These incidents lead to the following lessons learned :

✓ Impact of ISO 14000

It became clear that certification of a company according to ISO 14000 does not guarantee compliance behaviour. ISO 14000 is comparable with E-mas. However, due to these incidents, this certificate was finally withdrawn.

✓ Database system for maintenance and inspections :

During the operator's investigations, the Public Prosecutor and TNO, it became obvious that historical data about maintenance and inspections of the ACN plant were not traceable. Plant modifications were not incorporated in the

actual schemes of the ACN plant. Inspections results were often not transparent for outsiders. There was no system to monitor the execution of inspections under the authority of the plant manager.

The authorities ordered that the operator uses a database for planning and monitoring of all relevant inspections. Such system was introduced for the entire operator's production site, in this part of the Netherlands. The ACN plant was used as a pilot for this database system.

✓ Modification of the environmental permit procedure :

It appeared that there was a different inspection regime for installation parts constructed before and after 1984. The regime for the elder installations parts was less strict than the one for the newer parts. This was remarkable because inspection of elder installation should be stricter due to a higher risk factor.

It was decided to apply the same inspection regime for all plants, based on Seveso II. As a consequence, 42 environmental permits of the operator will be revised on this issue.