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Measures taken on 3 Dutch industrial sites to prevent emissions of chlorinated (micro)pollutants between 1985 and 2002

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Summary

This report discusses an overview of the measures taken by the three main ‘chlorine’ production locations in the Netherlands since the mid-1980s to prevent emissions from (by-)products. These sites were selected because of the fact that they are ‘home’ for most of the production processes that were a priority with regard to emissions to air and/or water and to ‘suspect’ products in the main phase of the chlorine chain study. The three companies are:

- Akzo Nobel Botlek¹,
- Shell Rotterdam² and
- Akzo Nobel Delfzijl³.

The end-of-pipe measurements of OVOC revealed little or no evidence of unknown emissions from the chlorine industry. This finding is consistent with this study into measures that the chlorine industry has taken in recent decades to minimise emissions to air and water. Virtually all of the plants that were investigated treat emissions to air with vent-gas incinerators and emissions to water with (advanced) biological and/or physical wastewater treatment plants. In general, these measures have led to large reductions of emissions of known chlorinated compounds. Furthermore, such measures are likely to prevent emissions of chlorinated micropollutants, a fact that was confirmed by the DR-CALUX measurements conducted within framework of the OVOC study.

The report arrives at the following general conclusions for the individual plants:

1. Akzo Nobel Botlek (chlorine production, including herbicide production at Nufarm and EDC/VCM production at Shin-Etsu): The OVOC DR-CALUX measurements of the effluent of the Biobot and one EDC sample showed DR-CALUX 2,4,7,8 TCCD equivalents below detection limit, with emissions to air passing through an incinerator. Contamination of products seems unlikely in light of previous product analyses, which showed negligible contamination levels of dioxins and other compounds.
2. Shell Nederland Chemie (AC/ECH production of Resolution and PVC production of Shin-Etsu): Emissions to air are incinerated. The discussion focused on emissions to water, which have been reduced to less than 1 ton per annum of EOCl at concentrations close to non-detectable levels. Dioxin emissions have been reduced to non-detectable levels.
3. Chemiepark Delfzijl (chlorine and chlorinated solvent production at Akzo Nobel Delfzijl, production of ethyleneamines at Delamine, and production of Twaron at Teijin Twaron). The production of chlorine and solvents are about to close down. Emissions to air are incinerated. Emissions to water are treated, but there is no biological wastewater treatment. There is no information to determine whether any contamination of products might be relevant.

More generally, the conclusions are:

¹ This site includes crop-protection chemical production, owned by Nufarm, and EDC/VCM production, owned by Shin-Etsu PVC B.V.

² The chlorine-related activities on this site are actually no longer owned by Shell. They now involve AC/ECH/Epoxy production by Resolution B.V and PVC production by Shin-Etsu PVC B.V.

³ This site includes production by joint ventures with Akzo Nobel or by former Akzo Nobel companies, particularly the ethylene amine production by Delamine and polyaramide production by Teijin Twaron B.V

1. The Dutch chlorine industry has taken a considerable number of end-of-pipe and in-plant reduction measures in the last 15 years. Virtually all emissions to air and water are now treated with vent-gas incinerators or advanced water treatment plants.
2. This has led to considerable reductions in the emission of known organochlorine compounds.
3. The types of measures taken are of a nature that they are likely to result in high reductions in emissions of chlorinated micropollutants.

Does this imply that the chance that chlorinated micropollutants will be emitted has been fully eliminated? This conclusion is not valid, as some issues remain that exceed the scope of the OVOC study. These issues involve the formation of micropollutants within processes, in combination with significant down-time for measures intended to reduce emissions to water or air, the unexpected contamination of product flows, and unanticipated errors in the handling of waste flows contaminated with micropollutants. This study was not designed to analyse these issues in more detail, and it can therefore provide no conclusions about the probability of these problems.

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1 Introduction

This report is one of the background studies which form a part of the Main Phase of the Research Programme Chlorine Chain Follow-up Studies (OVOC, see van Hattum et al., 1989.).

The major part of the Main Phase consisted of analytical research into emissions of chlorinated micropollutants from the Dutch chlorine chain. The main vehicle to perform this research was a sum parameter measurement on the basis of the DR-Calux method (bio-assay). This method basically detects dioxin-like responses, irrespectively of the specific compound present in a sample. By different clean-up methods, 'false positives' (i.e. compounds that give a positive response in the test, but do not have the persistence or bioaccumulative properties of dioxins) can be prevented. The DR Calux method hence gives insight if, apart from 'true' dioxins, other, yet unknown, compounds with dioxin-like properties are emitted.

The overall results of this research were rather reassuring: With a few exceptions, for most plants monitored the DR Calux response was below detection limit, could well be explained by known dioxin emissions, or was in absolute terms low. Only for some product samples questions had to be raised.

Initially, it was planned to concentrate the background studies of the Main Phase on:

1. Assessing the importance of current and former emissions of chlorinated micropollutants;
2. The importance of naturally produced organochlorine compounds compared to current emissions of chlorinated micropollutants.

This plan was based on the assumption that chlorinated micropollutants, when found, could be identified. However, since the actual emissions of chlorinated micropollutants seem to be very low, and cannot be identified, the original approach was seen as less useful by the guidance committee of the project. Hence, it was decided to reformulate the goal of the background studies:

1. The importance of current versus historical emissions would be analysed for dioxins.
2. The second question was left out since no identification of substances giving a positive DR Calux response could take place, and hence no comparison could be made with any natural production of such organochlorines. The Steering Committee of the project found it more relevant to answer a totally different question here. Experience shows that chlorine can be reactive. There is a large amount of documentation about unexpected chlorinated by-products found in various production processes (e.g. Thornton, 2000). If formed, these might still unknowingly be emitted. The analytical work in the Main Phase at least suggests that this problem is not present anymore. Historical research into measures taken by companies in the chlorine chains to prevent emissions of by-products could confirm this picture. Hence, this historical research was seen as more relevant than the original plan.

This report discusses for the three main ‘chlorine’ production locations in the Netherlands an overview of the measures taken by companies involved since the mid-1980s to prevent emissions of (by-)products. The focus on these three locations was based on the fact that these are ‘home’ for most of the production processes that were a priority with regard to emissions to air and/or water and to ‘suspect’ products in the Main Phase of the chlorine chain study⁴. It is structured as follows:

- Chapter 2 discusses shortly the main reasons for formation of by-products.
- Chapter 3-5 discuss for the three main ‘chlorine sites’ in the Netherlands (Akzo Nobel Botlek⁵; Shell Rotterdam⁶, and Akzo Nobel Delfzijl⁷) the measures taken, taking into account the main reasons for formation of by-products (and possibilities for their prevention) discussed in chapter 2.
- Chapter 6 draws overall conclusions.

The time available for this work was relatively limited (some 3 days per location). The work described in chapter 3-5 was done as follows:

- Process descriptions were made, mainly on the basis of the chlorine chain study (Tukker et al., 1995). For each process, in a box information about any chlorinated micro-emission data is given, referring to earlier work (Tukker, 2000a, 200b).
- Since around 1990 it is for many companies in the Netherlands common practice to produce annually an Environmental Report. Where available, the annual Environmental Reports were obtained from the companies at stake.
- Since the early 1990s, on a regular basis emission reduction covenants were signed between various industry branches, such as the chemical industry, and the Environment Ministry. Within the framework of these covenants, most

⁴ One other main location is Akzo Nobel Hengelo. Since in 2002 Akzo Nobel and the Environment Ministry decided to agree on closure of this plant within the framework of a reduction plan for chlorine transport, including this plant could not be regarded as a priority. The Delfzijl location is still included, though many of the current production processes will be re-arranged or re-structured as a consequence of the same agreement. We refer to chapter 5 of this report.

⁵ This site includes crop protection chemicals production owned by Nufarm, and EDC/VCM production owned by Shin-Etsu PVC B.V.

⁶ The chlorine-related activities on this site are actually not anymore owned by Shell. It concerns AC/ECH/Epoxy production by Resolution B.V and PVC production by Shin-Etsu PVC B.V.

⁷ This site includes production by joint ventures with Akzo Nobel or by former Akzo Nobel companies, particularly the ethylene amine production by Delamine and polyaramide production by Teijin Twaron B.V

companies covered in this report had to produce every 4 year a so-called Company Environment Plan, that evaluated emission reduction measures taken in the past period, and identified emission reduction measures to be taken in the next years. Where available, such Company Environmental Plans were collected as well.

- Face-to-face or telephone interviews were held with representatives of Akzo Nobel (covering the locations of Rotterdam Botlek and Delfzijl), Shin-Etsu (covering the EDC/VCM and PVC production at Rotterdam Botlek and Shell Pernis), Resolution (covering AC/ECH/epoxy production at Shell Pernis), Nufarm (covering crop protection chemical production at Rotterdam Botlek), Delamine and Teijin Twaron (covering ethylene amine production and Twaron production at Delfzijl)
- On the basis of all this information, a draft overview of measures taken was made.
- The interviewees were given the opportunity to react on this draft; comments and suggested additions were evaluated and the report was adapted on this basis.

2 Formation and emission of chlorinated by-products

There is already for a long time attention for the formation of by-products in processes where chlorine is used. Chlorine is reactive, and depending on the purity of the feedstocks used and process at stake, more or less complex mixtures of byproducts (often specific for the process) might be formed. Since in general a chlorinated compound tends to be more bioaccumulative and persistent than its non-chlorinated counterpart, formation of by-products in the chlorine industry tends to be a more critical issue than in the chemical industry in general (e.g. Thornton, 2000). Hence, over time, the chlorine industry has taken a variety of measures to prevent formation and emission of such by-products.

Various authors have suggested characteristics of processes that give an indication of the probability of formation of by-products (see e.g. the dioxin reviews of Bremmer, 1994, and Fiedler, 1994):

- The presence of active chlorine;
- The availability of precursors that, together with active chlorine, may easily form 'complex' compounds;
- The presence of a catalyst⁸ or UV-light; and/or
- High temperatures.

The logic behind these criteria is clear. First, chlorine must be available in an active form, since otherwise no (important) reaction will take place. Second, in production processes it is usually intended that chlorine reacts with another compound (e.g. the formation of EDC from chlorine and ethene). But since at technical scale feedstocks are never 100% pure, the chlorine will react as well with impurities in that other compound⁶. Third, UV light and catalysts might contribute to a partial breakdown of the non-chlorinated feedstock or other than the preferred reaction route. The same applies for high temperatures⁷. All these potential by-products formation routes can serve as handles to reduce the potential amount of by-products (e.g. not using elementary chlorine in the paper and pulp bleaching process, the use of very selective catalysts and /or of appropriate reaction conditions (UV/temperature characteristics), or working with more pure feedstocks).

If, for whatever reason, by-products are formed, in-process clean-up measures or end of pipe measures may be applied to prevent a flow of by-products ending up as emission or as impurity in the product. Examples here are the separation of by-products in EDC and incinerating these for HCl-generation, or tight water and air emission reduction measures.

⁸ The importance of catalyst was mentioned in the aforementioned literature. To some extent this is surprising, since catalysts tend to support and speed up specific reaction pathways, and normally reduce the amount of by-products.

⁸ For instance, if in raw materials already organic components are available with ring structures, there is a higher chance on formation of chlorinated aromatics. For instance, Fiedler (1994) claims that the chance of finding dioxins as a by-product in production of the following compounds decreases in the following order: chlorophenoles > chlorobenzenes > aliphatic organochlorines > inorganic chlorine compounds

⁸ Where as a general rule one has to acknowledge of course that in chemical reactions between two or more compounds there are always competing reaction pathways and yields never can be (though in many processes they might come close to) 100%.

Given the above, during the interviews with companies the following approach was chosen:

- The inputs of chlorine and main other feedstocks were followed from gate (input) to gate (output)
- It was discussed which measures had been taken between 1985 and 2002 in the following steps:
 - Use of more pure feedstock or change of feedstock
 - Change of process conditions (catalyst, temperature, reactor design, etc.)
 - New separation steps for separating the main product flow from any contaminants;
 - Changes in waste management of separated contaminants;
 - Changes in end-of-pipe measures concerning emissions to water and air.

The next chapters give per location and per main production unit a discussion of these issues. It has to be stressed that this report does not aim to give a complete overview of all emission reduction measures taken; we concentrated on emission reduction measures that are likely to have an effect on emissions of chlorinated substances only.

3 Akzo Nobel Botlek

3.1 Introduction

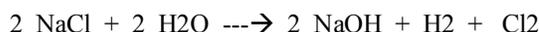
Akzo Nobel Botlek is by far the largest location for production of chlorinated compounds in the Netherlands. This location is home to the following production plants⁹

- Production of chlorine via membrane analysis;
- Production of VCM via EDC, which in turn is produced again from either chlorine and ethene, or oxychlorination of ethene and hydrogen chloride (HCl);
- Production of the crop protection chemicals MCPA and MCPC.

3.2 Production of chlorine

3.2.1 *Description of the process*

Chlorine and sodium hydroxide and hydrogen are produced by means of electrolysis of salt. The following reaction takes places:



In this process, the anode and cathode liquid have to be separated. This can be done by either mercury, a diaphragm, or a membrane. Since 1983, Akzo Nobel applies the membrane process in Rotterdam¹⁰. The production capacity was originally 250.000 tpa in 1983. In 2003 an expansion to 490 ktpa was realised, and by 2006 a further expansion to about 600 ktpa will be realised¹¹. The barrier between the electrodes is formed by an ion-exchanging membrane. This membrane conducts electric current through the transport of sodium ions. However, OH ions also diffuse through the membrane. These ions are neutralised by adding hydrochloric acid. The separation with the aid of membranes means that the strength of the caustic soda formed cannot be affected during its formation. The strength of the caustic soda is around 23% / 32% by weight and will therefore have to be increased by evaporation. The chlorine gas formed is cooled, dried with sulphuric acid and compressed and condensated. The hydrogen gas is washed to remove the caustic soda, and then again dried, cooled and compressed. The advantages of this process are:

- the process uses less energy than the other two processes;
- the caustic soda is very pure (compared with the diaphragm process);
- substances like asbestos and mercury are not used.

The disadvantages are the substantial investment costs involved and the degree to which the necessary purity can be achieved.

⁹ On this site also production of methylalkyls takes place. These processes are either chlorine-free, or use substances like ethylchloride in a condensation reaction to an inorganic compound, and such reactions were not regarded a priority in the main phase of the OVOC study.

¹⁰ Production of chlorine on this location started in 1961 via mercury electrolysis.

¹¹ These expansions in part are related to the agreement of Akzo Nobel with the Ministries of Environment and Economic Affairs to reduce chlorine transport, leading to the need for a higher on-site production in the Botlek area.

Box: Indications of formation of chlorinated micropollutants

In several literature sources the production of micropollutants has been indicated, though in small quantities.

Chlorine production plants have been an important source of dioxins, specifically in cases when graphite electrodes were used. Such electrodes are not used anymore in today's plants. Later, also dioxin formation was detected in the plastic tubes used for chlorine transport from the electrolysis cells. Replacing them by a different material solved that problem as well. For a Swedish plant based on mercury electrolysis (Hydro Polymers in Stenungsund plant), in former research we obtained a good insight into mass balances of the most important chlorinated micropollutants like dioxins chlorobenzenes and chlorophenoles. For a chlorine plant with a throughput of 114,300 tpa chlorine, the emissions for 1994 were (Tukker et al., 1996):

AOX: 2 kg/yr

Chlorobenzenes: 21 g/yr;

Chlorophenoles: 210 g/yr;

Dioxins/furans: 7 ug TEQ TCDD/yr.

Though the reported emissions of chlorinated micropollutants is rather low, sediment surveys near the Stenungsund plant show concentrations of HCB and other micropollutants. For this specific plant, at the time the sludge from water purification contained some dioxins and was landfilled, implying a disposal of some 13 g dioxins to a landfill per year. It has to be noted that this plant also produces EDC, VCM and PVC. This is irrelevant for this Dutch plant in Rotterdam Botlek since sewage sludge from waste water purification plants is incinerated.

3.2.2 *Measures taken between 1985 and 2002*

Below, the key measures taken to prevent formation or emission of chlorinated (by-) products are given.

Feedstock input:

In the chlorine production, relatively small amounts of NCl₃ are produced. Akzo Nobel used to remove this compound from chlorine by passing the chlorine flow through a CCl₄ (Tetra) scrubber. Tetra is a substance with a high ozone depletion potential and can only be used with a special permit within the framework of the the Montreal protocol. Contaminated tetra was sent for destruction in Akzo Nobel's CHC incinerator and replaced on a regular basis with new amounts. However, less than 10% of the tetra used ends up in the chlorine product . There is a slight chance, if the tetra is not removed in the customer's process, that it might be emitted to the atmosphere at the location of the chlorine users.

Akzo Nobel now uses another quality of salt, which greatly reduces the NCl₃ formation during chlorine production. The tetra scrubber step will be eliminated by 2005 (Akzo Nobel Botlek, 2003)

Process conditions:

No relevant changes in process conditions have been identified.

New separation steps:

As indicated above, a separation step making use of a tetra-scrubber will be eliminated by 2005.

Waste management:

No relevant changes in waste management practices have been identified. However, waste reduction programs are common practice.

Emission reduction measures (air and water)

A normal measure at almost any chlorine plant is to lead any vent gas from chlorine production through an absorber that contains a sodium hydroxide (NaOH) solution. In the absorber the chlorine is transformed into hypochlorite; the remaining other reaction products, nitrogen (N₂) and oxygen (O₂), are directly emitted to air (Akzo Nobel Botlek, 2003).

The chlorine plant has various over- and underpressure safety slots, that were filled with hexachlorobutadiene (a black-list substance). This substance was used since it does not react with chlorine. In the near future these safety slots will be replaced by mechanical devices which eliminates the need to use hexachlorobutadiene (Akzo Nobel Botlek, 2003).

Furthermore, a large number of other smaller measures like installation of leak-proof floorings, better detection and safety devices, introduction of more durable piping, for instance titanium piping, have been taken in the period since 1985 (Akzo Nobel Botlek, 2003).

3.2.3 *Comments*

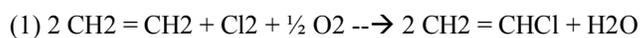
Virtually all of the measures identified above deal with major emissions of chlorinated compounds rather than micropollutants. As indicated in the box on page 12, in another chlorine production plant unexpected dioxin formation occurred by a reaction of chlorine with the specific plastic transport pipes used in that plant. The dioxin contamination was initially detected in landfilled sewage sludge of the waste water treatment. At Akzo Nobel Botlek it is unknown if such problems occur; the OVOC measurements which were done after end-of-pipe treatment did not show significant emissions. Furthermore, sewage sludge from Akzo Nobel's waste water treatment plant is incinerated, which should destroy any dioxins when present.

3.3 **Production of EDC and VCM****3.3.1** *Introduction*

Shin-Etsu is the sole producer of dichloroethane (EDC) and vinylchloride monomer (VCM) in the Netherlands. This company took over ROVIN v.o.f, the EDC/VCM/PVC producing joint venture of Shell and Akzo Nobel, per 1 January 2000. Shin Etsu produces EDC and VCM at the site of Akzo Nobel Botlek.

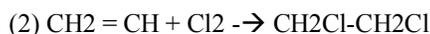
3.3.2 *Process description*

The vinylchloride monomer (VCM) is produced from ethene, chlorine and oxygen according to the following overall reaction:



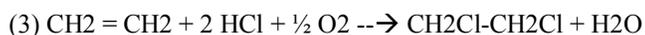
There are a number of distinct steps in this process, which are illustrated in figure 3.1. The intermediate product 1,2-dichloroethane (EDC) plays a central role in this process. EDC is prepared by direct chlorination or oxychlorination:

- in direct chlorination, ethylene and chlorine are used:



EDC acts as a solvent. The two reactants are added to the solution in almost equal molar measures at around 50°C. Iron is added into the process; the iron chloride formed acts as a catalyst.

- in oxychlorination, ethylene, hydrogen chloride and oxygen are used.



This reaction occurs at 220-240 °C and under increased pressure (4 bar). Copperchloride is used as a catalyst.

Water is separated from the EDC produced in a decanter. After this, EDC is washed with water and caustic soda to remove HCl, Cl₂ and contaminants that are soluble in water. Water is removed by phase separation in the wash step; the final part by distillation. Once removed, the water is cleaned using a stripper and a biological treatment with activated carbon (see chapter 3.5).

In the above reactions, chloroethane, trichloromethane, tetrachloromethane, 1,1,2-trichloroethane and tetrachloro methane¹², are produced as by-products as well as traces of chlorinated aromates. The EDC is cleaned of these contaminants by distillation. The by-products together account for less than 3.5% (ECETOC 1991). The by-products, together with highly chlorinated waste from third parties, are treated in an incinerator for liquid waste owned by Akzo Nobel (see § 3.3.3), during which HCl is recovered and then used again in the oxychlorination.

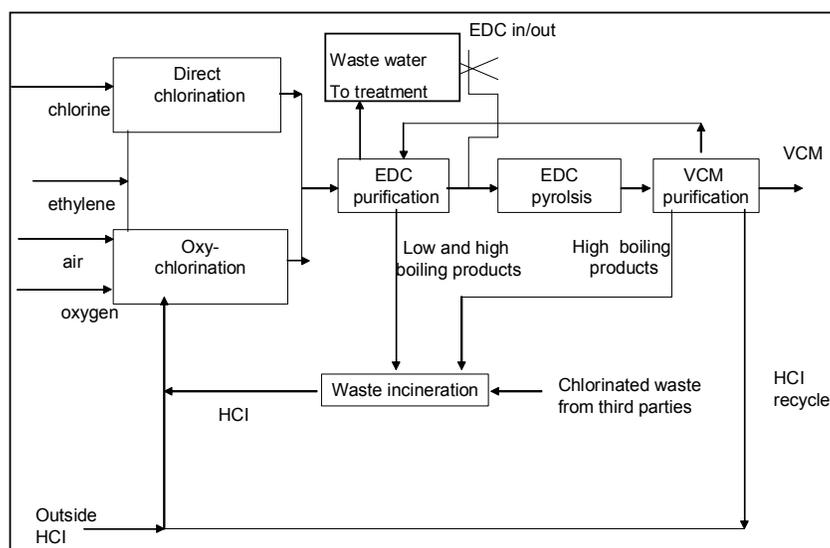
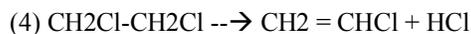


Figure 3.1: Schematic representation of the production of VCM (unbalanced)

¹² This is reflected by the 3rd Environmental Company Plan of Shin-Etsu.

After being treated, the EDC is converted into VCM by pyrolysis at around 500°C and 10 bar.



This produces various chlorinated and non-chlorinated by-products. These, together with non-reacted EDC, are returned to the process. The HCl that is released is used in the oxychlorination. During the process solid waste is released in the form of solids from process filters, calcium chloride from the drying of process flows and sewage sludge. This waste is incinerated as chemical waste at AVR-Chemie¹³.

Box: Indications of formation of chlorinated micropollutants

The EDC production, particularly via oxychlorination, is one of the focal points in the debate whether the chlorine industry is a source of chlorinated micropollutants. As indicated in the main text, there is little doubt that dioxins, and other PTB-like by products, are produced during EDC production (e.g. Evers and Olie, 1989 and Evers, 1996). The debate focuses on the quantities and the question whether the by-products do actually reach the environment or are destroyed or captured by emission reduction technologies (e.g. Fejes and Wennberg, 1994 and Fejes et al, 1996). A study by Schooneboom (1996) addresses the EDC/VCM/PVC production. Schooneboom reported initially on the basis of an other article a contamination of 55 ng/kg TEQ TCDD in EDC. A cross-check with original literature showed that a contamination of 55 ng/kg OCDF in commercial EDC was reported by Heindl and Hutzinger (1987). It is not clear if the sample was EDC from direct or oxychlorination. It appeared that this figure was mistakenly taken over as 55 TEQ TCDD in Schooneboom's report. A correction on this and some other errors has recently been published by the University of Amsterdam (Schooneboom, 1996). In terms of toxicity equivalents, 55ng/kg OCDF means 0.055 ng/kg TEQ. This would imply that the total Dutch EDC production via oxychlorination (approx. 900,000 tpa) would contain approx. 50 mg TEQ TCDD or less. Of the EDC produced in the Netherlands the vast majority is converted to PVC; approximated. 5% is sold as high pure EDC to third parties. Recent research reported by Carrol et al. (1996) confirmed the order of magnitude of concentrations reported by Heindl. The DR Calux results and GCMS identification in the Main Phase of the OVOC study also resulted in very low values of by-products in EDC. According to Shin-Etsu, dioxins formed in oxychlorination mainly end up in the waste water which is treated in the Biological waste water treatment, where they are absorbed to active carbon and sludge.. This is supported by the DR Calux measurements of the effluent of the Biobot which show low activity. Both solid waste streams are incinerated as chemical waste.

3.3.3 Measures taken between 1985 and 2003

Below, the key measures taken to prevent formation or emission of chlorinated (by-) products are given.

Feedstock input:

- As far as known no measures with regard to feedstock input have taken place or were deemed necessary.

¹³ Editor's note: AVR-Chemie is the most important Dutch hazardous waste management company.

Process conditions:

- The latest installed oxychlorination line (built in 1996) uses pure oxygen rather than air as input. In order to have the fluidized bed system work properly, vent gases are partially recirculated. The advantage of this system is that the all oxy gas flow is a factor 50 lower than of the two older oxychlorination reactors that have air as input. As explained below, all vent gases are treated in an oxy-vent gas incinerator. However, in case of discontinuity of this incinerator the (much smaller) vent gas flow from the oxygen-oxychlorination line can be re-directed to the VCM vent gas incinerator.
- Process conditions are continuously monitored and like any plant the process has been optimised over time to increase yields, etc. However, the losses to byproducts in absolute terms were always already relatively low (some 2-3%). It is not clear if also optimizations have taken place in order to reduce production of substances like dioxins.

New separation steps:

- The EDC wash water flow to the biological waste water treatment first is led through a steam stripper to remove volatile components. The steam stripper is operational the startup in 1971.
- A second steamstripper was built in 1996.

Waste management:

- EDC production at Botlek started in 1971. In the first few years, the EDC and VCM tars were incinerated at sea. This practice was stopped in 1975. Other management practices (landfill, dumping at sea) were not relevant.
- Soon after the start of the EDC and VCM production at location of Akzo Nobel Botlek in 1971, the so-called 'Kringloopinstallatie' (an incinerator for liquid chlorinated waste) was built. This installation came on stream in 1974. This installation would incinerate all CHC (chlorinated hydrocarbon) byproducts generated from EDC production and other liquid chlorinated waste (a.o. from Nufarm, but also from third parties). The installation basically converts CHC into CO₂ and HCl, that can be used in oxychlorination. This installation is still owned by Akzo Nobel.
- Since 1992, also the waste water flow from the CHC incinerator is treated in the biological waste water treatment (Akzo Nobel, 1998:).

Emission reduction measures (air and water)

- In 1991 a VCM vent gas incinerator was built. This incinerator is now part of the plant owned by Shin-Etsu. This incinerator deals with process rest gases, breathing losses, and losses from the EDC storage. This directly resulted in a CHC emission reduction of 95 % (Shin-Etsu, 2002). The vent gas incinerator has enough capacity to deal with vent gas flows, apart from irregular situations when major relief valves are blowing off. The availability of the incinerator, including the upstream ventheader system has been gradually increased to > 98,5%. When the incinerator is not available, the older vent gas scrubber system (based on washing vent gas with an NaOH solution) is used. Any micropollutants present in the vent gas will be destroyed. When the emission gases from this incinerator are cooled for heat recovery, traces of dioxins can be formed - the concentrations appeared to be just over the 0.1 ng TEQ/Nm³. For this reason, Shin-Etsu has now installed a dioxine-adsorber based on a wet

brown coal system, that reduced concentrations to $< 0.02 \text{ ng TEQ/Nm}^3$ (Shin-Etsu, 2003).

- In 1972 an oxy-vent gas incinerator was build. Availability is about 99%, target < 75 hour off-stream (Shin-Etsu, 2003). This incinerator deals mainly with the vent gas that comes from the three oxychlorination units, and is owned by Akzo Nobel. The two older units use air as input (both for supplying oxygen to the oxychlorination and as a basis for the fluidized bed system). The third unit built in 1996 uses pure oxygen as input, and has a vent gas recirculation system to ensure sufficient gas throughput through the fluidized bed. The ventgases (which still contains EDC) first go through an adsorber-stripper which captures most of the EDC present. The output from this plant goes to the oxy-vent gas incinerator.
- Fugitive emissions of substances like VCM now become a more important point of attention particularly after installation of the vent gas incinerators. There are about 12.000 flanges and 5.000 valves in the plant, plus a large number seals of pumps, compressors, etc.. By continuous monitoring and improvement Shin-Etsu targets this problem (Shin-Etsu, 2003)
- For waste water treatment of the whole site, a biological treatment plant has been build (see chapter 3.5).
- The oxychlorination unit built in 1996 is equipped with a closed cooling water system for all product coolers. This prevents emissions to water in case of leaking of one of the coolers.
- In 2001 a closed cooling water system for the direct chlorination unit was put into use.
- Possible emission of EDC through one of the other product coolers via cooling water are closely monitored.

Other

- Shin-Etsu has developed a risk-based inspection system. Benefits of risk-based inspection programs are: lesser downtime (which directly leads to lesser emission), lesser disturbances and incidents which also leads to lesser emissions.
- A large number of other measures have been taken, like installation of leak proof floorings, renewal and improvement of closed chemical sewer and contaminated water sewer, separation of sewer systems, enlargement of storage capacity for contaminated water (buffer before steam stripper and Biological treatment), better detection and safety devices, leak proof sample connections.

3.3.4

Comments

In principle all potential non-intentional outputs of the process are managed: gaseous emissions go to the two vent gas incinerators; waste flows to the CHC incinerator, and waste water from the EDC wash first is treated in strippers and after that in the so-called Biobot (see chapter 3.5). These systems are of course primarily built for main emissions such as EDC and VCM. However, if all these systems are operational for 100% of the time with their regular effectiveness, there seems a limited risk of emissions of chlorinated micropollutants. After all, they are destroyed in the incinerators or captured in the waste water treatment. The main risks seem to be a (potential) production of chlorinated by-products in the process (chlorination, oxychlorination and EDC-cracking), combined with:

- Outflow with the EDC wash water and insufficient effective treatment of the waste water flow. However, the measurements in the Main Phase of OVOC showed a virtual zero DR Calux response. This danger seems hence not relevant in practice.
- Emission with untreated vent gas during the 1-1.5% of the time that the vent gas incinerators are not operational.
- Outflow with the products: EDC or VCM (HCl is not relevant since it is totally re-used on site). Outflow with the products is relevant to a limited extent. For EDC, in the OVOC study, response just above the detection limited at 20 pg/kg was found in the DR Calux test, a bioassay that measures total dioxin-like activity. GCMS of EDC found some 50-500 µg/kg by-products in total, mainly chlorinated esters, -ethers and -benzene groups. For VCM, no DR Calux test or GCMS was done but at least dioxin measurements of PVC produced with VCM show also negligible values (see chapter 4.2).

3.4 Production of crop protection chemicals (MCPA, MCPP, D-MCPP and D-2,4 DP)

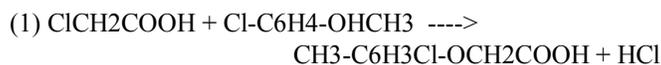
3.4.1 Introduction

At location of Akzo Nobel Botlek, Nufarm produces crop protection chemicals (CPCs). It concerns:

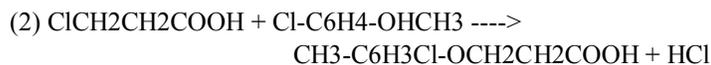
- MCPA: 2-methyl-4-chlorophenoxyacetic acid;
- MCPP: 2-methyl-4-chlorophenoxypropionic acid;
- D-MCPP: (+)-(R)-2-methyl-4-chlorophenoxypropionic acid;
- D-2,4 DP: (+)-(R)-2,4 dichlorophenoxypropionic acid.

3.4.2 Process descriptions

MCPA, 4-chloro-2-methyl-phenoxyacetic acid is produced by means of a reaction of monochloro acetic acid (MCA) with 2-methyl-4-chloro-phenol:



MCPP, 4-chloro-2-methyl-phenoxypropionic acid is produced by a reaction of chloropropionic acid with 2-methyl-4-chloro-phenol. :



The 2-methyl-4-chloro-phenol (chlorocresol) is produced by chlorination of o-cresol. The crude chlorocresol is purified, and the tars from the purification step are incinerated in Akzo Nobel's CHC incinerator. Waste water flows are treated in the biological waste water treatment (see section 5).

The production of D-MCPP is almost identical to the production of MCPP, but the isobutylester of (+S)- α -chloropropionic acid is used and very specific process conditions are applied in order to ensure that only the active, (+R) component is produced rather than the racemic mixture. The production of D-2,4 DP is almost

identical to the production of D-MCPP, but the raw material, 2,4-dichlorophenol, is imported.

MCA is acquired from elsewhere (especially the plant in Hengelo) or imported ; chloropropionic acid is imported. The chlorocresol, which act as intermediate product, is produced in situ and involve the use of chlorine. A small portion of the substance is released with the effluent. During the production processes of MCPA and MCPP (hydrogen) chloride is released with the effluent after extensive treatment via the central water treatment plant.

Figure 3.2 gives an overview of one of the processes mentioned above, i.e. the production of D-2,4 DP. Production volumes cannot be disclosed since Nufarm is the sole Dutch producer. The Dutch chlorine chain study gives a production volume of 14,5 ktpa as chlorine for MCA, MCPP and MCPA together. The Company Environmental Plan of Akzo Nobel of 1998 mentions a total production capacity of crop protection chemicals of 12 ktpa.

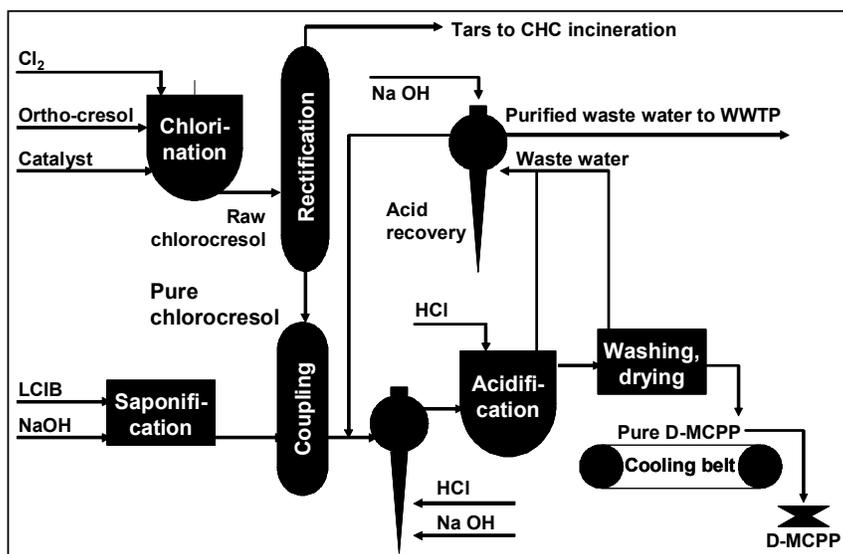


Figure 3.2.: Diagrammatic representation of the production of D-MCPP (Akzo Nobel, 1998).

3.4.3 Measures taken between 1985 and 2002

Below, the key measures taken to prevent formation of chlorinated by products are given.

Feedstock input:

Apart from input changes related to the start-up of the D-MCPP and D-2,4 DP plants no relevant changes in feedstock input have been identified.

Box: Indications of formation of chlorinated micropollutants

Emissions from the Akzo Nobel Botlek plant are listed in the chapter on EDC production. According to Fiedler (1994), the production of chlorinated compounds with ring structures, forms a relatively high risk with regard to by-products like dioxins. Schooneboom et al (1996) suggest a dioxin concentration in the product MCPA of 0.03 ng TEQ/kg . This would imply less than 0.5 mg for the total Dutch annual production. In a study into 'unexpected presence' of organochlorine compounds in the mid-eighties, Berbee (1987) found annual emissions of chlorotoluenes, hexanechloroethane, HCH chlorophenoles, and bromophenoles in the kg-range. That author considered both the EDC production and the MCPA/MCPP production as a potential source. It has to be noted these values may well be dated since the waste water treatment at Akzo Nobel has improved considerably since that time. Nufarm has submitted (confidential) test results of the raw waste water flows from the herbicide production which contained dioxins in the less than ppb range ($\mu\text{g}/\text{kg}$; which for dioxins still might be a relevant level)

Process conditions:

- The first CPC plant used a batch production system and was started in 1965. In 1976 this batch process was replaced by a continuous process.
- After a revamp, the plant became also operational for the production of D-MCPP per 1991, and for D-2,4 DP in 1992. These products consists only the active chemical rather than the racemic mixture, which implies a much more effective use of the active ingredient in the field (and hence less dispersion of organochlorines via the use of pesticides) (Akzo, 1990; Akzo Nobel, 1998)

New separation steps:

- Apart from the separation steps already included in the process description no new separation steps have been identified.

Waste management:

- An installation was build that could process the residues from the pesticide plant, allowing for incineration in the CHC incinerator (Akzo, 1990)

Emission reduction measures (air and water)

- Since 1987 all waste water is treated in the biological waste water treatment plant (see section 5).
- All processes take place in a building with a forced ventilation. Vent gases are washed to remover particularly o-cresol. Also, all process installations are connected to a vent gas washer.

3.4.4

Comments

In principle all potential non-intentional outputs of the process are managed: gaseous emissions go to vent gas scrubbers, waste flows to the CHC incinerator, and waste water from the washing step of the raw CPCs goes to the biological waste water treatment. The main risks of emissions of chlorinated micropollutants might lie in the fact of unintended production of micropollutants in critical processes like the chlorination of cresol and (to a lesser extent) the production of the raw pesticides, combined with (minor) irregularities or inefficiencies in waste water treatment and waste treatment. For dioxins the levels in the raw waste water flows seem to be in the

ppb range or less. Since no data are available on the waste water flow, it cannot be analysed if this results in a relevant mass flow of dioxins per annum.

3.5 Emission reduction measures for the whole location

There is a variety of measures that has an impact on emissions of the whole location:

- Building of a biological waste water treatment dealing with waste water from the VCM- and crop protection plant, as well as waste water from the CHC incinerator. This so-called Biobot is operational since 1986 and was gradually improved over time. The Biobot currently is preceded by two steam strippers to reduce CHC and other loads in the waste water. Waste water from the EDC/VCM production and CHC incinerator passes a sink tank to remove solid particles (particularly copper catalysts used in oxychlorination). In an aeration tank the waste water is purified by breakdown by micro-organisms and adsorption to active carbon (Akzo Nobel, 1998: 62). This resulted in reductions of (Akzo, 1990):
 - Emissions of 26 tpa CHCs to water to a level lower than the detection limit. The EOC1 emission is now below 100 kg per annum and consists mainly of chloroform and EDC (Akzo Nobel, 1998: 63).
 - Emissions of various other compounds (substances contributing to COD, copper) with 90%.

3.6 Overall conclusions

From the above, one could cautiously say that it is understandable that the OVOC study did not detect major emissions of chlorinated micropollutants (or at least dioxin-like activity via DR Calux). Under regular process conditions, all potential outputs in principle are treated via vent gas incinerators (air), an advanced biological waste water treatment combined with active carbon treatment, preceded by stripper and sink systems (water), and a dedicated incinerator for CHC waste equipped with advanced flue gas treatment. Any chlorinated micropollutants present are likely to be removed or destructed by these processes, and measurements in their outputs (as done in the OVOC study) basically confirm the effectiveness of removal and destruction¹⁴. Remaining risks of emissions of chlorinated micropollutants lies *in a combination* of the following points not covered by the OVOC study:

- Any production of micropollutants in production processes. Data on this are not known, but from the criteria mentioned in chapter 2 one can identify the EDC production (particularly via oxychlorination), the EDC cracking, and the chlorination of o-cresol in the CPC plants as the most relevant processes in this respect.
- Limitations of the mentioned end-of pipe measures. Here, the emissions during the relatively short down-times of the vent gas incinerators and, to a lesser extent fugitive emissions to air and a limited effectiveness of wastewater treatment seems to be most relevant in this respect.

Potential emissions via waste water and products are most probably not relevant. The dioxin contamination of the influent to the Biobot from the Nufarm plant is in the ppb

¹⁴ Or the absence of production of chlorinated micropollutants in these emission reduction devices.

range. Though this still could form a significant mass flow per annum, the OVOC DR Calux measurements of the effluent of the Biobot and an EDC sample showed DR Calux 2,4,7,8 TCCD equivalents below detection limit. The only other products possibly containing micropollutants leaving the Botlek location are VCM and herbicides. VCM is used for production of PVC; from other studies it is known that the amount of i-TEQ dioxins is low as well (see chapter 4). Herbicides have to comply with stringent regulations concerning product contaminants world-wide (e.g. on the basis of EU and US EPA regulations). In this context, Nufarm has to test its products on a regular basis on substances like dioxins; quantities of the different dioxin congeners are not-detectable.

4 Shell Rotterdam (Shin-Etsu and Resolution Europe B.V.)

4.1 Introduction

Shell Nederland Chemie B.V. at Rotterdam used to be an important producer of chlorinated chemical compounds. However, over the years, all chlorine-related activities have been sold (though still available on location) or closed. It concerns:

1. The production of epoxy resin via the production of ECH and AC (now performed by Resolution Europe B.V.);
2. The production of PVC from VCM (now owned by Shin-Etsu)
3. The production of pesticides (various drins; discontinued around 1990).

The next sections discuss process 1) and 2). Point 3) is not discussed anymore but in itself must have lead to a major reduction of emissions of problematic organochlorines to air and water.

4.2 Production of allylchloride, ECH and epoxy resin

4.2.1 Introduction

Epichlorohydrin (ECH, 1-Chlorine-2,3-Epoxypropane) is the most important raw material for the production of epoxy resin. In the Netherlands ECH is produced for this purpose by Resolution Europe B.V. (who took over production of Shell Nederland Chemie B.V. at the end of 2000). Until recently, ECH was also used as a raw material for glycerine in the Netherlands. This application was phased out at the end of the 1980s (SPIN 1993e). ECH is produced from chlorine and propene. An intermediate product is allylchloride (AC, 1-Chlorine-2-Propene); by-products (not only unintentional) are trichloropropane (TCP), dichloropropane and dichloropropene (DD-mix).

The production of AC, ECH and epoxy resin are dealt with in this paragraph. These products are all produced at the same locations. AC, ECH, TCP and DD are also used externally. The production of these products is one of the major chlorine consumers in the Netherlands (131 ktpa in 1990).

4.2.2 Process descriptions

Production of AC and ECH

Epichlorohydrine (ECH) is prepared via the intermediate products allylchloride (AC) and dichlorohydrine (DCH) from the raw material propene and chlorine. Figure 4.1 presents a diagram illustrating the process (Bremmer et al., 1988; Resolution, 2003).

Raw AC is produced from the raw materials propene and chlorine. The production units consist of two parallel reactor trains, one of which is always in operation while the other is cleaned.

During the reaction the by-products hydrochloric acid (HCl) and a blend of 1,3-dichloropropene and 1,2-dichloropropane (DD-mix) are produced. After separating a

propene/hydrochloric acid fraction in a pre-fractionator, AC is distilled to remove DD, among other things. The "light end" (LE) fractions are burned in two incinerators, during which hydrochloric acid is recovered.

Crude dichlorohydrine is then prepared from purified AC and hypochlorite, which is produced from chlorine and water. 1,2,3-trichloropropane is formed as a by-product of this.

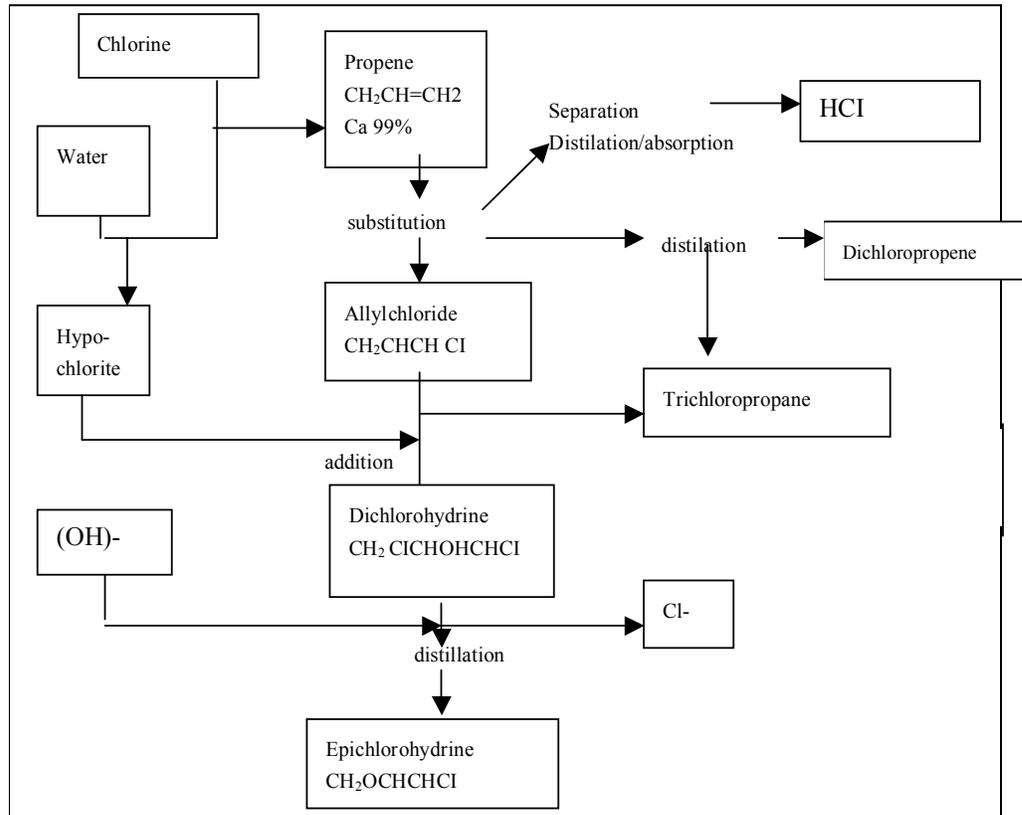


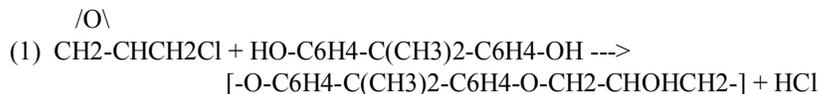
Figure 4.1 Diagram of production of AC, ECH, DD and TCP (Bremmer 1988)

ECH is formed by allowing the raw DCH to react with (OH)-. This produces inorganic (Cl)-, which is released to water. The crude ECH, which is contaminated with DCH and TCP, is stripped from the water with steam and then purified by distillation. DCH and TCP are produced during this process as bottom drainage. DCH is then recirculated internally.

The by-products of AC and ECH production, DD and TCP are purified. The 'heavy ends' (HE) of this purification are incinerated for chlorine or HCl recovery. Both the waste water flows from the crude allylchloride units and the ECH strippers are transferred after pre-treatment to the waste water treatment installation. The waste water is then successively cooled, neutralised with hydrochloric acid so that fixed substances dissolve, and finally decompose in the water treatment installation.

Internal use of ECH

ECH is used internally to produce epoxy resins. Epoxy resin is generally prepared by a reaction of ECH with bisphenol A under the influence of caustic soda and with the separation of NaCl (salt) according to:



Box: Indications of formation of chlorinated micropollutants

The process description already makes clear that the process leads to secondary products and waste flows.. In the mid-nineties, a thorough discussion was going on between Shell and RIZA about the extent to which emissions should be lowered. Various studies had shown that Shell emitted a wide range of unexpected by-products formed in the process (e.g. Berbee, 1987) and at that time the plant was one of the main emitters of EOX in the Netherlands. In the early nineties, there was a dioxin emission to air from the vent gas and waste incinerators at the Shell Chemie site of about 1 g/year. Better flue gas cleaning has reduced this number considerably. Hexachloropropylethers form the main part of the emissions to water. Due to the complexity of the emission to water, it is hardly possible to give here a better indication of substances that are emitted. All these emissions are (or at least were) mainly related to the AC/ECH production rather than the PVC production, discussed next. The Schooneboom (1996) study mentions on the basis of a review of Fiedler (1994) a possible contamination of ECH with dioxins of some 1.82 ng TEQ/kg. With a production volume of about 35,000 tpa (Tukker et al., 1995) this would imply a dioxin flow of some 0,063 g/annum. According to Resolution Europe a more realistic figure for possible ECH contamination is 0.01-0.04 ng i-TEQ/kg; with a production volume of 35 kt/a this would result in 0.4-1.4 mg/annum.

4.2.3 *Measures taken between 1985 and 2002*

Below, the key measures taken to prevent formation of chlorinated by- products are given.

Feedstock input:

The purity of propene, a major feedstock for AC production is increased from 96% to 99% or higher.

Process conditions:

Over time, the AC/ECH plant has been modernised and adapted, both for enhancing yields, reduction of energy used and reducing the amount of by-products. A major change occurred since 1999, when new or improved reactor technologies were implemented. Changes include:

- New reactor technology for AC. A first investment of around 40 million Euro was done in 1999; further adaptations are still going on.
- Improved DCH reactor technology (and additional investment of 8 million Euro to further reduce EOCl loads in 2002).

The new reactor technology for the AC production step resulted in higher yields of AC, and as a consequence less production of by-products like DD. The overall reaction principles did not change fundamentally. In general, there has been a continuous learning and adaptation process since the major 1999 changes. The improved DCH

reactor technology, in combination with the improved stripper efficiency (see below) led to a reduction of EOCl emissions from the ECH plant of 50% or more.

New separation steps:

Over time, various new or improved separation steps have been introduced to reduce the EOX flow in the waste water. These include:

- 1992, 1995 and 2002: Improved ECH stripper efficiency
- 1994: Hydrolysis tank for the effluent of the AC/ECH plant. In this tank, that has an alkaline environment at 90 °C, various chlorinated compounds present in the waste water are hydrolysed to non-chlorinated compounds and inorganic chloride(Cl)-.

Waste/by-product management:

- The by-product dichloropropene used to be sold as pesticide until the early/mid nineties. Since application of this material was banned for this use, it is incinerated for the recovery of chlorine or HCl or sold as raw material.
- Other by-products are applied as a raw material for other products: e.g. 2-chloropropane is used as raw material for other producers.

Emission reduction measures (air and water)

- Vent gases are incinerated in a vent gas incinerator.
- Emissions of chlorinated products are collected and incinerated. This has been normal practice since the plant was put on stream; however, in the late 1990s the flue gas cleaning of this combined waste/vent gas incinerator was dramatically improved to comply with the stringent dioxin standards in force for such installations.
- As indicated in paragraph 4.5, in 1983 a biological waste water treatment plant for the whole complex was implemented. This has led to a first reduction of EOX emissions (then 400 kg/day) with some 50-60%. Still, as indicated in the box shown before, the plant was one of the major emitters of EOX in the Netherlands. Via additional measures (partially described above) the emission volume was lowered over time.

Overall, the ECH/AC plant is now responsible for about 7 kg/day EOCl output which after biological treatment is some 1-3 kg/day or some one tpa to surface water coming close to non detectable levels. Due to various measures (closure of units, end of pipe measures, and in process measures) the emission of dioxins has been reduced to non-detectable levels to surface water in recent years (Resolution, 2003).

4.2.4

Comments

In principle all potential non-intentional outputs of the process are managed: chlorinated by-products are incinerated in a CHC incinerator with HCl recovery, the waste water fraction is pre-treated and goes to biological waste water treatment. The main risks of emissions of chlorinated micropollutants might lie in the fact of unintended production of micropollutants combined with (minor) irregularities or inefficiencies in waste water treatment and waste treatment, or output with products.. As for the products, only AC has been tested in the OVOC study. GCMS found some 480 µg/kg or <0,5 g/tonne of chlorinated by-products, mainly chloro(di-)propyl-ethers.

4.3 Production of PVC

4.3.1 Introduction

Shin-Etsu, who recently took over the ROVIN joint venture of Shell and Akzo, produces PVC at the location of Shell in Rotterdam. Shin-Etsu produces its VCM at Akzo Botlek and transports it to the production site by pipeline.

4.3.2 Processes

The VCM is fed to a reactor in doses, together with a suspension stabiliser, a pH buffer, an anti-foam agent and an initiator (organic peroxides). VCM reacts to PVC as follows:



When a conversion rate of 80 to 90% is reached, the polymerization is stopped with the aid of an inhibitor. After recovery of unconverted VCM, the suspension is filtered and temporarily stored. Residues of VCM are then stripped with open steam and transported to a gasometer. In fact, all water flows with a VCM content are treated in this way before being pumped to a water treatment plant. According to statements by the companies, after stripping the water is "VCM-free". In view of the high vapour pressure of VCM (3.4 bar at 20°C) this seems likely. There will probably be some emissions to water of the auxiliary substances (organic peroxides, interfacial active substances, inhibitor, methanol, pH buffers and anti-foam agent) (SPIN 1993e).

The VCM-free suspension is processed into dry PVC powder by centrifugation and drying. The air used for this is released into the atmosphere via a bag filter. VCM is recovered from various gas flows containing VCM using a condenser. PVC is produced in batches. Before the reactor is refilled it is first rinsed with water to remove residues of PVC.

During production, PVC is released as waste as a result of the filtering of the "lumps" formed in the suspension. These lumps are disposed of at an incineration plant for chemical waste. The cleaning of the reactors also produces PVC waste: a certain amount of PVC clings to the walls despite the fact that they have a coating to prevent this.

According to the Dutch chlorine chain study, the amount of PVC produced was 213 ktpa in 1993 (as chlorine).

Box: Indications of formation of chlorinated micropollutants

The production of PVC receives little attention in most of the literature on organic by-products containing chlorine (Stringer, 1994, Bremmer 1994). The emissions from the Shell site to water are over 2000 kg EOCl, but these are most likely related to the ECH-plant. For air, the Dutch Emission Registry lists only emissions of VCM.

Concerning micropollutants, there has been debate whether PVC contains dioxins. Schooneboom (1996) reported contamination of PVC with 0.86 to 8.69 ppt TEQ. This was based on a study by Swedish EPA in which two samples were taken (Allsop, 1994). Since the EDC-production by oxychlorination is in general indicated as the most suspected source of dioxins in the PVC-production, it is rather strange this reported contamination in PVC (produced from EDC) is higher than for EDC itself. In case the whole Dutch PVC use of about 250,000 tons were contaminated, this would represent an amount of 0.2 to 2 g TEQ TCDD. An extensive review by the ECVI, carried out by AEA laboratories shows that PVC is virtually free of dioxins and, taking into account the detection limits reached, certainly can not be contaminated with such levels (Wagenaar, 1996). Similar results were reported by Carrol et al. (1996); Isaksen (1996) reports similar results for PVC's precursor VCM. Wagenaar indicates it is quite difficult for laboratories to reduce background levels to sub ppt-levels, which might be an explanation of the 2 samples with higher levels.

4.3.3 *Measures taken between 1975 and 2002*

Below, the key measures taken to prevent formation and emissions of chlorinated (by-) products are given. It has to be noted, though, that unlike e.g. the EDC/VCM production or ECH production this process does not meet most of the criteria that makes it a 'high risk' process concerning formation of by-products. The main attention point always has been reduction of VCM-emissions. This was among others stimulated by the fact that in the 1970s it was discovered that exposure of workers to the on-site VCM concentrations normal at the time, could result in a rare form of liver cancer. This occupational health problem forced VCM and PVC producers to reduce emissions of VCM dramatically.

Feedstock input:

The main feedstock is VCM. No measures with regard to feedstock input have been identified or have been seen reported as potentially relevant in view of the production of chlorinated micropollutants.

Process conditions:

The production plant has been improved various times. The first units were installed in 1967 and 1972. These were improved, by 1980 so-called closed reactor technology was applied. In 1992 the old units were replaced. Emissions of VOS were diminished by reducing access points to the plant (Shin-Etsu, 2003).

New separation steps:

In 1977 suspension strippers were introduced to reduce the amount of VCM in PVC.

Waste management:

There are no large volume waste flows.

Emission reduction measures (air and water)

Most emission reductions had to do with the reactor technology (see above).

The stripped waste water flow is treated in the biological waste water treatment plant at the Shell site.

4.3.4 *Comments*

The information above suggests that the production of PVC from VCM in itself is less relevant from a perspective of potential emissions of chlorinated micropollutants. A comparison of the criteria in chapter 2 and the description of the reactions that take place in the process, indicates that the risk of formation of chlorinated micropollutants is relatively low. The main attention point in the plant has always been reduction of VCM emissions, particularly in view of occupational health protection.

4.4 **Emission reduction measures for the whole location**

The main emission reduction measure that was relevant for the whole location was the installation of a biological waste water treatment plant in 1983.

4.5 **Overall conclusions**

The description above indicates that concerning chlorinated micropollutants, the discussion mainly has to focus on the AC/ECH plant. Here, the main discussion always has been the relatively large EOCl emission to water that existed in the early 1980s (which may have been as large as 400 kg/day, or some 150 ton per annum). By 1990, the base year for the Dutch Chlorine chain study, this number was lowered to some 10 ton per annum. At this stage, less than 3 kg/day, so less than 1 ton per annum, of EOCl to water at concentrations close to non-detectable levels are emitted. Dioxin emissions were reduced to non-detectable levels.

There seems little doubt that in the AC/ECH production various by-products are formed. The outputs to waste, water and air are all managed and result in low measured emissions of known compounds, which probably explains the relatively low emissions with the DR Calux tests. If there are still emissions of chlorinated micropollutants, then they are more likely to be related with (minor) irregularities or inefficiencies in waste water treatment and waste treatment, or output with products. This study is not extended enough to confirm or deny this (hypothetical ?) problem.

5 Akzo Nobel Delfzijl

5.1 Introduction

Akzo Nobel Delfzijl is one of the three chlorine related sites of Akzo Nobel in the Netherlands. Here, Akzo Nobel, Akzo Nobel joint ventures, or former Akzo Nobel daughters produce:

- Chlorine;
- Chlorinated solvents;
- TDC and Poly-aramide
- Ethyleneamines

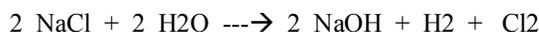
In the near future, rather substantial changes in the production structure will take place. For various reasons, the chlorinated solvent production is stopped by 2004 and the chlorine production, via the diaphragm process, will stop in the course of 2005. The NaOH produced via the diaphragm process (see below) has a relatively low quality, and the market for chlorinated solvents such as DCM is already under pressure since years. Furthermore, a substantial part of the chlorine currently produced in Delfzijl is actually used at other locations, most notably Rotterdam Botlek. The chlorine transport is under societal debate (despite the fact that regular risk calculations show acceptable risk levels). Therefore, early 2002, an agreement has been signed between Akzo Nobel and the Ministries of Economic Affairs and Environment to limit chlorine transport to an absolute minimum. Execution of this agreement will result in a relocation of chlorine production facilities in the Netherlands, which prompted Akzo Nobel to take a number of other strategic decision in relation. Execution is still pending due to the discussions in Brussels (Jan 2004). In short, the following changes will take place:

- The current chlorine production in Delfzijl will be closed by 2005. To serve existing clients, a smaller, new chlorine plant based on membrane technology will be build. Chlorine production in Rotterdam will be expanded.
- The mercury cell electrolysis in Hengelo and the related monochloroacetic acid (MCA) production will be closed. A new MCA plant will be built in Delfzijl.

5.2 Production of chlorine

5.2.1 *Description of the process*

Chlorine and sodium hydroxide and hydrogen are produced by means of electrolysis of salt. The following reaction takes places:



In this process, the anode and cathode liquid have to be separated. This can be done by either mercury, a diaphragm, or a membrane. Akzo Nobel applies the diaphragm process in Delfzijl. In the diaphragm process the electrolytes are separated by an asbestos diaphragm. The diaphragm separates the chlorine from the caustic soda and hydrogen gas produced during the electrolysis of brine. The cathode process results in a solution of caustic soda in brine, from which soda can be prepared.

The chlorine produced is cooled, washed and dried. The aqueous washing liquid is discharged to water. After this, the chlorine is purified with tetra and liquefied. Gaseous emissions from this process are incinerated in the vent gas incinerator of the chlorinated solvent production plant (Akzo Nobel Delfzijl, 1998). Chlorine containing vent gases are destructed by reaction with NaOH to hypochlorite.

5.2.2 *Measures taken between 1985 and 2002*

Below, the key measures taken to prevent formation of chlorinated (by-) products are given, mainly taken from (Akzo Nobel, 1998: V-8).

Feedstock input:

No measures with regard to changes in the feedstock input have been identified.

Process conditions:

No major measures relevant for this study with regard to changes in process conditions have been identified.

New separation steps:

No major measures relevant for this study with regard to new separation steps have been identified.

Waste management:

Various recycling options have been implemented, see below.

Emission reduction measures (air and water)

- The main chlorine-containing emissions to water consist of salt, sodium chlorate (NaClO_3) and active chlorine. Additionally, some chloroform and tetra in the kg range is discharged. These emissions have not been reduced in the period 1985-1996 (Akzo Nobel Delfzijl, 1998). In 1999, recycling of bleach lye was introduced which led to a substantial reduction of the active chlorine emissions to water (with 75%)
- The chlorine destruction installation has been changed from a batch- to a continuous operating system.
- Various measures were taken to reduce diffuse emissions of a.o. tetra.

5.2.3 *Comments*

Virtually all of the measures identified above deal with major emissions of chlorinated compounds rather than micropollutants. As indicated in the box on page 12, in another chlorine production plant unexpected dioxin formation occurred, which was initially detected by contamination in landfilled sewage sludge of the waste water treatment. At Akzo Nobel Delfzijl it is unknown if such problems occur; the OVOC measurements which were done after end-of-pipe treatment did not show significant emissions. Furthermore, sewage sludge from Akzo Nobel's waste water treatment plant is incinerated, which should destroy any dioxins when present. Given the plans to close the plant and replace it by a smaller one on the basis of membrane technology, the discussion above has become obsolete in the mean time. For the future situation a similar analysis as made for the Rotterdam plant probably is valid (see chapter 3.2).

5.3 Production of chlorinated solvents

5.3.1 Introduction

Akzo Nobel is the only Dutch producer of chlorinated solvents (halogenated hydrocarbons - HHCs). Dichloromethane (DCM) and chloroform are produced in Delfzijl via the intermediate product methylchloride, . Until mid-1990 tetrachloroethene (PER) and Carbontetrachloride (Tet) were also produced in a combined PER/tetprocess. The following sub-section describes the steps in the process in greater detail (SPIN 1994, Bremmer et al., 1988).

5.3.2 Process description

Figure 5.1 illustrates the production of chlorinated hydrocarbons. Methanol and a return flow of HCl-gas react to methyl chloride and water. The gaseous reaction mix is cooled so that most of the water condenses. The surplus HCl dissolves in this water so that a hydrochloric acid solution is produced. This is stripped of methanol, and processed to 30% hydrochloric acid. The methylchloride gas is dried with concentrated sulphuric acid and used entirely in the methylene-chloroform factory.

In this factory, the methyl chloride reacts with chlorine to DCM and chloroform. The by-products tetra and HCl are produced. By using an excess of methylchloride all chlorine is removed in the reaction. The reaction mixture is separated by condensation into a liquid and a gas phase. The gas phase consists mainly of hydrogen chloride (HCl) and methyl chloride and is largely fed back into the methyl chloride production.

The liquid phase is separated by means of distillation into HCl, methylchloride, dichloromethane, chloroform and tetra. HCl and methylchloride are recycled to the chlorination reactor. Until 1990 propylene was chlorinated to Tetra and PER in the PER/ Tetra plant. The by-product HCl was processed to 30% hydrochloric acid.

The (by-)products dichloromethane, chloroform, Tetra and Per (until 1990) are washed with 10% caustic soda to neutralise residues of chlorine and HCl and dried. As a last step, the damp, purified chlorohydrocarbons, are dried.

Since mid-1990 Akzo Nobel has been using an incinerator to process waste gas flow containing chlorohydrocarbons. These are waste gases from storage tanks and the methylene chloride/chloroform factory. The waste gases from the incinerator are conveyed to an absorber where hydrochloric acid is produced, which is either processed and sold or neutralised and released. After absorption, the waste gases are fed through an alkali scrubber and then released into the outside air. The waste flow created here, chlorine bleaching soda, is processed in the electrolysis factory.

All aqueous effluents from the process containing chlorinated hydrocarbons are treated in a water purification unit consisting of a sedimentation section, a steam stripping section and a carbon black absorption section.

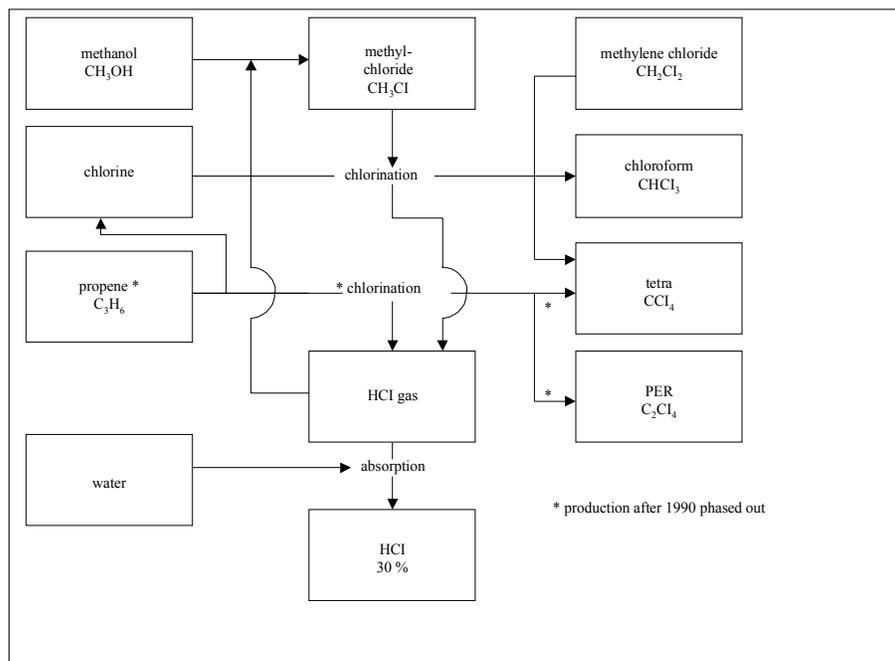


Figure 5.1 Diagram of the production of halogenated hydrocarbons

Box: Indications of formation of chlorinated micropollutants

The process description already makes clear that the process leads to by-products, that have to be separated from the main product. Some residual emissions of HCB and HCBd were by-products from the already decommissioned production of PERC and tetra. In a study into 'unexpected presence' of organochlorine compounds in the mid-eighties, Berbee (1987) found annual emissions of chlorotoluenes, hexanechloroethane, HCH chlorophenoles, and bromophenoles in the kg-range. This author linked that to the aforementioned production of tetra and PERC. Hence, the emissions of these substances probably are mainly related to the historical production of PERC and tetra. No further literature data have been found on micropollutants in specific for DCM and chloroform production. From another producer (ICI) of similar solvents (i.e. PERC and trichloroethene), some sources indicate that production wastes contain a significant amount of dioxins (ENDS, 1997). Fiedler et al. (1994) reported for PERC dioxin concentrations of 0,055 ng OCDD/g (equalling 0,055 pg TEQ/g); for a PERC use of 2600 tpa in the Netherlands in 1990 this would imply a contamination of 0,1 mg TEQ TCDD/yr. The 'Basisdocument Chloorbenzenen' (Slooff et al, 1991) indicates that the fraction of high boilers in PERC (which includes chlorobenzenes) would be at most 10 mg/kg. With 2600 tpa PERC use in the Netherlands in 1990, this would equal some 20-30 kg chlorobenzenes at most. However, this finding for PERC cannot be translated to the production of other solvents.

5.3.3 *Measures taken between 1985 and 2002*

Below, the key measures taken to prevent formation of chlorinated (by-) products are given.

Feedstock input:

No measures with regard to changes in the feedstock input have been identified.

Process conditions:

- In March 1990 the PER-Tetra plant was closed (Akzo Nobel Delfzijl, 1998). This resulted in lower emissions of CHCs, and particularly the emissions of hexachlorobenzene (HCB) which was produced as a byproduct/continaminant.

New separation steps:

- In the period 1985-1990 a steam stripper became operational that reduced the emission of halogenated hydrocarbons to the seawater canal from 18 ton to less than 41 kg pa in 1992, a reduction of over 90%.

Waste management:

No major measures relevant for this study with regard to waste management have been identified. However, waste reduction programs are common practice.

Emission reduction measures (air and water)

- An installation that reduces HCB emission to the seawater canal was build, resulting in a reduction of 70 kg to 0,6 kg/annum.
- In the period 1985-1990 a vent gas incinerator became operational that treated vent gases of the chlorinated solvent production and the diaphragm electrolysis. This resulted in substantial reductions of emissions of CHC to air (some 80-90%). No major reductions were realised after the incinerator became operational.
- In 1993 filters were added to the quench of this incinerator, in order to capture solid particles in the effluent to which dioxins could be attached.
- Measures were taken to enhance availability of the vent gas incinerator.

5.3.4 *Comments*

The PER/Tetra plant, which probably was the most critical part of the plant in the view of formation of chlorinated micropollutants, has been closed for over a decade now. Vent gases are incinerated. All aquous effluents from the process containing chlorinated hydrocarbons are treated in a water purification unit consisting of a sedimentation section, a steam stripping section and a carbon black absorption section. The solvent plant as such has been closed recently, making any discussion on chlorinated micropollutants obsolete.

5.4 Production of TDC and aramide

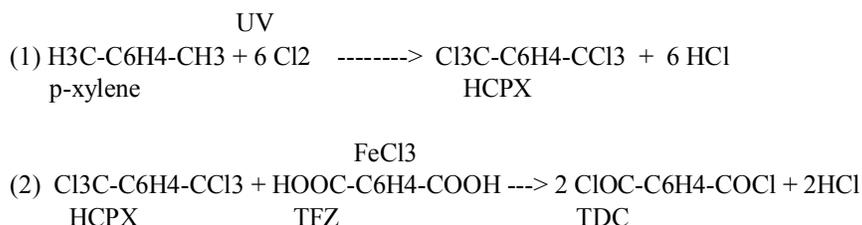
5.4.1 Introduction

The Aramidemaatschappij V.O.F. (later: Aramide Products) in Delfzijl produces terphthaloyldichloride (TDC) from p-xylene and chlorine. This is a raw material for aramide. The next sub-section describes the process in more detail. The process description is based on (Assies 1991) and material from the TNO Plastics and Rubber Institute (KRI) (Preston 1985, Volbracht 1976 and 1989). The company is established on the Akzo Nobel premises in Delfzijl. In 2000 this plant was taken over by Teijin, and since 2001 it is called Teijin Twaron B.V.

5.4.2 Process descriptions

Production of TDC

TDC is produced via the following reactions:



P-xylene is chlorinated in batches to hexachloro-P-xylene (HCPX). To prevent side-reactions and rust forming, the process is conducted in an inert tetra atmosphere. The reaction is catalysed by UV light. Waste flows containing tetra are neutralised with NaOH and separated and then the tetra layer is distilled. The tetra vapour is cleaned in a caustic soda scrubber and fed back into the process.

After the chlorination, terephthalic acid (TFZ) is added to HCPX in a batch reactor (reaction 2). The waste gas from this reaction contains N₂, HCl, TDC, HCPX and PTA. This mixture goes to the HCl processing system. Raw TDC is conducted to an evaporator and then to a distillation column. The vapour is condensed and this produces quality TDC. Distillation residue and incidental off-spec batches, in 1990 was processed elsewhere as chemical waste (including at Akzo Nobel in Botlek with recovery of HCl). These flows are now incinerated in a Teijin Twaron incinerator. Figure 5.2 illustrates the preparation of TDC.

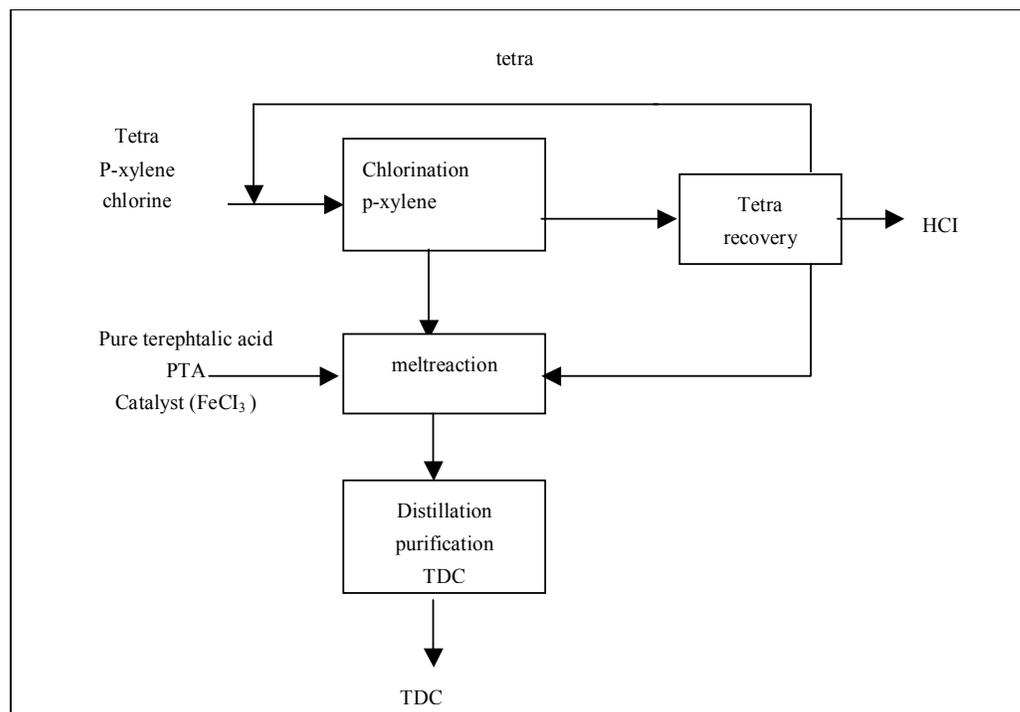


Figure 5.2 Diagram of TDC production

Production of aramide

Poly p-phenylene terephthaloyl amide (PPTA) is the raw materials for super-strength fibres, such as Twaron®. (Teijin Twaron) and Kevlar (DuPont). These fibres will be referred to as aramide fibres for short. Aramide is synthesised from equimolar quantities of p-phenylenediamine (PDD) and terephthalic acid dichloride (TDC) in an N-methylpyrrolidon (NMP)/calcium chloride mixture. The process is performed in batches.

In the first step, liquid or finely ground TDC is mixed with a solution of PPD in NMP/ CaCl_2 . Because the reaction is strongly exothermic, the reaction mix is cooled. Together with the other components of the reaction medium, the aramide formed creates a highly viscous jelly-like mass, from which the polymer, after intensive mixing with water, is settled, filtered off, washed and dried. The filtrate is neutralised with calcium hydroxide during which the HCl bound to NMP is converted into water and CaCl_2 . Regeneration occurs partly by liquid-liquid extraction with dichloromethane (DCM) and otherwise by evaporation. The top product consists of water, CaCl_2 and traces of NMP and DCM, which is further processed. Some of the CaCl_2 is fed back into the process. The remainder is released to water. The intermediate product NMP is also fed back into the process. The bottom product consists of DCM, NMP and water. This is distilled in a separate column.

Box: Indications of formation of chlorinated micropollutants

No specific information about the formation of chlorinated micropollutants has been found in literature for this process.

5.4.3 *Measures taken between 1985 and 2002*

Below, the key measures taken to prevent formation of chlorinated (by-) products are given (Chemiepark Delfzijl, 2000 and 2001, and Teijin Twaron, 2003).

Feedstock input:

- No measures with regard to changes in the feedstock input have been identified. Research is ongoing to enable the replacement of tetra by 2010.

Process conditions:

- Emissions of tetra have been reduced from over 3 tpa in 1999 to 435 kg/a in 2000, particularly due to better process management of an active carbon filter and better air flow management of the installation and introduction of a control programme for diffuse emissions detection

New separation steps:

- In various stages, active carbon filters have been placed to reduce tetra emissions (see also below under emission reduction measures).

Waste management:

- All of the waste (distillation residue during the production of TDC) generated is incinerated in an on-site incinerator.

Emission reduction measures (air and water)

- The PPD factory has
 - an incinerator for vent gases, that includes a dust filtration unit.
 - An active carbon filter for adsorption of aniline;
 - A 'vapour return system' for aniline and MMC
- The TDC factory has:
 - An incinerator, that include a ventgas wash column and a dust filtration unit;
 - Ventgas stripper to remove tetra and P-xyleen from water
 - Vent gas washing systems for reducing HCl and chlorine;
 - Active carbon filters for absorption of tetra
- Furthermore, the polymerisation factory and the recovery have filters for dust prevention and active coal filters for DCM absorption.
- There is no biological treatment of the final waste water flow. Emissions to water are managed via particularly process-internal measures and various separation steps:
 - An aniline-separator and active carbon columns;
 - A chlorine destruction installation;
 - A stripper for tetra and para-xylene
 - A steam stripper for DCM in the recovery factory
 - Filters in the waste water flow of the TDC/PPD incinerator, and an active carbon filter for removal of solid particles (that might include dioxins).

5.4.4 *Comments*

Emissions to air are dealt with via active carbon columns and treatment of the vent gas from the incineration installation by a washing column and dust filter unit. Emissions to water are treated, but there is no biological waste water treatment. There is no information to judge if any contamination of products might be relevant.

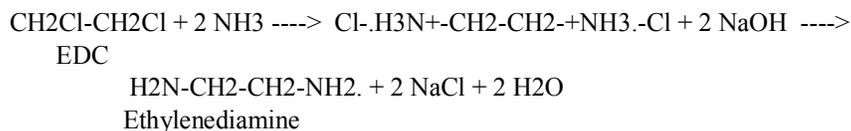
5.5 **The production of ethylene amines**

5.5.1 *Introduction*

Delamine is a joint venture of Akzo Nobel and Tosoh and produces ethylene amines at the Akzo Nobel location in Delfzijl. The following sub-section describes the stages in the production process. The description is based on the SPIN document for this process (SPIN 1993c; Chemiepark 2000 and 2001).

5.5.2 *Process descriptions*

Ethylene amines are produced by the ethylenedichloride process. This involves ethylenedichloride (EDC) reacting at 140 °C and 140 bar with an excess of ammonia (NH₃). The by-product vinylchloride produced during the process is incinerated. The reaction produces a mix of aminohydrochloride salts. Some of the possible reactions are:



These salts are neutralised with caustic soda, creating free ethylene amines and inorganic salts (primarily NaCl). After the amines of the organic salts have been separated with the aid of solvent extraction, the various fractions of ethylene amines are separated and purified by means of distillation.

The proportions of the reaction products can be varied by using the NH₃ excess and reactor dimensions. Reaction products might be: ethylenediamine (EDA), piperazine (PIP) diethylenetriamine (DETA), aminoethylpiperazine (AEP), triethylenetetramine (TETA), tetraethylenepentamine (TEPA) and other polyamines.

A diagram of the process is given in Figure 5.3.

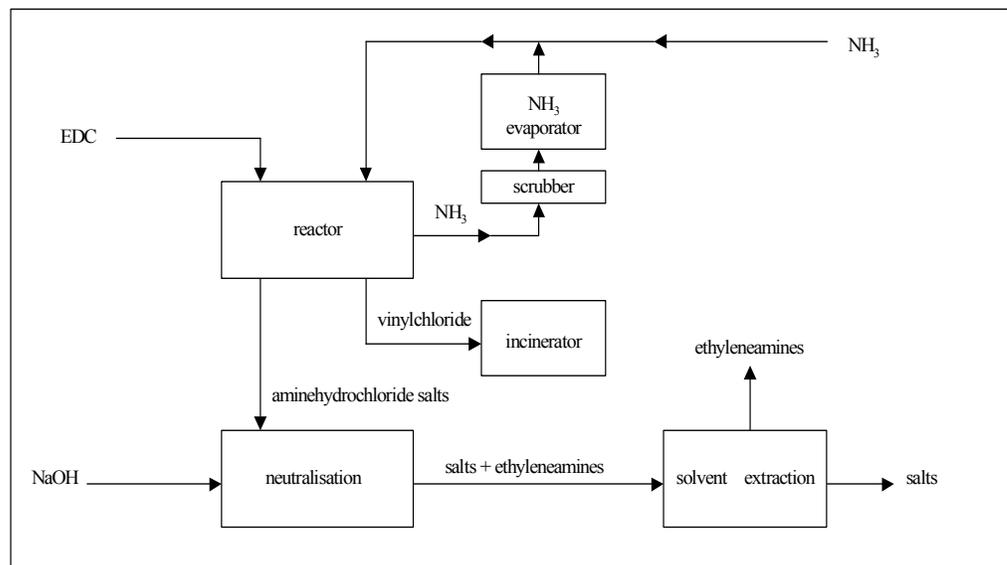


Figure 5.3 Diagram of the production of ethyleneamines

Box: Indications of formation of chlorinated micropollutants

No specific information about the formation of chlorinated micropollutants has been found in literature for this process.

5.5.3 Measures taken between 1985 and 2002

Below, the key measures taken to prevent formation of chlorinated (by-) products are given.

Feedstock input:

- No measures with regard to changes in the feedstock input have been identified.

Process conditions:

- Waste water is discharged. Delamine has implemented some process measures (a.o. re-use of process water) to limit emissions.

New separation steps:

- A filter system has been installed to treat the waste water of the incinerator, in order to remove suspended particles to which contaminants are often attached. Part of this filter is an active carbon adsorption unit that removes all chlorinated micro-pollutants.

Waste management:

- Delamine succeeded in finding market applications for all its amine outputs, including the by-products.

Emission reduction measures (air and water)

- A vent gas incinerator is available that deals with vent gases from the process, in which small amounts of VCM are produced.
- Waste water is treated with active carbon to remove chlorinated micro pollutants and traces of amines.

5.5.4 *Comments*

The characteristics of the process (low temperature, condensation reaction) do not suggest a major threat of generation of chlorinated micropollutants. The EDC reacts with NH₃ to ethylene amines. The main alternative reaction path apparently is some conversion of EDC into VCM under HCl release. Emissions to air are prevented by a vent gas incinerator that will deal with any chlorinated micropollutants formed. Waste water is treated with active carbon to remove chlorinated micro pollutants and traces of amines.

5.6 **Emission reduction measures for the whole location**

Unlike for Akzo Nobel Botlek or Shell Rotterdam, there are no emission reduction measures relevant for the whole location. There is no central biological and/or physical waste water treatment. Each plant has its own air emission abatement system(s).

5.7 **Overall conclusions**

Most information is available for the chlorine production and solvent production. However, these plants have been or will be closed on short notice and any danger with regard to emissions of chlorinated micropollutants hence has become irrelevant. Given the nature of the reaction at the Delamine plant, there seems to be a low risk that micropollutants are formed here. Neither the products nor the water effluents were a priority in the analytical program of the OVOC study. As for Teijin Twaron, emissions to air are dealt with via a vent gas incinerator. During down time of this incinerator any emissions to air of any chlorinated micropollutants could be feasible. Emissions to water are treated, but there is no biological waste water treatment. There is no information to judge if any contamination of products might be relevant.

6 Discussion and conclusions

6.1 Introduction

In the set-up of the study it was agreed that in the BOVOC study measurements would be done end-of-pipe. No in-plant measurements would be done. The innovation compared to traditional analytical measurement approaches was that a bio-assay would be used that in principle detects a large spectrum of compounds with dioxin-like activity (the DR Calux). The OVOC study hence was not meant to quantify any formation of such micropollutants in the different processes. Literature available suggests that in various processes such by-products are formed. Also, analytical measurements on specific substances found some unexpected presence of by-products in e.g. chlorinated solvents.

6.2 Discussion

The end-of-pipe measurements of OVOC found no or hardly any evidence of unknown emissions from the chlorine industry. This is consistent with this study into measures that the chlorine industry took the last decades to minimize emissions to air and water. Virtually all plants covered treat emissions to air by vent gas incinerators, and emissions to water by (advanced) biological and/or physical waste water treatment plants. These measures in general led to large reductions of emissions of known chlorinated compounds. Furthermore, such measures can be expected to prevent emissions of chlorinated micropollutants, which was confirmed by the biological and chemical measurements done within framework of the OVOC study.

Does this imply that the chance on emissions of chlorinated micropollutants can be seen as fully absent? This conclusion cannot be drawn, since there are some issues out of the scope of the OVOC study. It concerns the situation where there is a process in which micro-pollutants are formed, in combination with significant down-times of emission reduction measures to water or air, an unexpected contamination of product flows, or an unexpected improper handling of waste flows contaminated with micropollutants. This study was not designed to analyse this, and hence cannot conclude in any way about the probability of this problem.

6.3 Conclusions per plant

On the basis of the chapters, following specific conclusions for the individual sites apply:

4. Akzo Nobel Botlek (chlorine production, including herbicide production at Nufarm and EDC/VCM production at Shin-Etsu): The dioxin contamination of the influent to the biological waste water treatment plant (Biobot) from the Nufarm plant is in the ppb range. Though this still could form a significant mass flow per annum, the OVOC DR Calux measurements of the effluent of the Biobot and an EDC sample showed DR Calux 2,4,7,8 TCCD equivalents below detection limit. The only other products possibly containing micropollutants leaving the Botlek location are VCM and herbicides. VCM is

used for production of PVC; from other studies it is known that the amount of i-TEQ dioxins is low as well (see chapter 4). Herbicides have to comply with stringent regulations concerning product contaminants world-wide (e.g. on the basis of EU and US EPA regulations). In this context, Nufarm has to test its products on a regular basis on substances like dioxins; quantities of the different dioxin congeners are not-detectable.

5. Shell Nederland Chemie (AC/ECH production of Resolution and PVC production of Shin-Etsu): the discussion mainly has to focus on the AC/ECH plant. Here, the main discussion always has been the relatively large EOCl emission to water that existed in the early 1980s (which may have been as large as 400 kg/day, or some 150 ton per annum). By 1990, the base year for the Dutch Chlorine chain study, this number was lowered to some 10 ton per annum. At this stage, less than 3 kg/day, so less than 1 ton per annum, of EOCl to water at concentrations close to non-detectable levels are emitted. Dioxin emissions were reduced to non-detectable levels.
6. Chemiepark Delfzijl (chlorine and solvent production at Akzo Nobel Delfzijl, production of ethyleneamines at Delamine, and production of Twaron at Teijin Twaron). Most information is available for the chlorine production and solvent production. However, these plants have been or will be closed on short notice and any danger with regard to emissions of chlorinated micropollutants hence has become irrelevant. Given the nature of the reaction at the Delamine plant, there seems to be a low risk that micropollutants are formed here. Neither the products nor the water effluents were a priority in the analytical program of the OVOC study. As for Teijin Twaron, emissions to air are dealt with via a vent gas incinerator. During down time of this incinerator any emissions to air of any chlorinated micropollutants could be feasible. Emissions to water are treated, but there is no biological waste water treatment. There is no information to judge if any contamination of products might be relevant.

6.4 General conclusions

In view of the above, this report comes to the following general conclusions:

1. The Dutch chlorine industry has taken a considerable number of end-of-pipe and in-plant reduction measures in the last 15 years. Virtually all emissions to air and water are now treated with vent-gas incinerator or advanced water treatment plants.
2. This has led to considerable reductions in the emission of known organochlorine compounds.
3. The type of measures taken are of a nature that they are likely to result in high reductions in emissions of chlorinated micropollutants;
4. The low or absent DR-CALUX responses in most air or water samples is therefore logical in view of the emission reduction measures that have been adopted.

Any remaining uncertainties about emissions of chlorinated micropollutants have to do with issues that exceed the scope of the OVOC study, i.e., a combination of the formation of micropollutants in processes (not measured as a part of the OVOC program) and down-times of temporarily sub-optimal performance of end-of pipe measures. In general, OVOC samples were taken under normal process conditions.

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