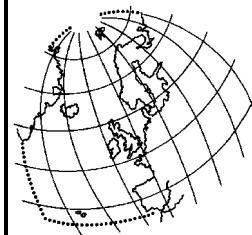


# Oslo and Paris Commissions 1996



## Best Available Techniques for the Vinyl Chloride Industry

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## 1 Introduction

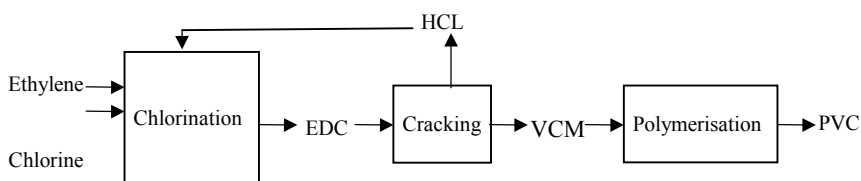
1.1 OSPAR 1994 agreed that the vinyl chloride industry has a potential to release significant amounts of organohalogens to the environment, and that it would be useful to look thoroughly into the sector starting with developing a background document which could serve as the basis for a PARCOM Recommendation on Best Available Techniques (BAT).

1.2 The vinyl chloride industry sector includes, for the purpose of this background document, the production of the intermediate compound 1,2-dichloroethane (EDC), the monomer vinylchloride (VCM) and the suspension polymer polyvinylchloride (s-PVC). Production of ethylene and chlorine, the raw materials for EDC, is not included. Nor is the processing of raw PVC to compounds for the manufacture of soft or rigid products nor the subsequent steps in the PVC life cycle including waste disposal.

1.3 PARCOM Recommendation 94/4 on Best Available Techniques for the Organic Chemical Industry, which applies to the whole Organic Chemical Industry, constitutes the underlying basic principles for the present background document and future work on the vinyl chloride-industry.

## 2 The vinyl chloride industry

2.1 Vinyl chloride is made by reacting ethylene with  $\text{Cl}_2$  and HCl to EDC. This compound is cracked to hydrogen chloride and VCM. The polymerisation process occurs in the presence of catalysts and other chemicals under controlled temperature conditions. Both fully integrated plants (from raw materials to PVC) and non-integrated plants exist. **Figure 1** gives a very simplified overview of the production processes (see Figure 2 for more details).



**Figure 1: Main steps in the production of EDC, VCM and PVC**

2.2 Environmental concerns are related to the releases of EDC, VCM and a range of chlorinated compounds to air and water, and as disposed wastes.

2.3 PVC is used for applications such as building materials, piping, packaging, automobiles and electrical appliances.

2.4 EDC, VCM and PVC are made on a much larger scale than any other chlorinated product. The potential and actual releases to the environment of chlorinated organic compounds from this industry are significant.

2.5 According to the European Council of Vinyl Manufacturers (ECVM), the production capacity for PVC in 1993 was 4,94 million tonnes per year in OSPAR countries (estimated 22,8 million tonnes per year world wide). **Table 1** contains a survey of the VCM and PVC industries in OSPAR countries. VCM and/or PVC is produced in all OSPAR countries except Denmark, Iceland and Ireland.

**Table 1: Production capacities for VCM and PVC in OSPAR countries (3)\*, 1993**

Country	VCM		PVC	
	No. of plants	Tonnes/year	No. of plants	Tonnes/year
Belgium	3	970 000	2	320 000
Finland	0	0	1	90 000
France	4	1 250 000	7	1 250 000
Germany	8	1 655 000	9	1 565 000
Netherlands	1	510 000	2	550 000
Norway	1	470 000	1	90 000
Portugal	0	0	1	110 000
Spain	2	415 000	5	410 000
Sweden	1	110 000	1	125 000
Switzerland	0	0	1	45 000
United Kingdom	2	400 000	4	385 000
Total	22	5 780 000	34	4 940 000

2.6 About 85 % of the PVC is produced by the suspension polymerisation process. About 15 % is produced by the emulsion process.

2.7 Current (1993) sales of the West European vinyl chloride industry has been estimated at 8 030 million DEM. The average cost of environmental protection is about 5 % of sales (3)\*.

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\* Figures in brackets refer to the references listed on page 43

### 3 Environmental issues

#### 3.1 Environmental impact

3.1.1 The environmental concerns relate mainly to the actual or potential contribution of identified and non-identified organohalogens to air, water and soil. More specifically:

- a. formation and releases into water of any substance that is toxic, persistent and liable to bioaccumulate:
  - small quantities of polychlorinated dioxins (PCDD), furanes (PCDF) and e.g. hexachlorobenzenes are identified in internal process streams and in effluents and wastes from the production of VCM (24);
  - in addition the waste streams contain small amounts of several complex chloro-organics which are only partially identified and quantified. Some qualitative studies are reported by Greenpeace (10);
  - copper ions are usually present in the waste water due to the use of copper as catalyst at VCM plants;
- b. waste generation, storage and disposal (EDC-tar, disposal of sludge containing organohalogens);
- c. risk of severe pollution in case of accidents;
- d. contaminated groundwater from underground effluent pipes leakages;
- e. emissions of large quantities of VCM to atmosphere from point sources and fugitive sources (apply both for VCM plants and PVC plants);
- f. emissions of large quantities of EDC to atmosphere from both point sources and fugitive sources (VCM plants);
- g. formation and releases of other volatile chlorinated hydrocarbons e.g. carbontetrachloride, chloroform and 1,1,2-trichloroethane.

3.1.2 The releases into water and air of organohalogens from the vinyl chloride industry in the OSPAR area have been calculated in **Table 2** below from data provided by the Association of Plastics Manufacturers in Europe (APME) (7). However, according to the information compiled during the elaboration of this background document, the figures in the table seem to be too high for “state of the art” plants.

**Table 2: Releases of chlorinated organics from the vinyl chloride industry**

Substances	Medium	Emissions* in gram per tonne s-PVC
Chlorinated organics	Water	3
Chlorinated organics	Air	510

\* Cumulative emissions, (including the emissions from the manufacture of VCM) based on the operation of 8 s-PVC-plants. (Nominal production capacity of PVC in OSPAR countries, 1993: 4 940 000 tonnes/year)

Comparison with emission factors related to other industrial sectors releasing chlororganic substances is difficult because available data from other sectors are not equally updated.

3.1.3 The above table gives no information on releases of particular hazardous substances like dioxins and HCBs. According to the European Council of Vinyl Manufacturers (ECVM) (3) releases of chlorinated dioxins and furans are less than 0,1 g (as I-TEQ) per 100 000 tonnes produced VCM. Dioxins and furans isomer patterns are dominated by the octa-chlorodibenzofurans (OCDF). It is *inter alia* reported by Spain (4) that about 99% of the dioxin-like compounds emitted in the effluents of the oxychlorination process of EDC productions are polychloro-dibenzofurans (PCDFs), of which OCDF represents about 90% by weight. The toxicity equivalent factor for OCDF is 0,001 in the commonly used international toxicity equivalent model (I-TEQ), in which model the most toxic isomer, 2,3,7,8-TCDD is 1.

3.1.4 In **Appendix 5**, an example of the dioxins/furans-isomer patterns analysed in the effluent from one VCM plant is shown. Greenpeace states in one of their reports (8) that dioxin releases to the environment can be as much as 5-10 g per 100 000 tonne VCM produced. The figures reported by Greenpeace cannot be regarded as representative for plants in the OSPAR Convention Area, according to information compiled for this background document. Dioxin releases to air and water reported from *inter alia* Norwegian and Swedish plants are in the range of 0,03-0,2 g (I-TEQ)/year (21). In the annual report of 1992 from Akzo Nobel (25), emissions to air of dioxins are reported to be in the range 3 to 20 mg TEQ per year. For the two first mentioned plants, it is also reported that the total formation of dioxins in the internal process streams are about 8 g/year and 40 g/year respectively. Most of the dioxins are found in the "heavy-ends" fraction (cf. paragraph 4.10.2.3 concerning dioxins in waste).

3.1.5 Numerous studies on the impact on human health from occupational exposure to VCM in PVC plants have been carried out, but very few studies addressing the local environmental impact of the manufacture of VCM/PVC are known.

3.1.6 Evers *et al* (14), in a recent study on polychlorinated dibenzo-p-dioxin and dibenzofuran residues in estuarine and coastal North Sea

sediments, have analysed sediments from the North Sea and from estuaries of the rivers Rhine, Meuse, Scheldt, Ems and Humber for dioxins using a congener-specific procedure. It was found that dioxins in sediments in parts of the North Sea (*inter alia* the Wadden Sea) originate primarily from industrial operation discharges related to the production of chloroaliphatic compounds (e.g. VCM plants) and the chlor-alkali industry along the river Rhine.

3.1.7 In a Swedish study (15), high concentrations of some chlorinated hydrocarbons (e.g. HCB) were found in marine sediments along the coast of an industrialised area (Stenungsund, Swedish west coast), including a VCM/PVC plant. However, the study could not draw any conclusion on a possible link between the VCM/PVC factory and the polluted sediments.

3.1.8 In the mid-1980s, the Swedish environmental authorities undertook a comprehensive study (6) of the environmental impact in Stenungsund where five petrochemical plants were located, including one plant producing VCM and PVC. No particular local impact from the VCM/PVC industry was detected.

3.1.9 A preliminary conclusion that might be drawn from the above mentioned studies is that local environmental impact or health damage directly linked to the manufacture of PVC and its intermediates have not been observed (except for earlier cases of damage to human health due to occupational exposure to VCM). However, the manufacturing processes contribute to the environmental burden of organohalogenes.

## 3.2 Pollutants and their properties

3.2.1 Among the wide spectrum of organohalogenes identified in air and water effluent streams in the vinyl chloride industry, the major components are 1,2-dichloroethane (EDC) and vinylchloride monomer (VCM).

### Typical properties of EDC

- liquid at ambient temperature, b.p. 83°C;
- lost from water by evaporation, which is a more significant sink than biodegradation;
- measured concentrations in biosphere and hydrosphere do not provide any sign of bioaccumulation;
- acute and chronic toxicity towards aquatic organisms;
- predicted lifetime in the atmosphere is about 50 days;
- EDC is eliminated from the atmosphere through photo-oxidation processes, no effect is expected on the ozone layer;

- carcinogenic<sup>1</sup>;
- low solubility in water.

### Typical properties of VCM

- VCM is a gas at ambient temperature, b.p. 13°C and has a relatively low solubility in water;
- VCM entering aqueous systems tends to evaporate, volatilisation half time from surface waters is a few hours or less. Evaporation is a more significant sink than biodegradation;
- in groundwater where volatilisation cannot occur, VCM will hydrolyse slowly, half time in the order of 10 years;
- adsorption of VCM to sediments and soils is not significant;
- bioaccumulation of VCM is not significant;
- relatively low acute and chronic toxicity towards aquatic organisms;
- final atmospheric degradation products are CO<sub>2</sub> and HCl;
- predicted half time in the atmosphere, due to photo-oxidation, is 36 hours or less;
- VCM in sediment and soil can be decomposed by methane-oxidising bacteria;
- carcinogenic.

Descriptions of other relevant substances occurring in waste streams from the vinyl chloride industry are given in **Appendix 4**.

## 3.3 Environmental regulations

### 3.3.1 National regulations

3.3.1.1 Regulations applicable to the manufacture of VCM and PVC are in force in all producing countries in Europe. In most Contracting Parties to the Paris Convention, discharges of chlororganic substances to water are regulated by EC Directives (16, 17). Standards for air emissions are in several Contracting Parties identical with the German *TA-Luft*.

3.3.1.2 Spain has recently prepared a study (4) on the manufacture of VCM and PVC including a comparison of national regulations in Europe on the typical pollutants released from this particular sector. An overview is given in **Appendix 3**.

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<sup>1</sup> Regarded as carcinogenic only by certain countries. Regarded as potentially carcinogenic by other countries.

### **3.3.2 International commitments**

3.3.2.1 The EC Directive (16) regulates discharges of chlorinated substances to water from VCM and EDC production. In addition, the production of monomers and polymers exceeding 1 tonne/day will most probably be subject to the provisions of an EC Directive on Integrated Pollution Prevention and Control, once adopted (23).

3.3.2.2 EDC (1,2 dichloroethane) is on the Third North Sea Declaration list of substances, inputs of which via rivers and estuaries should be reduced by 50% or more between 1985 and 1995. Chloroform, carbontetrachloride, 1,1,1 and 1,1,2-trichloroethane, which occur in the process-stream and in the waste/by-product EDC-tar, are among the substances on the Third North Sea Declaration list of substances whose inputs via rivers and estuaries and emissions to air should be reduced by 50% or more by 1995, or by 1999 at the latest, provided that the application of Best Available Technology, including the use of strict emission standards, enables such reductions. Chlorinated dioxins are among the substances on the Third North Sea Ministerial Declaration (1990) list which should be reduced by 70% or more for total inputs (via all pathways).

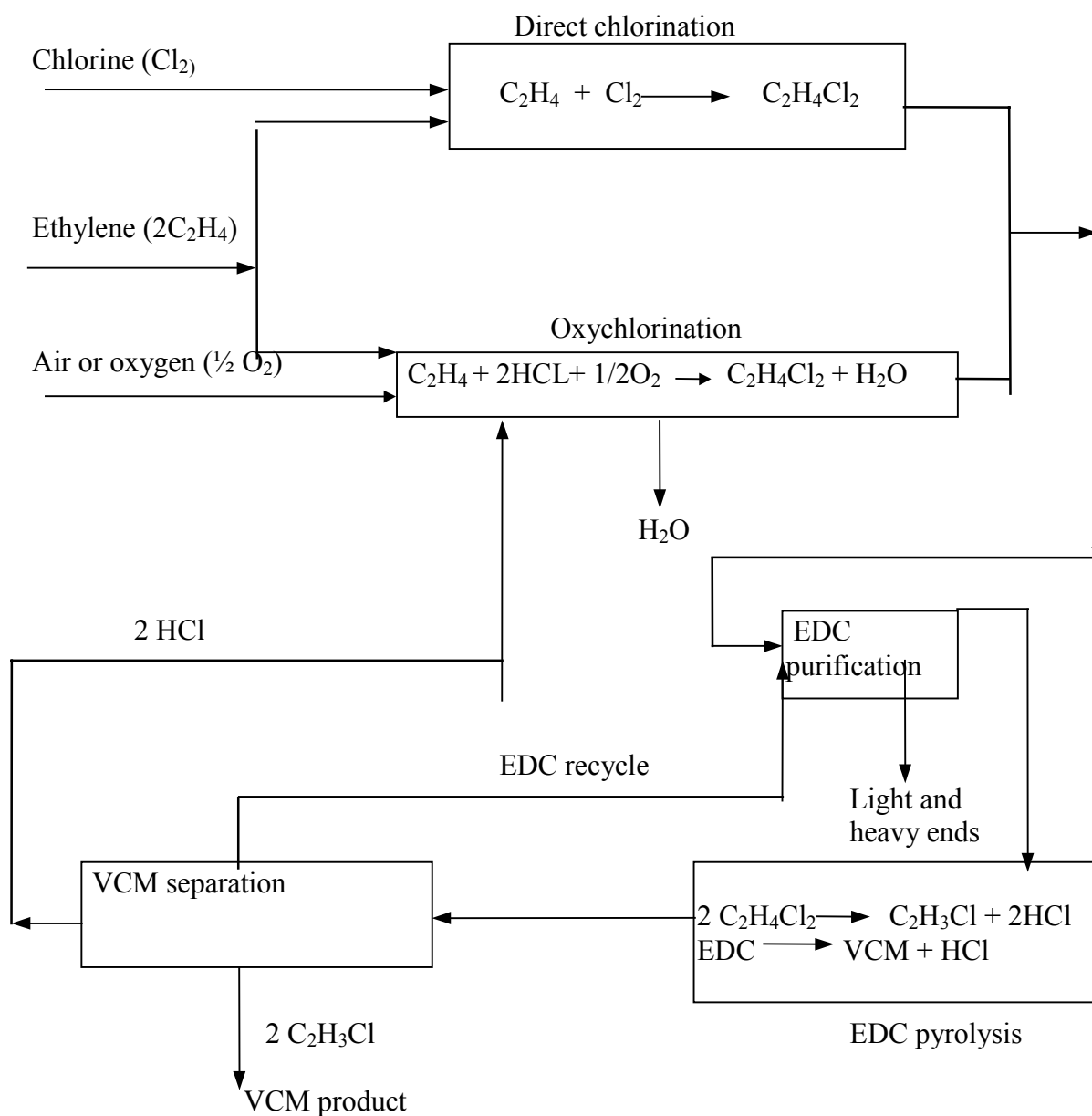
3.3.2.3 Following the Montreal protocol, the European States have decided that the use of carbon tetrachloride shall cease from 1 January 1995, and the use of 1,1,1, trichloroethane shall be reduced by 50% by 1 January 1994 and shall cease from 1 January 1996.

3.3.2.4 The VOC protocol under the UN ECE Convention on Long-range Transboundary Air Pollution states that the Parties shall reduce their VOC emissions by at least 30% by the year 1999 (19).

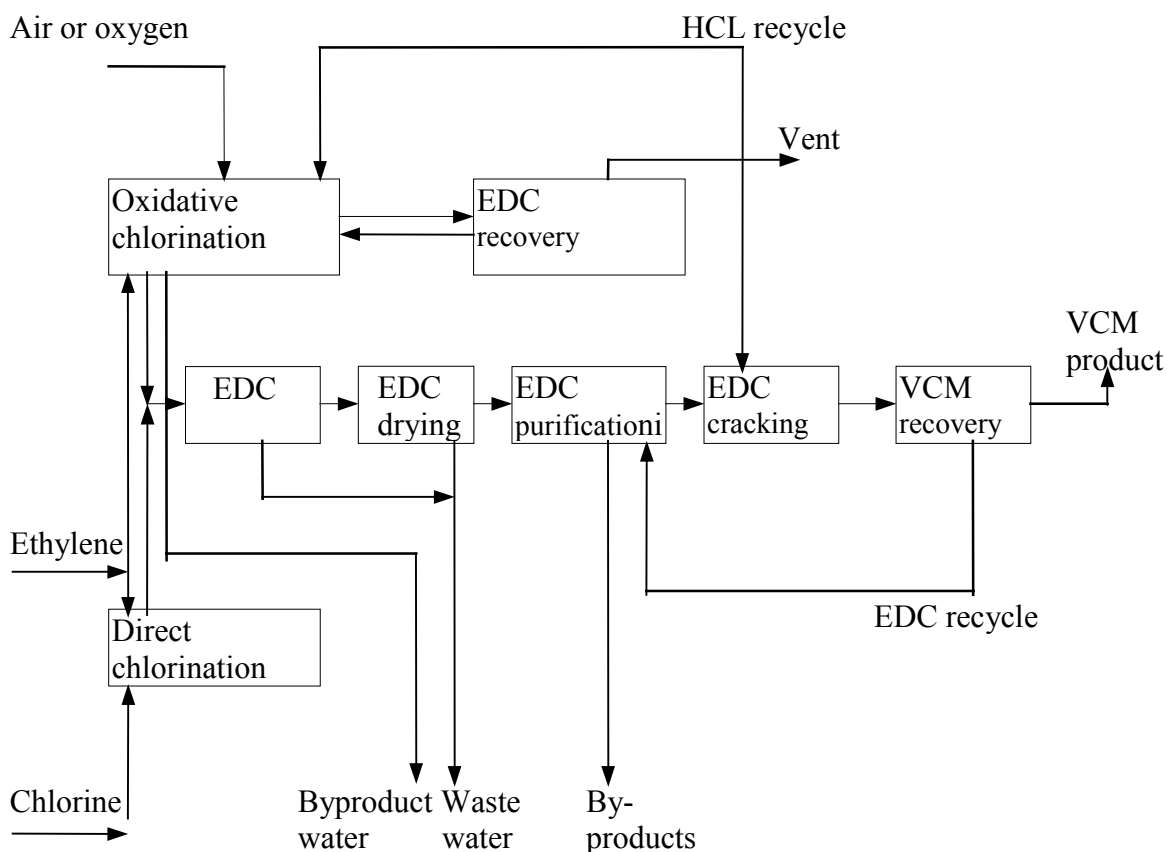
## 4 Ethylene dichloride and vinyl chloride monomer production

### 4.1 Overview

4.1.1 The main chemical reactions involved in production of EDC from chlorine and ethylene are shown in **Figure 2**. A block flow diagram is shown in **Figure 3**.



**Figure 2: Balanced VCM process (5)**



**Figure 3: Block flow diagram of balanced VCM process (5)**

4.1.2 The term “balanced process” refers to plants using a stoichiometric feed of ethylene and chlorine, and consuming HCl formed during EDC cracking by recycling to the process. Chlorination of ethylene takes place in two steps, namely, direct chlorination and oxychlorination.

## 4.2 Feedstock and auxiliary chemicals

4.2.1 Some plants use outside HCl (gas), which may be available as a waste or byproduct, as chlorine feed to the oxychlorination step. Further, a plant may be in a position either to sell HCl recovered from process waste incineration, or to use it in the oxychlorination step.

4.2.2 Air used as oxygen source in oxychlorination generates a considerable waste gas flow, due to the nitrogen content. By using pure oxygen, the waste gas flow is reduced, the reaction temperature is lower and the yield of EDC probably increases. Plants using outside HCl containing inert gases can obviously not take full advantage of using pure oxygen. In some cases, the use of pure oxygen excludes the use of external HCl with any impurities as feedstock, so that this aspect has to be thoroughly considered before conversion from air to pure oxygen for existing plants can be recommended. Pure oxygen for oxychlorination

will probably be selected at most new plants to be planned today, when pure oxygen is available at a reasonable cost.

## **4.3 Processes**

### **4.3.1 Direct chlorination**

4.3.1.1 EDC is produced in a reactor in which ethylene and chlorine are injected and react with ferric chloride as a catalyst. An alternative process using a sodium ferrate catalyst may reduce generation of byproducts. Other alternative catalysts are also under development.

4.3.1.2 Direct chlorination is carried out with a slight excess of ethylene or chlorine. The reaction product consists of more than 99 % of 1,2 dichloroethane and less than 1 % of other chlorinated hydrocarbons (predominantly 1,1,2 trichloroethane and ethyl chloride).

4.3.1.3 Direct chlorination can alternatively be carried out at high or low temperature. High temperature direct chlorination allows recovery of about 60 % of the heat of reaction, and comparatively lower selectivity. Low temperature chlorination may require washing of crude EDC with water. Both alternatives can be considered BAT. High temperature will probably be selected at a new plant.

4.3.1.4 No water is formed by the chemical reactions during direct chlorination.

### **4.3.2 Oxychlorination**

4.3.2.1 In oxychlorination gaseous phase EDC is synthesised from HCl, ethylene and oxygen or air in contact with a copper salt catalyst. Water is formed by the reaction. The reactor can either be fixed or fluidised bed. In fluidised bed reactors, copper salts are transferred to the process waste water because of abrasion of the catalyst which can vary significantly. HCl is recycled from the cracking unit.

4.3.2.2 Oxychlorination is an exothermic process, the heat of reaction is recovered by the generation of steam. The reaction products and catalyst particles are separated from the process off-gas flow by cooling and condensing. Separation of final traces of EDC from the process off-gas can be performed with an adsorption or absorption process, including recovery by stripping. The process off-gas from oxychlorination is the main source of air pollutants from VCM production.

4.3.2.3 After condensation, water separates from EDC and other organic chlorinated hydrocarbons because EDC and most other chlorinated organic compounds have low solubility in water. Exceptions are chloral, chloro-ethanol and other soluble chlorinated byproducts which accumulate in the water-phase and have to be converted under specific pH and temperature conditions into substances that are biodegradable or removable by stripping. The separated water-phase is treated by steam stripping for recovery of the small content of dissolved

EDC (< 1 %). In the fixed bed process, the catalyst must be exchanged at intervals.

4.3.2.4 Octo-chlorodibenzofurane and other dioxin related compounds are formed by the oxychlorination reactions. These compounds are concentrated in the heavy end residues from EDC distillation and in the catalyst matrix. Data from two different plants show that the total formation of dioxins in the internal process streams are in the range 6-40 g/year (fluid and fixed bed-respectively) and that the major fraction of dioxins follows the heavy ends (21). Although more dioxins are formed in fixed beds, there is virtually no carry over to the effluent systems as there is for fluidised beds.

4.3.2.5 Purified EDC and oxychlorination process off-gas do not contain significant amounts of dioxin compounds.

4.3.2.6 Oxidising HCl formed in the EDC cracking step to Cl<sub>2</sub> would allow the elimination of the oxychlorination step. The main environmental advantage would be the avoidance of the introduction of water needed for the purification of EDC (and hence waste water contaminated by organics), because EDC produced in direct chlorination could be directly fed to the pyrolysis furnace. In addition, the off-gas flow from the oxychlorination step would be eliminated. Nevertheless, no commercially available process exists at present and, accordingly, such techniques do not comply with criterion 2b of Appendix 1 of the OSPAR Convention. Furthermore, corrosion and safety problems have been mentioned by ECVI as arguments against these techniques.

4.3.2.7 Rapid cooling of the pyrolysis gases is of major importance for reducing the formation of tars and heavy components.

### **4.3.3 EDC purification**

4.3.3.1 The EDC to be purified originates from the following sources:

- direct chlorination (dry crude EDC);
- oxychlorination (wet crude EDC);
- recycled EDC from VCM production;
- outside sources (outside EDC).

4.3.3.2 EDC purification includes:

- washing to remove traces of HCl, chlorine and iron compounds;
- light-ends distillation to remove water and chlorinated organic byproducts with a boiling point lower than EDC;
- heavy-ends distillation to remove chlorinated organic byproducts with a boiling point higher than EDC and tars;

- light-ends and heavy-ends processing to recover EDC, to remove water from the light-ends or in some cases to separate feedstock from other chlorination processes.

4.3.3.3 Distillation columns for EDC purification can have overhead off-gas flows of inerts with non-condensed EDC and other volatile chlorinated organic compounds.

4.3.3.4 When molecular sieves are applied for drying light-ends, regeneration with inert hot gas will give emissions of the adsorbed components.

4.3.3.5 Process water originates in the EDC purification from acid and caustic wash, overhead product from azeo-distillation and light-ends processing. These process effluents contain EDC and other chlorinated organic compounds.

#### **4.3.4 VCM Production**

4.3.4.1 VCM is produced from purified EDC by thermal cracking in heated furnaces, at about 500°C, with conversion rates of 50-65 %. HCl and unconverted EDC, and byproducts, are separated from VCM by distillation. Unconverted EDC is transferred to EDC purification and recycled to the cracker furnaces for the production of VCM.

4.3.4.2 Separated HCl is recycled as chlorine feed to oxychlorination. Most of the volatile byproducts are removed via the HCl flow to oxychlorination. VCM product is transferred to VCM storage. The VCM production section has no water effluent, except when caustic water is applied for the removal of traces of HCl from the VCM product. Normally there is no off-gas in this section. Coke is formed during thermal EDC cracking.

### **4.4 Plant design**

#### **4.4.1 Air pollution prevention**

4.4.1.1 The chemical reactions and separation processes are carried out continuously, in closed equipment.

4.4.1.2 The process vessels are equipped with vents to prevent pressure build up by inert gases. These vents can also be operated to depressurise and flush equipment during emergencies and prior to maintenance. All vents can be connected to air pollution control equipment, except:

- vents for gases containing explosive mixtures of organic compounds and oxygen;
- major relief vents which, due to large flow, will extinguish flares and incinerators.

4.4.1.3 To prevent leaks from unconnected vents, rupture disks in combination with safety valves on the high pressure side are employed. The pressure between the rupture disc and the safety valves is monitored

to detect any leaks. As the processes in the VCM plants are continuous, gas holders for the purpose of equalising fluctuating flows are normally not used. The benefit of a gas holder depends on gas flow stability and the capacity of recovery systems and incinerators.

4.4.1.4 Technical provisions to prevent and minimise leaks causing fugitive emissions of air pollutants include:

- valves: bellow or double packing seals or equally efficient equipment;
- pumps: double seals with liquid barrier, magnetic driven or canned;
- compressors and vacuum pumps: double seals with liquid barrier, magnetic driven or canned;
- agitators: double seals with liquid barrier, magnetic driven or canned;
- flanges (connectors): minimise number, high quality gaskets.

Magnetic driven or canned designs may not yet be proven technology for large capacity units. Flanges are not critical, compared to the other components.

4.4.1.5 Closed collection systems (sewers) for contaminated process effluent water prevent the emission of volatile components to the atmosphere.

#### **4.4.2 Water pollution prevention**

4.4.2.1 Leaking process effluent water systems are observed as a problem at several VCM plants. Sewage systems made from corrosion resistant materials and designed to prevent leaks reduce the risk. To facilitate inspection and repair, BAT for contaminated effluent water collection systems at new plants and retrofitted systems are, alternatively:

- pipes and pumps etc. placed above ground;
- pipes and pumps placed in ducts accessible for inspection and repair.

4.4.2.2 Measures for water pollution prevention include separate effluent collection systems for:

- contaminated process effluent water;
- potentially contaminated water from leaks and other sources, including cooling water and surface run off from process plant areas, etc;
- uncontaminated water.

Water consumption should be reduced by internal measures.

4.4.2.3 A sufficiently large buffer tank installed upstream of the treatment plant for contaminated process waste water will secure stable operation of the process waste water treatment and function as a reservoir (dump tank) for water not satisfying maximum concentration limits before discharge.

## **4.5 Storage, loading and unloading facilities**

### **4.5.1 Storage**

4.5.1.1 Chlorine and ethylene feedstock are in general supplied by pipeline from nearby production facilities. The plant will then need storage facilities for EDC, by-products including light- and heavy-ends, HCl and VCM. Tanks must be designed and maintained to prevent leaks and prevent soil and water pollution caused by leaks. EDC and by-products are stored at atmospheric pressure in tanks exposed to ambient temperature. The gas phase will be partly saturated with EDC and volatile chlorinated by-products. Off-gas can occur by vapour displacement from filling of tanks, by nitrogen supply for inert blanketing and by breathing due to temperature variations. When tank vents are equipped with refrigerated reflux condensers or connected to gas recovery and/or the gas incinerator, releases to atmosphere are prevented.

4.5.1.2 HCl is stored, in the process, in buffer tanks at low temperature and under pressure.

4.5.1.3 VCM is alternatively stored in refrigerated tanks at atmospheric pressure, or in pressurised tanks at ambient temperature. Off-gas will only occur when there is an excess of inerts (nitrogen) introduced with the VCM input and removed with the VCM output, or from vapour return from loading operations. In normal practice, this is seldom the case. Emissions are prevented by providing tanks with refrigerated reflux condensers or by connecting to VCM recovery. Wet EDC and light-ends storage can have water phases to be drained. The drained water phase contains EDC and light-ends and should be collected for treatment.

### **4.5.2 Loading and unloading of VCM**

4.5.2.1 Emission of VCM during loading/unloading operations can occur from the decoupling of pipe-connections, when VCM between the connections is not evacuated before decoupling. Provisions are required to purge coupling connections to VCM recovery.

4.5.2.2 Plants loading VCM only into trucks, railcars or ships equipped with vapour return systems on their tanks avoid releases from the mobile tanks as the gas phase flows of the supplying and receiving VCM tanks are in balance. Care must be taken to avoid any increase in oxygen content in order to prevent the formation of vinyl polyperoxide.

## **4.6 Process control and automation**

4.6.1 Efficient process control, to achieve stable operations and high yields, is important to achieve good environmental performance. This includes pollution control equipment which should not be considered “add-on” operations of less importance than the production equipment.

4.6.2 In plants where monitoring results for environmental parameters are continuously available to operators and management, as documentation of performance and as input to improvements, swift corrective action can be taken and extraordinary releases prevented.

## **4.7 Operations**

4.7.1 Most plants today have established an environmental management system. For EDC/VCM plants, the following aspects are particularly important:

- regular inspection and instrumental monitoring to detect leaks and fugitive emissions to the atmosphere, water and ground;
- swift action to correct leaks when detected;
- ensuring that emissions from depressurising, emptying, purging and cleaning of equipment are treated in air or water pollution control equipment before discharge.

## **4.8 Treatment of air pollutants**

### **4.8.1 Sources of air pollution**

4.8.1.1 The major sources of emissions to air from EDC/VCM plants are leakages from flanges, valves and in some cases open drainage systems leakage (fugitive emissions), while emissions from stacks connected to air pollution control equipment are in general small. Only the air based oxychlorination reaction entails a large off-gas flow, due to the unreacted nitrogen when air is used as oxygen source. Reducing emissions of chlorinated organic components to the atmosphere starts with the separation of these components from the inert gas flow and recycling them to the process where they can either be reused or collected in the liquid residues.

4.8.1.2 The following sources (vents) can be connected to recovery of chlorinated organic compounds:

- direct chlorination reactor;
- oxychlorination reactor;
- distillation columns and driers for by-products including light- and heavy-ends;
- VCM/EDC separation;
- VCM purification;

- vacuum pumps;
- sampling systems;
- tanks and pipelines for EDC, VCM and by-products;
- contaminated waste water collecting system;
- buffer tank for contaminated waste water.

#### **4.8.2 Technologies for treatment of air pollutants**

4.8.2.1 Efficient methods for the recovery of chlorinated organic compounds and ethylene are:

- recycling to the process;
- refrigeration and condensation;
- adsorption in solvents, followed by stripping;
- adsorption on solids, followed by desorption.

4.8.2.2 Efficient methods for the further reduction of chlorinated compounds and ethylene concentrations in off-gas from recovery are:

- thermal incineration;
- catalytic incineration.

Catalytic incineration is restricted to low concentrations of organic compounds, as off-gas temperatures will otherwise be too high and inactivate the catalyst. Higher concentrations can be treated during limited periods of time.

4.8.2.3 After incineration, the HCl formed from the chlorinated organic compounds is available for treatment by absorption:

- in water/hydrochloric acid for recovery of HCl from concentrated gases;
- in alkaline solution for HCl emission reduction in diluted gases, including off-gas from recovery.

4.8.2.4 Concentrations of ethylene are high during start-up periods, emissions to the air can be reduced in these periods if the incinerators have sufficient capacity. Incinerators with sufficient capacity for all operating conditions, including start-up when ethylene concentrations are high, reduce the emissions to air in these periods.

#### **4.8.3 Performance of air pollution control equipment**

4.8.3.1 According to ECVM (3), typical concentrations in treated off-gas from plants employing BAT are as shown in **Table 3**.

**Table 3: Maximum emission levels in treated off-gas (ECVM (3))**

VCM	5 mg/Nm <sup>3</sup>
EDC	5 mg/Nm <sup>3</sup>
ethylene	150 mg/Nm <sup>3</sup>
HCl (as total chloride ion)	30 mg/Nm <sup>3</sup>
chlorine	5 mg/Nm <sup>3</sup>
dioxin (I-TEQ)	0,1 mg/Nm <sup>3</sup>

These maximum concentrations are monthly averages (no single measurement higher than twice these values), except the dioxin value which is an annual average. Nm<sup>3</sup> refers to wet volume at 0°C and 1 bar.

4.8.3.2 According to other available information, which is summarised and evaluated in **Appendix 1**, some plants report emissions which are lower than those reported by ECVM. Reported achievable emission levels are shown in **Table 4**.

**Table 4: Emission levels reported from some of the plants**

Sum of EDC and VCM from point sources	< 1 mg/Nm <sup>3</sup>
HCl from point sources	< 10 mg/Nm <sup>3</sup>
Dioxin (I-TEQ) from point sources	< 0,1 ng/Nm <sup>3</sup>
Volatile chlorinated hydrocarbons from fugitive sources	< 5 kg/h (and in working atmosphere: EDC < 2 ppm (8 mg/Nm <sup>3</sup> ) and VCM < 1 ppm (2,6 mg/Nm <sup>3</sup> ))

The figures on EDC, VCM and HCl represent annual averages, while figures on dioxins and fugitive emissions relate to maximum levels (spot sampling). Figures on working atmosphere relate to 8 h average maximum level.

#### **4.8.4 In-plant monitoring of air pollutants**

##### **4.8.4.1 Monitoring of stack emissions includes:**

- continuous, on line instrumental monitoring of O<sub>2</sub>, CO and temperature;
- sampling at intervals for C<sub>2</sub>H<sub>4</sub>, VCM, EDC, Cl<sub>2</sub>, HCl and dioxin.

##### **4.8.4.2 Monitoring of fugitive emission concentrations can include:**

- continuous, on line instrumental monitoring of C<sub>2</sub>H<sub>4</sub>, VCM and EDC at numerous (i.e. 10-20) points in the plant airspace;
- spot checks of VCM and EDC with hand-held instruments, to detect leaks;

- personal monitors (i.e. activated carbon buttons) for VCM.

4.8.4.3 Fugitive releases arise from incidents such as spillage or plant failure, or uncontained releases from processes operating under normal conditions. The chances of incidents occurring should be minimised by management and maintenance programmes.

4.8.4.4 Measurement of mass emission from fugitive sources is difficult, but can give a useful indication of the actual amount of emissions from fugitive leakages for comparison with emissions from other sources. At some plants measurements by tracer (SF<sub>6</sub>) technique are carried out once or twice a year, but this method has limitations and can be applied primarily for “isolated” plants.

#### **4.8.5 Cost of air pollution control**

4.8.5.1 ECVI (3) reports two examples of the typical costs of installed off-gas treatment equipment at the oxychlorination step after EDC-recovery, of balanced VCM plants, namely:

- oxygen process: 12 million DEM;
- air process: 28 million DEM.

### **4.9 Treatment of water pollutants**

#### **4.9.1 Sources of water pollutants**

4.9.1.1 Contaminated effluent water streams to be connected to water treatment systems originate from:

- reaction water from oxychlorination;
- wash water and condensate from EDC purification;
- other condensates;
- water seal flushes from pumps, vacuum pumps and gasholders;
- cleaning water from maintenance operations;
- water separated in wet EDC and light-ends storage tanks.

4.9.1.2 Categories of components relevant for effluent treatment are:

- EDC and other volatile chlorinated organic compounds;
- non-volatile chlorinated organic compounds;
- organic compounds, such as sodium formate and glycol;
- copper (when oxychlorination with fluidised-bed technology);
- dioxin related components.

#### **4.9.2 Technologies for treatment of effluent water**

4.9.2.1 Volatile chlorinated organic compounds such as EDC, VCM, chloroform and carbon tetrachloride can be effectively removed by steam or air stripping to concentrations in the effluent of less than 1 mg/l. The stripped compounds can be recycled to the process.

4.9.2.2 Relevant non volatile water soluble chlorinated organic compounds are 2-chloroethanol and chloral. These components, formed in the oxychlorination process, can be converted into components such as sodium formate and glycol, under the right conditions of temperature, pH and residence time. Sodium formate and glycol are biodegradable compounds.

4.9.2.3 Discharge of biodegradable compounds can be reduced efficiently by aerobic biological treatment.

4.9.2.4 To obtain the copper precipitation, treatment of the effluents at pH 11-12 (copper hydroxide precipitation) is required. In the same way, a high pH value promotes the hydrolysis of chloral and chloroethanol to strippable chloroform or easily biodegradable (ethylene glycol and sodium formate) products. The installation of a biological treatment requires the previous neutralisation of the effluent with the consequent chloride formation. Therefore, the nature of the receiving waters can determine the decision about the final treatment.

4.9.2.5 Discharge of copper with effluent water can be reduced by alkaline precipitation and separation by settling, to concentrations in the effluent of maximum 2 mg/l (ECVM (3)). Lower concentrations are reported by some other plants, and might be necessary for effective biological treatment. Electrolysis is alternatively or additionally applied at some plants where the effluent water contains ammonia.

4.9.2.6 Dioxin and related compounds generated during oxychlorination have a strong affinity to particle surfaces. The presence of dioxin related components in effluent from EDC production is influenced by the technology used in the oxychlorination process. With fixed bed oxychlorination there is virtually no carry over of copper catalyst which can be contaminated with dioxin. When fluid bed technology is applied, a significant portion of these components will be removed in the copper precipitation, together with the catalyst residues (metal sludges). Additional removal of dioxin related components can be achieved by flocculation and settling or filtration. Further removal of the dioxin related components may take place by adsorption on active sludge during biological treatment. Adsorption on activated carbon is used at some plants as additional treatment or as stand-by installations to be used when emission standards for chlorinated compounds cannot otherwise be complied with.

#### **4.9.3 Performance of effluent treatment installations**

4.9.3.1 ECVM (3) has provided data on annual values for a number of components in effluent water from VCM plants applying BAT. These

values are referred in **Table 5** below. ECVM indicates also that the concentration in the discharges from some of these plants are lower than the values in this table.

**Table 5: Performance of effluent treatment installations (ECVM (3))**

Component	Concentration
VCM	0,1 mg/l
EDC	5 g/tonne of EDC purification capacity (or 2,5 mg/l)
Dioxins	1 µg I-TEQ TCDD/tonne of EDC oxychlorination capacity
Copper	1 g/tonne of EDC oxychlorination capacity 2 mg/l (only relevant for oxychlorination with fluidised bed)
Chloroform	1 mg/l or 1 g/tonne of EDC purification capacity
Trichloroethane 1,1,2	0,5 mg/l
Hexachlorobutadiene	10 µg/l (microgram/litre)
Hexachlorobenzene	10 µg/l (microgram/litre)

ECVM explains that the EDC purification capacity is applied as reference for specific mass discharge of EDC, because this discharge is mainly related with the processing in this section. The production capacity of EDC by oxychlorination is applied as reference for the specific mass discharge of dioxins and copper, because those components are primarily related with the oxychlorination process. The values given for VCM, EDC and chloroform are before biological treatment. The values for the other substances are given for the final discharge.

4.9.3.2 According to other available information, which is summarised and evaluated in **Appendix 1**, some plants report discharges which are considerably lower than those reported in the table above. The achieved concentrations are given in **Table 6**.

**Table 6: Reported achievable concentrations in emissions to air at some of the plants**

Component	Concentration	Comment
Total chlorinated hydrocarbons	< 1 mg/litre	after stripper, (before bio-treatment)
Dioxins	< 0,1 ng/litre	final discharge
ΣHexachlorobenzene + pentachlorobenzene	< 1 µg/litre	final discharge
Hexachlorobutadiene	< 1 µg/litre	final discharge
Copper, total	< 1 mg/litre	final discharge
COD	< 125 mg/litre	

The values given for total chlorinated hydrocarbons refer to the concentration after stripper (unit prior to biotreatment). The other figures refer to final discharge (in this case, after on-site biological treatment). Figures on dioxins, HCB, HCBd are based on spot samples, while the other figures represent daily averages. A biological test programme carried out at one of these plants showed that after biological treatment the waste water was moderately toxic, not showing bioaccumulating tendency, but contained a fraction of persistent substances (26).

#### **4.9.4 Monitoring of effluent water streams**

4.9.4.1 Inlet water to treatment plants is monitored for the purposes of treatment plant operations. Continuous on-line monitoring for flow, pH and temperature is frequently applied. Treated effluent water monitoring could include:

- continuous on-line monitoring of flow and pH;
- continuous flow proportional sampling for solids, EDC, TOC, COD and Cu;
- periodic sampling for VCM, dioxins, hexachlorobenzene, hexachlorobutadiene and other chlorinated organic compounds.

In addition, AOX (Adsorbable Organic Halogenated Compounds) or EOX (Extractable Organic Halogenated Compounds) are used as control parameters in some countries. Potentially contaminated water would often have continuous EDC monitors, with detection limit 1 mg EDC/l and connected to an alarm.

#### **4.9.5 Cost of effluent water treatment**

4.9.5.1 As an example, the installed cost of a 40 m<sup>3</sup> water per hour waste water stripping plant is 5,9 million DEM (3).

## **4.10 Wastes**

### **4.10.1 Waste sources and categories**

4.10.1.1 The main process wastes are:

- light-end fractions;
- heavy-ends fractions/EDC tar;
- sludge from waste water treatment;
- hydrochloric acid from incineration of EDC tar;
- copper catalyst residue from fixed bed oxychlorination;
- coke from EDC cracking.

4.10.1.2 The main by-products of the EDC/VCM production process are light-ends and heavy-ends fractions from the EDC purification units. The total amount of light- and heavy-ends produced is approximately 0,03 tonnes per tonne VCM produced. Some of the light-ends and heavy-ends fractions can be used as feedstock for other chlorination processes, but this option is declining due to reductions in the use of e.g. chlorinated solvents. The heavy-ends fraction, the sludge from chemical and biological waste water treatment (at fixed bed oxychlorination plants) and the catalyst residues (at fluidised bed oxychlorination plants) contain dioxin compounds.

### **4.10.2 Waste treatment**

4.10.2.1 As a general principle, first priority should be given to waste minimisation and recycling to the process. Further waste minimisation (minimisation of chlorinated byproducts) could be achieved by the following options for plant design:

- use of pure oxygen instead of air in the oxychlorination process (on the other hand, the option of recycling HCl is less available (cf. § 4.2.2);
- (future) use of sodium ferrate as catalyst;
- use of direct chlorination (not balanced with oxychlorination);
- developing new processes avoiding oxychlorination (5).

4.10.2.2 Recycling is applied by some plants using the HCl from the incineration of heavy-ends and light-ends in the oxychlorination process. Alternatively, HCl from the incineration of heavy-ends and light-ends is made commercial grade for external sale. Some plants dispose of the recovered HCl in water recipients, directly or neutralised. In any case, destruction of liquid by-products can be performed by incineration on-site and in compliance with the achievable release levels referred to in sections 4.8 and 4.9.

4.10.2.3 One VCM plant has recently found that the contents of dioxins in the sludge from its waste water treatment system are 7 µg/kg (dry

weight) and 400 µg/kg (dry weight) in the sludge from the biological and chemical treatment, respectively. These sludges are disposed of in landfills. About 1 200 tonnes/year of the biological sludge (since 1983) and about 720 tonnes (covering a period of 4-5 years) of metal-bearing sludge have been deposited (separately from each other) in these landfills (22). Another plant has reported that the sludge from their chemical and biological treatment plant contains approximately 0,4 g dioxins/year. These figures indicate variations in the amount of dioxins in disposed sludge from 0,4-8 g dioxins/year.

4.10.2 4 Alternative options for the disposal of dioxin-contaminated sludges and cokes are destruction in chemical waste incinerators or deposition in controlled, chemical waste landfills. If sludges or coke contain significant quantities of dioxin and other stable chlororganic compounds, incineration would be considered as the long-term solution.

#### **4.10.3 Cost of waste treatment**

4.10.3.1 A liquid waste incinerator of 5 000 tonnes per year capacity for light- and heavy-ends fractions, including HCl and steam recovery, is reported to cost 14 million DEM.

## **5 Polyvinyl chloride production**

### **5.1 Overview**

A simplified block diagram of PVC production is shown in **Figure 4** (page 26).

### **5.2 Feedstock and auxiliary chemicals**

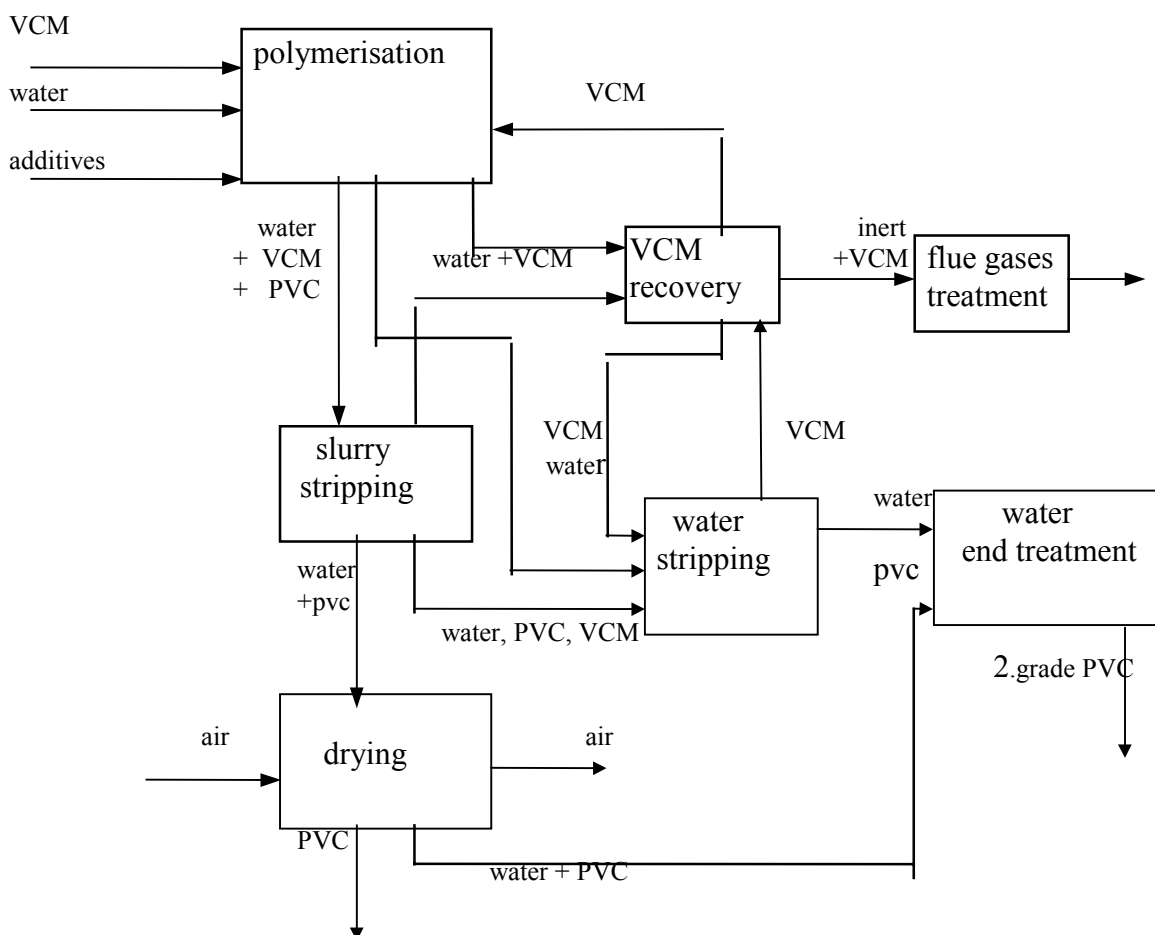
5.2.1 The main feedstock to the reactor consists of:

- VCM;
- demineralised water, for suspension or emulsion;
- initiators for the reaction (e.g. organic peroxides);
- surfactants and colloids to promote stability of suspension and to control PVC quality;
- other additives to improve the quality of the products (alcohols, cellulose derivatives and other water soluble biodegradable compounds).

### **5.3 Processes**

5.3.1.1 This report concentrates on suspension polymerisation, which is the most applied process. Suspension, emulsion and mass polymerisation are different with respect to air pollution. Suspension polymerisation and emulsion polymerisation are quite similar regarding

water pollution. Mass polymerisation is a dry process and there is no process effluent water.



**Figure 4: Block diagram of PVC production (4)**

### 5.3.2 Polymerisation

5.3.2.1 The polymerisation reaction is exothermic and performed batchwise in a stirred tank reactor with cooling to remove reaction heat. The reactor could be of either closed or open type. Modern plants have closed reactors, and conversion of existing open reactors is taking place.

5.3.2.2 When the required conversion is reached, residual VCM is vented to VCM recovery before transfer of the PVC polymer slurry to the stripping operations. This removal of excess VCM can be performed either in the reactor itself or in a blowdown-tank between reaction and stripping operations.

### **5.3.3 Stripping and drying**

5.3.3.1 The polymer suspension is saturated with VCM in the water phase and in the polymer particles. This residual VCM is usually removed in a separate system by stripping with steam. The residual VCM concentration in PVC particles from suspension polymerisation is low.

5.3.3.2 The efficiency of the stripping operation is important because most of the VCM remaining will be emitted to the atmosphere during drying. Suspension grade PVC at a BAT plant contains less than 20 g VCM per tonne PVC after stripping (3).

5.3.3.3 Overhead steam from the stripping operation, including VCM, is partly condensed. The condensate can be returned to the stripping system. Alternatively, the condensate can be transferred to the water stripper of the effluent treatment or other sections of the process, to recover contained VCM and to prevent VCM emission from this effluent. The stripped polymer slurry is centrifuged and transferred to the drying section.

### **5.3.4 VCM recovery**

5.3.4.1 The non-condensed VCM and steam are transferred to the condensing section of the VCM recovery system. Recovered VCM is reused as feedstock for polymerisation. The condensers for steam and VCM in the recovery system can be cooled by a multistage combination of normal cooling water and refrigeration. The efficiency of VCM recovery by condensation is determined by the right combination of low temperature and increased pressure. The gas flow to VCM recovery will fluctuate, as a consequence of batchwise polymerisation and consecutive operations.

5.3.4.2 The control of emissions of VCM to the environment is determined by:

- effective removal of VCM from reactors before opening;
- effective stripping of VCM from polymer suspension or emulsion;
- efficiency of VCM recovery;
- efficiency of final treatment of exhaust gas;
- provisions to prevent incidental emissions;
- provisions and procedures to control fugitive emissions.

## **5.4 Plant design**

### **5.4.1 Air pollution prevention**

5.4.1.1 During polymerisation, polymer deposits tend to be formed at the reactor wall. With open reactor technology, reactors must be opened after every batch for mechanical cleaning, visual inspection and the introduction of additives. Before opening, the reactor is steam flushed and degassed. However, any residual VCM remaining in the reactor before opening will be lost to the environment if additional measures are not taken.

5.4.1.2 With closed reactor technology, which is a technology used only for suspension PVC, reactors and operations are modified in such a way that it is not necessary to open the reactor after every batch for those purposes. In this situation the frequency of opening of the reactor can be reduced to levels of up to once per 100 batches, depending on the type of PVC being produced. The closed reactor technology is considered BAT for all new (future) plants. Emissions connected with the periodic opening should be taken into account.

5.4.1.3 At well run open reactor plants, obtaining BAT emission levels is possible (3). Whether a specific plant is achieving this emission level has to be documented by monitoring.

5.4.1.4 The off-gas sources to be connected to the VCM recovery system are:

- inert flushing vents from reactors, other process vessels and pumps in the polymerisation section;
- non-condensed steam from the overhead of the slurry stripper;
- overhead steam from the effluent stripper;
- vents from tanks containing VCM.

5.4.1.5 Minimising emissions to air implies connection to air pollution control equipment of all vents except:

- vents for gases containing explosive mixtures of organic compounds and oxygen;
- major relief vents which due to large flow will extinguish flares and incinerators;
- off-gas from PVC driers (normally not connected because of low concentrations, high volume).

To prevent leaks from unconnected vents, rupture disks in combination with safety valves on the high pressure side are employed. The pressure between the rupture disc and the safety valves are monitored to detect any leaks.

5.4.1.6 Preventing and minimising leaks causing fugitive emissions of air pollutants are achieved by using:

- valves: bellow or double seals or equally efficient equipment;
- pumps: double seals with liquid barrier, magnetic driven or canned;
- compressors and vacuum pumps: double seals with liquid barrier, magnetic driven or canned;
- agitators: double seals with liquid barrier, magnetic driven or canned;
- flanges (connectors): minimise number. High quality gaskets.

Magnetic driven or canned designs may not be proven technology yet for large capacity units. Flanges are not critical, compared to the other components.

#### **5.4.2 Water pollution prevention**

5.4.2.1 The water consumption should be reduced by internal measures, and, because of intermittent emptying of polymerisation reactors, effluent water streams should be collected in a closed equalising tank. VCM in water from the polymerisation reactors is removed in a separate stripper. With efficient stripping, concentrations lower than 1 mg VCM per litre in the effluents can be attained as a yearly average.

### **5.5 Storage, loading and unloading facilities**

5.5.1 VCM is alternatively stored in refrigerated tanks at atmospheric pressure, or in pressurised tanks at ambient temperature. Off-gas will only occur when there is an excess of inerts (nitrogen) introduced with the VCM input and removed with the VCM output, or from vapour return from loading operations. In normal practice, this is seldom the case. VCM emissions are prevented by equipping tanks with refrigerated reflux condensers or by connection to VCM recovery.

### **5.6 Process control and automation**

5.6.1 Efficient process control, to achieve stable operation and high yields, is important to achieve good environmental performance. This includes pollution control equipment, which should not be considered “add-on” operations of less importance. Swift corrective actions to prevent extraordinary releases can be ensured if monitoring results for environmental parameters are continuously available to operators and management.

## **5.7 Operations**

### **5.7.1 Control of accidental emissions of VCM**

5.7.1.1 Accidental emission of VCM could occur when the reaction rate during polymerisation exceeds the normal and emergency control limits. If normal control provisions should fail, the reaction energy has to be relieved by emergency venting of VCM to the atmosphere or to the gas holder.

5.7.1.2 Additional provisions to prevent emergency discharge of VCM to atmosphere are required such as:

- computer control for reactor feeds and operational conditions;
- emergency power for agitation;
- emergency reactor cooling capacity;
- controlled emergency vent capacity to the VCM recovery system;
- chemical inhibitor systems to stop reaction.

With these provisions, the runaway situation can be controlled before any VCM emission occurs.

### **5.7.2 VCM removal before opening reactors**

5.7.2.1 Procedures for effective removal of residual VCM from reactors are:

- depressuring of the reactor by venting to VCM recovery;
- draining the liquid contents to closed vessels;
- rinsing and cleaning of the reactor with water;
- draining of this water to the effluent stripping system;
- steaming and/or flushing of the reactor with inert gas to remove residual traces of VCM, with transfer of the gases to VCM recovery.

5.7.2.2 These procedures will ensure a very low level of VCM left in the reactor which will be slowly vented off to the ventilation system after opening of the reactor.

5.7.2.3 In some existing plants with small reactors, off spec charges are released to the equalising tank. Prevention of off spec charges by quality assurance measures including automatic weighing and feeding is thus important.

## **5.8 Treatment of air pollutants**

### **5.8.1 Sources of air pollutants**

5.8.1.1 VCM is the dominant air pollutant emitted from PVC plants. In addition, there could be some emission of PVC dust from PVC driers. The sources emitting directly to the atmosphere, normally with no VCM gas cleaning, are:

- ventilation air outlets from buildings containing polymerisation reactors (large flow, low VCM concentration);
- outlets for humid air from PVC driers (large flow, low VCM concentration);
- fugitive sources, mainly leakages from valves, pumps and flanges etc.

The only source subject to VCM gas cleaning is off-gas from the VCM recovery system.

### **5.8.2 Technologies for treatment of air pollutants**

5.8.2.1 Removal and recovery of VCM is achieved with systems such as absorption with organic solvents or adsorption with active carbon. Incineration under controlled conditions is an additional or alternative option. Gas streams containing PVC dust can be efficiently treated in textile filters or by well-designed cyclone separators.

### **5.8.3 Performance of air pollution control equipment**

5.8.3.1 Fugitive emissions represent only a few per cent of the total emission of VCM to the atmosphere (3). Based on measurements, and on estimates for fugitive sources which are difficult to measure, ECVI recommends for a plant employing BAT and producing s-PVC a total maximum long time average emission level of 100 g VCM/tonne s-PVC including fugitive emission. Plants employing BAT could achieve total air emissions of less than 70 g VCM/tonne suspension PVC including fugitive emissions (cf. **Appendix 1**).

### **5.8.4 In-plant monitoring of air pollutants**

5.8.4.1 Monitoring of stack emissions could include continuous, on line instrumental monitoring of VCM, O<sub>2</sub>, CO and temperature, whilst monitoring of fugitive emissions includes:

- continuous, on line instrumental monitoring of VCM at 10-20 points in the plant airspace;
- spot checks of VCM with hand held instruments, to detect leaks;
- personal monitors (i.e. activated carbon buttons) for VCM.

No data has been found with regard to the cost of air pollution control.

## **5.9 Treatment of water pollutants**

### **5.9.1 Sources of water pollutants**

5.9.1.1 Waste streams from PVC plants are not known to contain any organohalogenated compounds which are toxic, persistent and liable to bioaccumulate. The main effluent in the production process comes from the water required for suspending PVC in the reactor. Process water streams containing VCM should be collected in a closed collection system to be processed in the water stripper to remove and recover the residual VCM in:

- condensates from overhead suspension stripper, if any;
- condensates from the VCM recovery system;
- water from VCM / water phase separators;
- cleaning water from reactor cleaning;
- seal flushes from pumps or gasholder;
- effluents from vacuum systems;
- contaminated cooling water and surface run off.

These flows are collected in the VCM recovery system, where VCM is removed by steam stripping to less than 1 mg VCM per litre.

### **5.9.2 Technologies for treatment of effluent water**

5.9.2.1 Stripped effluents are transferred to a system for removal of suspended and emulsified solids and/or biotreatment. Suspended and emulgated PVC particles can be separated by traditional technologies such as filtration, flocculation and settling. Biological treatment can be an effective technology for reducing the discharge of biodegradable organic compounds.

### **5.9.3 Performance of effluent treatment installations**

5.9.3.1 According to ECVM (3) 5g VCM per tonne PVC production capacity is discharged. This discharge is based on 1 mg VCM/litre, measured at the outlet from effluent water stripping and does not take into account the effect of biological treatment. The outlet concentration of organic substances, expressed as COD, from an efficient biological treatment plant is reported to be 125 mg COD per litre. Achievable emission levels are given in **Table 7**.

**Table 7: Performance of effluent treatment installations (ECVM (3))**

Before biological treatment	< 1 mg VCM/litre
At effluent water outlet	< 125 mg COD/litre
Particles at effluent water outlet	< 30 mg PVC/litre

#### **5.9.4 Monitoring of effluent water streams**

5.9.4.1 Monitoring programmes will normally include flow recording and continuous flow proportional sampling, with samples being analysed for VCM, COD (or BOD) and suspended solids. No data have been found with regard to the cost of effluent water treatment.

### **5.10 Wastes**

#### **5.10.1 Waste sources and categories**

5.10.1.1 Wastes generated in PVC plants are:

- off spec PVC, including deposits removed from reactors;
- PVC sludge from mechanical treatment of effluent water;
- sludge from biological treatment of effluent water.

#### **5.10.2 Waste treatment**

5.10.2.1 Waste consisting of PVC should as first choice be used as raw material for products. Remaining PVC wastes and sludge could be placed on landfills or destroyed in a chemical waste incinerator.

### **5.11 PVC product**

5.11.1 After drying, PVC normally contains residual VCM as shown in **Table 8**.

**Table 8: Content of VCM in different PVC grades**

Food and medical grades	< 1 g VCM/t PVC (less than 0,5g in practice)
Common grades	< 5 g VCM/t PVC
Special grades	< 10g VCM/t PVC

## **6 Best available techniques for VCM plants - summary and conclusions**

### **6.1 Introduction**

6.1 The identified elements comprising BAT for the manufacture of VCM are summarised in this chapter. The text is extracted from Chapter 4.

### **6.2 Process**

6.2.1 In the oxychlorination step, the use of oxygen is considered to be the BAT for new plants but air can be used in some specific cases. Either fluid bed or fixed bed reactors can be considered as BAT provided that, in the fixed bed installations, it is demonstrated that the control of hazardous emissions leads to the same performance as fluid beds as regards the environmental impact. (Although more dioxins are formed in fixed beds, there is virtually no carry over to the effluent systems as there is for fluid beds). In future, direct chlorination with sodium ferrate or other catalysts may reduce the formation of chlorinated byproducts.

### **6.3 Plant design**

6.3.1 All vents are connected to air pollution control equipment, except vents for gases containing explosive mixtures of organic compounds and oxygen and major relief vents which, due to large flow, will extinguish flares and incinerators. There are also unconnected vents equipped with rupture disks on the high pressure side, to prevent leaks.

6.3.2 Leaks causing emissions of air pollutants can be prevented and minimised by selecting:

- valves: bellow or double seals or equally efficient equipment;
- pumps: double seals with liquid barrier, magnetic driven or canned;
- compressors and vacuum pumps: double seals with liquid barrier, magnetic driven or canned;
- agitators: double seals with liquid barrier, magnetic driven or canned;
- flanges (connectors): minimise number, high quality gaskets.

6.3.3 Separate effluent collection systems for:

- contaminated process effluent water;
- potentially contaminated water from leaks and other sources, including cooling water and surface run off from process plant areas etc.;

- uncontaminated water.

6.3.4 In order to prevent emissions of volatile components to the atmosphere, closed collection systems (sewers) for contaminated process effluent water should be installed. Sewers system made from corrosion resistant materials and designed to prevent leaks should be installed.

6.3.5 For new plants and for retrofitted plants, pipes and pumps etc. should be placed above the ground. For existing plants, pipes and pumps should be placed in ducts, so as to be accessible for inspection and repair.

## **6.4 Storage facilities**

6.4.1 Storage facilities can be tanks designed so as to prevent leaks and to prevent soil and water pollution caused by leaks or loading of VCM only into trucks, railcars or ships equipped with a vapour return system on their tanks in order to minimise emissions to air.

## **6.5 Process control and automation**

6.5.1 Monitoring results for environmental parameters should be continuously available to operators and management.

## **6.6 Operations**

6.6.1 An environmental management system should be established. The operational requirements should include:

- regular inspection and instrumental monitoring to detect leaks and fugitive emissions to atmosphere, water and ground;
- swift action to correct leaks when detected;
- ensuring that emissions from depressurising, emptying, purging and cleaning of equipment are treated in air or water pollution control equipment before discharge.

## **6.7 Treatment of air pollutants**

6.7.1 The following sources (vents) should be connected to recovery of chlorinated organic compounds:

- direct chlorination reactor;
- oxychlorination reactor;
- distillation columns and driers for by-products including light- and heavy-ends;
- VCM/EDC separation;
- VCM purification;
- vacuum pumps;
- sampling systems;

- tanks and pipelines for EDC, VCM and by-products;
- contaminated waste water collecting system;
- buffer tank for contaminated waste water.

6.7.2 Efficient methods for the recovery of chlorinated organic compounds and ethylene should be used, such as:

- recycling to the process;
- refrigeration and condensation;
- adsorption in solvents, followed by stripping;
- adsorption on solids, followed by desorption.

6.7.3 Efficient methods for the further reduction of concentrations of chlorinated compounds and ethylene in off-gas from recovery such as thermal incineration and catalytic incineration should be used.

6.7.4 Concentration of HCl formed from the incineration of chlorinated organic compounds by absorption can be reduced by:

- in water/hydrochloric acid for recovery of HCl from concentrated gases;
- in alkaline solution for HCl emission reduction in diluted gases, including off-gas from recovery.

6.7.5 Incinerator capacity for all operating conditions, including start-up when ethylene concentrations are high, reduces emissions to air in these periods.

6.7.6 Reported achievable concentrations in treated off-gas from VCM plants employing BAT are shown in **Table 9** (cf. para 4.8.3.2).

**Table 9: Reported achievable concentrations**

Sum of EDC and VCM from point sources	< 1 mg/Nm <sup>3</sup>
Dioxins from point sources (I-TEQ)	< 0.1 ng/Nm <sup>3</sup>
HCl from point sources	< 10 mg/Nm <sup>3</sup>

6.7.7 Monitoring of stack emissions could include continuous, on line instrumental monitoring of O<sub>2</sub>, CO and temperature and sampling at intervals for C<sub>2</sub>H<sub>4</sub>, VCM, EDC, Cl<sub>2</sub>, HCl and dioxin.

6.7.8 Reported achievable fugitive release levels are shown in **Table 10**.

**Table 10: Fugitive emissions**

Volatile chlorinated hydrocarbons from fugitive sources	< 5 kg/h
EDC in working atmosphere	< 2 ppm (8 mg/Nm <sup>3</sup> )
VCM in working atmosphere	< 1 ppm (2,6 mg/Nm <sup>3</sup> )

6.7.9 Monitoring of fugitive emission concentrations could include:

- continuous, on line instrumental monitoring of C<sub>2</sub>H<sub>4</sub>, VCM and EDC at 10-20 points in the plant airspace;
- spot checks of VCM and EDC with hand held instruments, to detect leaks;
- personal monitors (i.e. activated carbon buttons) for VCM;
- when practicable: measurements of mass emission, e.g. by tracer technique.

## 6.8 Treatment of water pollutants

6.8.1 Contaminated effluent water streams to be connected to a treatment plant include:

- reaction water from oxychlorination;
- wash water and condensate from EDC purification;
- other condensates;
- water seal flushes from pumps, vacuum pumps and gasholders;
- cleaning water from maintenance operations;
- water separated in wet EDC and light-end storage tanks.

6.8.2 Volatile chlorinated organic compounds such as EDC, VCM, chloroform and carbon tetrachloride can be effectively removed by steam or air stripping to concentrations in the effluent of less than 1 mg/l, before biological treatment. Stripped material (EDC, VCM etc.) should be condensed and recovered, or incinerated.

6.8.3 Discharge of copper with effluent water can be reduced by alkaline precipitation and separation by settling, to concentrations in the effluent below 1 mg/l. Electrolysis could be employed as alternative treatment e.g. in cases where the effluent water contains ammonia.

6.8.4 The presence of dioxin related components in effluent from EDC production is influenced by the technology used in the oxychlorination process. When fluid bed technology is applied, a significant portion of these components will be removed in the copper precipitation, together with the catalyst residues (metal sludges). Additional removal of dioxin

related components can be achieved by flocculation and settling or filtration and/or may take place by adsorption on active sludge during biological treatment or as additional treatment at the outlet from biological plant.

6.8.5 Where biological treatment is applied, reported achieved maximum discharges of effluent water from VCM plants are as shown in **Table 11** (cf. para. 4.9.3.2).

**Table 11: Reported achieved maximum discharges of effluent water**

Total chlorinated hydrocarbons	1 mg/litre
Dioxins	0,1 ng/litre
ΣHexachlorobenzene + pentachlorobenzene	1 µg/litre (microgram/litre)
Hexachlorobutadiene	1 µg/litre (microgram/litre)
Copper, total	1 mg/litre
COD	125 mg/litre

6.8.6 Treated effluent water monitoring could include:

- continuous on-line monitoring of flow and pH;
- continuous flow proportional sampling for solids, EDC, OC, COD/BOD and Cu;
- periodic sampling for VCM, dioxins, hexachlorobenzene, hexachlorobutadiene and other chlorinated organic compounds.

Potentially contaminated water outlets should have continuous EDC monitors, with detection limit 1 mg EDC/l and be connected to an alarm system.

## 6.9 Wastes

6.9.1 First priority should be given to waste minimisation and recycling to the process. Incineration in a chemical waste incinerator is recommended for destruction of sludge from waste water treatment and coke from EDC cracking. Deposition in a safe chemical waste landfill is an option for sludge from waste water treatment, coke from EDC cracking and spent copper catalyst, providing that the contents of organohalogens in the wastes are not significant.

## **7 Best available techniques for s-PVC plants - summary and conclusions**

### **7.1 Introduction**

7.1 The identified elements comprising BAT for the manufacture of s-PVC are summarised in this chapter. The text is extracted from Chapter 5.

### **7.2 Processes**

7.2.1 The closed reactor technology is considered BAT for all new (future) plants. For new plants the open process can be considered only when producing specialities (small lots etc). The PVC slurry at the inlet to the driers at BAT plants should have a maximum residual VCM content of 20 g VCM per tonne suspension PVC (yearly average).

### **7.3 Plant design**

7.3.1 The off-gas sources connected to the VCM recovery system include:

- inert flushing vents from reactors, other process vessels and pumps in the polymerisation section;
- non condensed steam from the overhead of the slurry stripper;
- overhead steam from the effluent stripper;
- vents from tanks containing VCM.

7.3.2 All vents connected to air pollution control equipment, except:

- vents for gases containing explosive mixtures of organic compounds and oxygen;
- major relief vents which due to large flow will extinguish flares and incinerators;
- off-gas from PVC driers.

To prevent leaks from unconnected vents, rupture disks on the high pressure side are employed.

7.3.3 Prevention and minimising leaks causing fugitive emissions of air pollutants could include:

- valves: bellow or double seals or equally effective measures;
- pumps: double seals with liquid barrier, magnetic driven or canned;
- compressors and vacuum pumps: double seals with liquid barrier, magnetic driven or canned;

- agitators: double seals with liquid barrier, magnetic driven or canned;
- flanges (connectors): minimise number, high quality gaskets.

7.3.4 Because of intermittent emptying of polymerisation reactors, effluent water streams would be collected in a closed equalising tank.

## **7.4 Storage, loading and unloading facilities**

7.4.1 VCM is stored in refrigerated tanks, at atmospheric pressure, or in pressurised tanks at ambient temperature. The tanks should be connected to VCM recovery.

## **7.5 Process control and automation**

7.5.1 Swift corrective action to prevent extraordinary releases can be ensured if monitoring results for environmental parameters are continuously available to operators and management.

## **7.6 Operations**

7.6.1 Additional provisions to prevent emergency discharge of VCM to atmosphere are:

- computer control for reactor feeds and operational conditions;
- emergency power for agitation;
- emergency reactor cooling capacity;
- controlled emergency vent capacity to the VCM recovery system;
- chemical inhibitor systems to stop reaction.

7.6.2 Procedures for effective removal of residual VCM from reactors are:

- depressuring of the reactor by venting to VCM recovery;
- draining the liquid contents to closed vessels;
- rinsing and cleaning of the reactor with water;
- draining of this water to the effluent stripping system;
- steaming and/or flushing of the reactor with inert gas to remove residual traces of VCM, with transfer of the gases to VCM recovery.

7.6.3 Prevention of off spec charges by quality assurance measures includes automatic weighing and feeding. An environmental management system should be established and in operation.

## **7.7 Treatment of air pollutants**

7.7.1 The only source subject to VCM gas cleaning is off-gas from the VCM recovery system. Removal and recovery of VCM is achieved with systems such as absorption with organic solvents or adsorption with active carbon. Incineration under controlled conditions is an additional or alternative option. Gas streams containing PVC dust can be efficiently treated in textile filters or by well-designed cyclone separators.

7.7.2 A reported achievable total maximum long time average emission level for a suspension PVC plant applying BAT is 70 g VCM/tonne suspension PVC including fugitive emission.

7.7.3 Monitoring of stack emissions could include continuous, on line instrumental monitoring of VCM, O<sub>2</sub>, CO and temperature, whilst monitoring of fugitive emissions could include:

- continuous, on line instrumental monitoring of VCM at numerous (i.e. 10-20) points in the plant airspace;
- spot checks of VCM with hand-held instruments, to detect leaks;
- personal monitors (i.e. activated carbon buttons) for VCM.

## **7.8 Treatment of water pollutants**

7.8.1 Process water streams containing VCM and collected in a closed collection system to be processed in the water stripper to remove and recover the residual VCM include:

- condensates from overhead suspension stripper, if any;
- condensates from the VCM recovery system;
- water from VCM/water phase separators;
- cleaning water from reactor cleaning;
- seal flushes from pumps or gasholder;
- effluents from vacuum systems.

7.8.2 VCM is removed by steam stripping to less than 1 mg VCM per litre. Stripped effluents are transferred to a system for the removal of suspended and emulgated solids and/or biotreatment. Suspended and emulgated PVC particles can be separated by traditional technologies such as filtration, flocculation and settling, etc. In situations where residual additives in the effluents require consideration, biological treatment can be an effective technology for reducing the content of biodegradable organic compounds.

7.8.3 Reported achievable maximum discharge levels from a plant employing BAT are shown in **Table 12** (cf. § 5.9.3.1).

**Table 12: Reported achievable discharge levels**

Before biological treatment	1 mg VCM/litre
At effluent water outlet	125 mg COD/litre
Particles at effluent water outlet	30 mg PVC/litre

These emission levels do not imply that biological treatment is always necessary.

7.8.4. Monitoring could consist of flow recording and continuous flow proportional sampling, and the analysis of samples for VCM, COD and suspended solids.

## **7.9 Wastes**

7.9.1 Waste consisting of PVC should as first choice be used as raw material for products. Remaining PVC wastes and sludge could be placed in landfills or destroyed in a chemical waste incinerator.

## **7.10 Residual VCM in dried PVC**

7.10.1 The values of residual VCM in PVC-grades achieved after drying are shown in **Table 13**.

**Table 13: Residual VCM in dried PVC**

Food grade and medical grade	<1 g VCM/t PVC (less than 0,5g in practice)
Common grades	< 5 g VCM/t PVC
Special grades	< 10g VCM/t PVC

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## Appendix 1

### 1 Background data for the determination of release values achievable for VCM plants applying BAT

#### 1.1 Releases into water

Basis for calculation: Average waste water volume for VCM plants: 1,1 m<sup>3</sup>/tonne prod. (9)

##### 1.1.1 Chlororganic compounds

- a. volatile chlorinated hydrocarbons: (e.g. EDC, VCM, Chloroform, Carbontetrachloride, 1,1,1-trichloroethane, 1,1,2-trichloroethane, methylchloride):
  - EDC is the major substance in the effluent.
  - according to ECVN (3), BAT includes steam stripping of water effluent resulting in EDC concentrations of less than 1 mg/l as a monthly average. It is reported from one plant, producing about 450 000 tonnes VCM/year, that the effluent after stripper and before biological treatment normally contains less than 0,1 mg EDC/l. Due to further evaporation, adsorption on biosludges and dilution effects, the concentration in outlet from biological treatment is likely to be lower than 0,1 mg/l.
  - a study made for the EC in October 1989 (9), as part of the preliminary work on EC Directive 90/415, gives concentrations less than 1 mg/l from one plant with regard to total chloroderivates. (No indications are provided on the type of mean value and conditions of measurement). The example refers to the production of 200 000 tonnes VCM/year.
  - EC Directive (16): the ELVs valid from 1 January 1995: EDC < 2,5 mg/l or 5 g/tonnes prod. EDC are by now complied with by most plants within the PARCOM area (ECVN (3)).
  - German regulations ("Annex 22") (20) require AOX from tributary streams to be not higher than 1 mg/l.
- b. other chlorinated compounds:
  - it is documented from at least one plant that dioxins occur at < 0,1 ng/l and HCB (include 4 other substances, i.e. 5CB)-level << 1 µg/l at the outlet from the biological treatment plant (24).
  - EC Directive (17) requires release limits of HCB and HCBd < 1,5 mg/l, monthly mean.

Applying BAT means that a concentration limit < 1 mg/l for the sum of all chlorinated organic compounds (including e.g. EDC, dioxins, HCB, HCBu) and concentration limits < 0,1 ng/l for dioxins and < 1 µg/l for HCB and HCBd may be achievable. Thus, total releases into water of chlorinated organic compounds from a BAT plant would be in the order of 1 g/tonne VCM. These conclusions should nevertheless be considered carefully given the few data available.

### 1.1.2 Copper (Cu)

According to Spain (4): Cu < 0,5 mg/l for soluble Cu is achievable. Total Cu < 1 mg/l (daily average) is achieved in final discharge at one plant with fluidised bed technology.

Cu discharges to water < 0,5 mg/l soluble Cu, and 1 mg/l total Cu is achievable.

### 1.1.3 Chemical oxygen demand (COD)

COD < 125 mg/l is considered an achievable emission level for the organic chemical industry in general. COD could be significantly lower.

COD < 125 mg/l is achievable.

## 1.2 Releases into air - point sources

### 1.2.1 Chlororganic compounds

- a. volatile chlorinated hydrocarbons:
  - emissions of both EDC and VCM < 5 mg/m<sup>3</sup> from point sources (vents) are achievable at most plants. Emission standards for EDC and VCM are 5 mg/m<sup>3</sup> in several Member States;
  - one plant has in their annual report published emissions figures for EDC and VCM < 0,5 mg/m<sup>3</sup> [annual average]. This plant uses thermal incinerator for all off-gases (25);
- b. other chlorinated organic compounds:
  - it is generally accepted that the emission of dioxins from incinerators operated at optimal combustion conditions is < 0,1 ng/m<sup>3</sup>. This is also the case for incinerators in VCM plants (including incinerators for destroying chlorinated byproducts) (24). Release levels for HCB and “comparable substances” < 5 ng/m<sup>3</sup> are well documented and should be associated with BAT.

When BAT is employed, the sum of EDC and VCM from point sources could be < 1 mg/m<sup>3</sup>. Emission of dioxins is < 0,1 ng/m<sup>3</sup>.

### 1.2.2 Hydrogen chloride

- HCl < 30 mg/m<sup>3</sup> is achieved at most plants and also recommended as BAT-level by ECVM.
- HCl < 10mg/m<sup>3</sup> is achieved in plants using alkaline wet scrubber or recovery of HCl.
- According to Spain (4) BAT implies HCl < 10 mg /m<sup>3</sup>.
- ELV at 10 mg/m<sup>3</sup> is used for some new waste incineration plants and is therefore proved achievable.

HCl < 10 mg/m<sup>3</sup> is achievable in a BAT-plant

## 1.3 Releases into air - fugitive emissions

### 1.3.1 Volatile chlorinated compounds

- Emission data from *monitoring* of fugitive emission are known only from a few plants. Substances released by fugitive emissions are: EDC, VCM, CCl<sub>4</sub>, CHCl<sub>3</sub>, 1,1,2 and 1,1,1-trichloroethane (=“Σ Chlorinated hydrocarbons”). EDC is the dominant substance.
- Emission levels have been reduced as monitoring experiences have been gained.
- According to the result of the monitoring programmes carried out at one plant producing about 450 000 tonnes/year, the amounts of fugitive emissions have varied from 8-15 kg/h of “Σ Chlorinated hydrocarbons” to less than 5 kg/h of “Σ Chlorinated hydrocarbons”.
- One plant of more than 400 000 tonnes VCM/year capacity reports total emissions to air of 14 g VCM per tonne VCM. This figure includes point and fugitive sources and is based on measurements and estimates.

Fugitive emission is less dependent on production capacity and annual productions than on plant design and operation. The last figure (Σ = 5 kg/h) indicates the emission level that should be achieved in a relatively large VCM plant applying BAT.

## 2 Release values achievable for s-PVC plants applying BAT

### 2.1 Releases into water

(Waste water volume for s-PVC plants: 4-5 m<sup>3</sup> /tonne s-PVC, (9))

#### 2.1.1 VCM

- BAT includes efficient steam stripping of water effluent, resulting in VCM < 1 mg/l.
- ECVM (3) identifies achievable levels for BAT plants as VCM < 1 mg/l and < 5 g/tonne s-PVC.
- Examples of better performances have not been available.
- The recommended level is in a BAT plant achieved *before* biological treatment.

Effluent from PVC plant applying BAT contains < 1 mg VCM/l before biological treatment

### 2.1.2 COD

- Information from one modern plant producing > 200 000 tonnes/year indicates that discharge levels of total organic carbon (TOC) ranges from 100-200 mg/l (0,5-1 kg/tonne s-PVC) before the effluent enters biological treatment plant.
- For a new plant, discharges < 0,4 kg TOC/tonne s-PVC (yearly average) was expected. This plant suggested the correlation between TOC and COD to be 1:3.6 (meaning COD < 1,5 kg/tonne s-PVC), still before entering biological treatment plant.
- ECVI recommends COD < 125 mg/l as BAT-level (meaning approx. 0,63 kg COD/tonne s-PVC).
- COD < 125 mg/l is also being considered as a level applicable to the whole organic chemical industry. This level can be achieved without biological treatment.

COD < 125 mg/l is achievable for BAT plants.
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### 2.1.3 Suspended solids (SS)/(PVC-particles)

- For a new plant producing 200 000 tonnes s-PVC, discharges of PVC-particles (as SS) < 100 g/tonne-PVC was regarded as a realistic target. (In this case the concentration in water discharge would be < 20 mg/l).
- According to Spain (4) PVC particles are regarded as solids in general and a concentration limit < 30 mg/l should be achievable.
- The same level is recommended as BAT by ECVI (3).
- Examples are known of old plants which discharge > 2 800 g SS/ tonne PVC produced (differences in analytical methods could be an explanation for the large difference as compared with the best plants).

SS < 30 mg/l for PVC-particles is achievable in a BAT-plant.
--

## 2.2 Releases into air

### 2.2.1 VCM

- For one new s-PVC plant a total emission of VCM < 1,5 kg/h (equals < 70 g VCM/tonne s-PVC) was predicted, including all point and fugitive sources emitting VCM during normal operations.
- Another modern s-PVC plant has reported on total emission of VCM < 65 g VCM/tonne PVC and included in this figure outlet of recovery units, driers and fugitive emissions.
- Spain (4) recommends VCM from outlet of driers < 20 g/ tonne s-PVC (and also that working area concentration < 3 ppm).
- Residual VCM in s-PVC slurry after stripping (and at the inlet of the drying section) should be less than 20 g VCM/tonne s-PVC (3).

- ECVM (3) recommends a BAT-level < 100 g VCM/tonne s-PVC.

In a s-PVC plant applying BAT, the achievable level of total VCM-releases (including all vents, off-gases, ventilation air and fugitive emissions) is estimated < 70 g VCM/tonne s-PVC.

## 2.3 Residual VCM in dried PVC

2.3.1 For most general applications residual VCM < 5 g VCM/tonne PVC, and < 0,5 g VCM/tonne PVC for food and medical application are achieved (3). This applies for both s-PVC and emulsion-PVC, with the exception of special grades PVC where residual VCM can be higher (less than 10 g/tonne s-PVC).

Residual VCM in common grade PVC are in general less than 5 g per tonne PVC and less than 0,5 g per tonne PVC for food and medical applications.

## Appendix 2

### Overview of emission limit values recommended by ECVM (3)

**Table A.1 VCM plants**

Substances	Emissions to air (point sources) mg/m <sup>3</sup>	Emissions to water	
		mg/l (max.)	g/tonne EDC
VCM	<5	0,1 *	
EDC	<5	2,5 mg/l *	5 g/tonne EDC
Chloroform	-	1 *	
1,1,2-tri-chloroethane	-	0,5	
Cu		0,5 mg/l for soluble and 2 mg/l for total Cu	1 g/tonne oxygen capacity
COD		125 mg/l	
Dioxins	<0,1 ng/m <sup>3</sup>	1 µg TCDD/tonne EDC pur.cap (including releases to air & water)	
HCl /Cl <sub>2</sub>	<30 +5		
Ethylene	<150		
Hexachloro-benzene (HCB)		10 µg/l	
Hexachloro-butadiene (HCBu)		10 µg/l	
Methyl-chloride	<1		

\* before biological treatment

**Table A.2 s-PVC plants**

	Emissions to air (point emissions)	Discharges to water
VCM	100 g/tonne s-PVC	1 mg/l ( 5 g/tonne prod.capacity)
PVC-dust		
PVC-particles		
COD		125 mg/l

## Appendix 3

## Overview of national regulations in force (1994)

(These tables do not allow a fair judgement of “strict” or “less strict” regulations in the different countries unless exact knowledge is available on which sources are included/excluded, whether values represent maximum or average values and other conditions/limitations).

Table A.3 VCM plants - discharges to water

	VCM	EDC	AOX	Dioxin HCB HCBu	COD or TOC	Cu	SS
EC Directive (16)		2,5 mg/l 5 g/tonne (both monthly average) *					
Belgium		EC Dir. Water volume : 2,5 m <sup>3</sup> /tonne production capacity.	15 mg/l TOX (Cl). Refers to water volume 1,1 m <sup>3</sup> /tonne production capacity				
France		EC Directive	3 mg/l		COD < 15 mg/l		
Finland	30 kg/month (6 month moving average)						
Germany		EC Directive	Annex 22: <0,1 mg/l or < 20 g/tonne production capacity				
The Netherlands		EC Directive					
Norway		0.35 mg/l; 1,7 kg/week (0,18 g/ tonne VCM production capacity)			TOC: 100 mg/l	1 mg/l and 1,7 kg week	
Portugal		EC Directive			COD < 40 mg/l		SS <60 mg/l
Spain		EC Directive					
Sweden	300 kg/year	< 1000 kg/year (under revision)					
Switzer-land	(Has no VCM production)	-	-	-	-	-	-
United Kingdom	< 1mg/l (expected)		Sum chlorinated < 2 mg/l				

\* Values applicable from 1 January 1995 for installations producing both EDC and VCM  
Tonne = production capacity of EDC including recycled EDC

**Table A.4 VCM plants - emissions to air**

	VCM	EDC	dioxins
Belgium	< 5 mg/m <sup>3</sup>	< 5 mg/m <sup>3</sup> (mass flow > 100g/h)	
Germany	< 5 mg/m <sup>3</sup> (d.a)	< 20 mg/m <sup>3</sup> (daily average, mass flow > 100 g/h)	
France	< 5 mg/m <sup>3</sup> (d.a)	< 20 mg/Nm <sup>3</sup> (mass flow < 100g/h)	
The Netherlands	< 5mg/m <sup>3</sup> (h.a)	< 5 mg/m <sup>3</sup> , hour average	
Norway	< 1 kg/h (approx. 20g/t VCM)	< 1 kg/h	0,1 ng/m <sup>3</sup> *
United Kingdom	< 5 mg/m <sup>3</sup>	proposal : < 20mg/m <sup>3</sup> mass flow < 100 g/h	
Switzerland		(has no VCM prod.)	
Portugal	0,1 mg/m <sup>3</sup> (appealed)		

\* for incineration of liquid byproducts from EDC production

**Table A.5 PVC plants - emissions to air**

	VCM
Belgium	< 5 mg/m <sup>3</sup>
Germany	< 5 mg/m <sup>3</sup> (daily average) and/or: 10 mg/kg mass-PVC 100 mg/kg s-PVC (homo) 400 mg/kg s-PVC (co) 1500 mg/kg emul- PVC
France	< 5 mg/m <sup>3</sup> (daily average) and/or: 50 mg/kg mass PVC 1200mg/kg emul-PVC 1500 mg/kg Co-po-PVC
Finland	1000 mg/kg s-PVC 4000 mg/kg emul-PVC
The Netherlands	< 5mg/m <sup>3</sup> (hour average)
Norway	< 20 kg/h (s+emul PVC) = approx. 2000 mg/tonne (s- + emul.)
United Kingdom	< 5 mg/m <sup>3</sup> (all vents) and 100 mg/tonne s-PVC 1500 mg/tonne PVC + 200 mg/tonne PVC reactor opening emission- emulsion
Switzerland	5 mg/m <sup>3</sup> (all vents)
Portugal	0,1 mg/m <sup>3</sup> (appealed)

## Appendix 4

### Pollutants and their properties

(Source: Report on data for priority hazardous substances in Norway, SFT, 1993:23)

#### Typical properties of 1,2-dichloroethane (EDC)

- Liquid at ambient temperature, b.p. 83°C
- Lost from water by evaporation, which is a more significant sink than biodegradation
- Measured concentrations in biosphere and hydrosphere do not provide any sign of bioaccumulation
- Chronic toxicity towards aquatic organisms
- Predicted lifetime in the atmosphere is about 50 days
- EDC is eliminated from the atmosphere through photooxidation processes, no effect is expected on the ozone layer
- Carcinogenic

#### Typical properties of vinylchloride monomer (VCM)<sup>2</sup>

- VCM is a gas at ambient temperature, b.p. 13°C and has a relatively low solubility in water
- VCM entering aqueous systems tends to evaporate, volatilisation half time from surface waters is a few hours or less. Evaporation is a more significant sink than biodegradation
- In groundwater where volatilisation cannot occur VCM hydrolyses slowly, half time in the order of 10 years
- Adsorption of VCM to sediments and soils is not significant
- Bioaccumulation of VCM is not significant
- Relatively low acute and chronic toxicity towards aquatic organisms
- Final atmospheric degradation products are CO<sub>2</sub> and HCl
- Predicted half time in the atmosphere, due to photo-oxidation, is 36 hours or less
- VCM in sediment and soil can be decomposed by methane-oxidising bacteria
- Carcinogenic

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<sup>2</sup> Source: ECVM (3)

**Typical properties of chloroform**

- B.p. 76,7°C
- Not liable to bioaccumulate
- Acute toxicity (1,6-105 mg/l)
- Carcinogenic
- Very slow degradability in surface water, moderate in aerobic environment
- Atmospheric life time: 60-100 years

**Typical properties of 1,1,1-trichloroethane**

- B.p. 74°C
- Not liable to bioaccumulate
- Moderate acute toxicity (7,5-280 mg/l)
- Degradability, abiotic: water - half-life 25 weeks
- Degradability, biotic: not easily degradable
- Life-time in atmosphere: 5,7-10 years
- Half-time, atmosphere: 140 weeks
- Carcinogenic in mice, not in rats

**Typical properties of hexachlorobenzene**

- B.p. 332°C
- Liable to bioaccumulate
- High acute toxicity (< 0,03 mg/l-0,32 mg/l)
- Persistent
- Carcinogenic

**Typical properties of carbontetrachloride**

- B.p. 76,7°C
- Not liable to bioaccumulate
- Acutely toxic (1,6-70 mg/l)
- Carcinogenic
- Lifetime atmosphere: 60-100 years
- Hydrolysis, half-time: 7000 years
- Very slowly degradable, in particular in surface water

**Typical properties of hexachlorobutadiene**

- B.p. 210-220°C
- Liable to bioaccumulate
- High acute toxicity (0,1-1,9 mg/l)
- Easily degradable (biotic)
- Metabolites mutagenic

**Typical properties of 1,1,2 trichloroethane<sup>3</sup>**

- B.p. 113°C
- Not bioaccumulative
- Biodegradable in specific aerobic conditions
- Half life in troposphere 1-2 months
- Not able to reach the stratospheric region and no ozone depletion potential
- Moderate acute toxicity (19-430 mg/l)

**Typical properties of dioxins (polychlorinated dibenzo-dioxins and -furanes)  
(as TCDD-equivalents)**

- B.p. above 900 ° C
- High acute toxicity
- Liable to bioaccumulate
- Liable to undergo biological magnification
- Persistent

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<sup>3</sup> Source: ECVN (3)

## Appendix 5

### Dioxin isomer patterns of effluent from VCM plants

(Example: Effluent from scrubber, VCM plant. Reported to Norwegian Pollution Control Authorities from a Norwegian VCM plant. Date of report: 25 July 1990).

Component	ng/l	Recovery (%) of the added 13 C-marked standards
volume (litre) per sample	2,84	
1378/1379-tetra-CDF	< 0,006	
1278-tetra-CDF	< 0,006	
2378-tetra-CDF	0,036	41
Sum-tetra-CDF	0,036	
12368/13479-penta-CDF	0,027	
12478-penta-CDF	0,017	
12378/12348-penta-CDF	0,048	
23478-penta-CDF	0,062	50
Sum penta-CDF	0,203	
123478/123479-hexa-CDF	0,190	54
123678-hexa-CDF	0,143	
123789-hexa-CDF	0,05	
234678-hexa-CDF	0,083	
Sum hexa-CDF	0,94	
1234678-hepta-CDF	0,80	55
1234789-hepta-CDF	0,24	
Sum hepta-CDF	1,4	
Octa-CDF	12,3	
Sum PCDF	14,9	
2378-tetra-CDD	< 0,01	84
Sum tetra CDD		
12378-penta-CDD	< 0,016	33
Sum penta CDD	< 0,016	
123478-hexa-CDD	< 0,016	
123678-hexa-CDD	< 0,016	57
123789-hexa-CDD	< 0,016	
Sum hexa-CDD	< 0,016	
1234678-hepta-CDD	< 0,016	54
Sum hepta-CDD	< 0,016	
Octa-CDD	0,18	62
Sum PCDD	0,18	
2378-TCDD equivalents*	0,10	

\* Nordic model (comparable with I-TEQ)