

GUIDELINES ON BEST AVAILABLE TECHNIQUES AND PROVISIONAL GUIDANCE ON BEST ENVIRONMENTAL PRACTICES

relevant to Article 5 and Annex C
of the Stockholm Convention on
Persistent Organic Pollutants

Specific chemical production processes
releasing chemicals listed in Annex C



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MAY 2007, GENEVA, SWITZERLAND

C O N T E N T S

SECTION I: INTRODUCTION

- I.A** PURPOSE
- I.B** STRUCTURE OF DOCUMENT AND USING GUIDELINES AND GUIDANCE
- I.C** CHEMICALS LISTED IN ANNEX C: DEFINITIONS, RISKS, TOXICITY
- I.D** ARTICLE 5 AND ANNEX C OF THE STOCKHOLM CONVENTION
- I.E** RELATIONSHIP TO THE BASEL CONVENTION
- I.F** RELATIONSHIP TO OTHER ENVIRONMENTAL CONCERNS

SECTION II: CONSIDERATION OF ALTERNATIVES IN THE APPLICATION OF BEST AVAILABLE TECHNIQUES

- II.A** CONSIDERATION OF ALTERNATIVES IN THE STOCKHOLM CONVENTION
- II.B** THE STOCKHOLM CONVENTION AND NEW SOURCES
- II.C** AN APPROACH TO CONSIDERATION OF ALTERNATIVES
- II.D** OTHER CONSIDERATIONS OF THE STOCKHOLM CONVENTION

SECTION III: BEST AVAILABLE TECHNIQUES AND BEST ENVIRONMENTAL PRACTICES: GUIDANCE, PRINCIPLES AND CROSS-CUTTING CONSIDERATIONS

- III.A** GUIDANCE
- III.B** GENERAL PRINCIPLES AND APPROACHES
- III.C** CROSS-CUTTING CONSIDERATIONS:
 - (i) CHEMICALS LISTED IN ANNEX C: FORMATION MECHANISMS
 - (ii) WASTE MANAGEMENT CONSIDERATIONS
 - (iii) CO-BENEFITS OF BEST AVAILABLE TECHNIQUES FOR CHEMICALS LISTED IN ANNEX C
 - (iv) MANAGEMENT OF FLUE GAS AND OTHER RESIDUES
 - (v) TRAINING OF DECISION MAKERS AND TECHNICAL PERSONNEL
 - (vi) TESTING, MONITORING AND REPORTING

SECTION IV: COMPILATION OF SUMMARIES FROM THE SOURCE CATEGORIES INCLUDED IN SECTIONS V AND VI

SUMMARIES OF SECTION V: SOURCE CATEGORIES INCLUDED IN PART II OF ANNEX C

SUMMARIES OF SECTION VI: SOURCE CATEGORIES INCLUDED IN PART III OF ANNEX C

SECTION V: GUIDANCE/GUIDELINES BY SOURCE CATEGORIES: SOURCE CATEGORIES IN PART II OF ANNEX C

- V.A** WASTE INCINERATORS
 - (i) MUNICIPAL SOLID WASTE, HAZARDOUS WASTE AND SEWAGE SLUDGE
 - (ii) MEDICAL WASTE
- V.B** CEMENT KILNS FIRING HAZARDOUS WASTE
- V.C** PRODUCTION OF PULP USING ELEMENTAL CHLORINE OR CHEMICALS GENERATING ELEMENTAL CHLORINE
- V.D** THERMAL PROCESSES IN THE METALLURGICAL INDUSTRY
 - (i) SECONDARY COPPER PRODUCTION
 - (ii) SINTER PLANTS IN THE IRON AND STEEL INDUSTRY
 - (iii) SECONDARY ALUMINIUM PRODUCTION
 - (iv) SECONDARY ZINC PRODUCTION

SECTION VI: GUIDANCE/GUIDELINES BY SOURCE CATEGORIES: SOURCE CATEGORIES IN PART III OF ANNEX C

- VI.A** OPEN BURNING OF WASTE, INCLUDING BURNING OF LANDFILL SITES
- VI.B** THERMAL PROCESSES IN THE METALLURGICAL INDUSTRY NOT MENTIONED IN ANNEX C PART II
 - (i) SECONDARY LEAD PRODUCTION
 - (ii) PRIMARY ALUMINIUM PRODUCTION
 - (iii) MAGNESIUM PRODUCTION
 - (iv) SECONDARY STEEL PRODUCTION
 - (v) PRIMARY BASE METALS SMELTING

| | |
|-------------|---|
| VI.C | RESIDENTIAL COMBUSTION SOURCES |
| VI.D | FOSSIL FUEL-FIRED UTILITY AND INDUSTRIAL BOILERS |
| VI.E | FIRING INSTALLATIONS FOR WOOD AND OTHER BIOMASS FUELS |
| VI.F | SPECIFIC CHEMICAL PRODUCTION PROCESSES RELEASING CHEMICALS LISTED IN ANNEX C |
| VI.G | CREMATORIA |
| VI.H | MOTOR VEHICLES, PARTICULARLY THOSE BURNING LEADED GASOLINE |
| VI.I | DESTRUCTION OF ANIMAL CARCASSES |
| VI.J | TEXTILE AND LEATHER DYEING (WITH CHLORANIL) AND FINISHING (WITH ALKALINE EXTRACTION) |
| VI.K | SHREDDER PLANTS FOR THE TREATMENT OF END-OF-LIFE VEHICLES |
| VI.L | SMOULDERING OF COPPER CABLES |
| VI.M | WASTE OIL REFINERIES |

Section VI.F

Guidance/guidelines by source category:
Source categories in Part III of Annex C

**Part III Source category (f):
Specific chemical production processes releasing chemicals listed
in Annex C**

| | | |
|-------------|---|----------|
| VI.F | Specific chemical production processes releasing chemicals listed in Annex C | 9 |
| 1. | Process description | 9 |
| 1.1 | Introduction to organic chemical processes | 9 |
| 1.2 | Co-product hydrogen chloride | 10 |
| 1.3 | Direct chlorination | 11 |
| 1.4 | Oxychlorination | 11 |
| 1.5 | Main product isolation | 14 |
| 1.6 | By-product destruction | 15 |
| 1.7 | Summary: What organic processes have in common | 15 |
| 1.8 | Inorganic chemical processes | 17 |
| 2. | Potential sources of chemicals listed in Annex C | 18 |
| 2.1 | Oxychlorination process | 20 |
| 2.2 | Other process contact with elemental chlorine | 21 |
| 2.3 | Titanium dioxide, chlorine process | 21 |
| 2.4 | By-product destruction | 21 |
| 2.5 | Products | 22 |
| 3. | Alternative processes that avoid formation of chemicals listed in Annex C | 22 |
| 3.1 | General considerations | 22 |
| 3.2 | Titanium dioxide, sulphate process | 22 |
| 4. | Primary and secondary measures | 24 |
| 4.1 | Production approaches reducing emission of chemicals listed in Annex C | 24 |
| 4.2 | Primary measures | 25 |
| 4.3 | Secondary measures: Best available techniques for waste treatment practices | 27 |
| 5. | Summary of measures | 28 |
| 6. | Performance standards and measures | 28 |
| 6.1 | Performance standards | 28 |
| 6.2 | Performance measures | 29 |
| | References | 32 |

Annexes

| | |
|---|----|
| Annex I. Synthesis of commodity chemicals | 30 |
|---|----|

Illustrations

| | |
|---|----|
| Figure 1. General process overview..... | 10 |
| Figure 2. C ₁ and C ₂ processes | 12 |
| Figure 3. Oxychlorination flow diagram | 13 |
| Figure 4. By-product destruction..... | 15 |
| Figure 5. Block diagram of generic organic process | 16 |
| Figure 6. Chloride process for manufacturing titanium dioxide | 18 |

VI.F Specific chemical production processes releasing chemicals listed in Annex C

■ Summary

This section focuses on processes for the manufacture of industrial chemicals that could theoretically give rise to persistent organic pollutants (particularly those chemicals listed in Annex C of the Stockholm Convention). Most of the processes described share common steps, including chlorination of organic or inorganic raw materials, purification of the products, separation of product streams (usually by distillation), destruction of high-molecular-weight side products and recycle or sale of hydrogen chloride. Efficient separation and destruction of chlorinated organic side products, which may include persistent organic pollutants, is key to best available techniques applicable to these processes, as is the associated guidance for any incorporated incineration processes. For certain products, modernized manufacturing processes that reduce formation of persistent organic pollutants are also presented. A range of performance standards associated with best available techniques are provided relevant to the individual processes.

1. Process description

1.1 Introduction to organic chemical processes

This section focuses on processes for the manufacture of industrial chemicals that could theoretically give rise to chemicals listed in Annex C of the Stockholm Convention. Chlorination processes are used in the synthesis of hundreds of industrial and specialty chemicals (Wiley Interscience 2000; World Chlorine Council 2002). Chlorine chemistry may also be used in processes where the final product contains no chlorine atoms. Under modern conditions of operation, however, these processes are typically not a major source of emission of chemicals listed in Annex C (UNEP 2003; EPA 2001).

Many of the general principles developed here – including more efficient use of raw materials and minimization of by-products and waste – are principles that support both better economic and environmental performance, consistent with modern principles of what is called green chemistry and engineering. They can also be applied to the much larger number of manufacturing processes used to produce a wide range of fine (low-volume speciality) chemicals, including pesticides and pharmaceuticals. Production of such chemicals can depend on the unique properties of chlorine that make it a valuable synthetic tool.

A list of some of the processes leading to industrial chemicals is included in annex I to this section (Wiley Interscience 2000). It is beyond the scope of this section to attempt to define best available techniques and best environmental practices for each of these processes individually; rather, the processes will be examined for what they have in

common and how those common practices can be addressed to reduce the formation, and particularly the release, of chemicals listed in Annex C of the Stockholm Convention.

Most of the processes involve a hydrocarbon, saturated or unsaturated, treated with elemental chlorine and in most processes also a catalyst. Reactions can be electrophilic additions to olefins, chlorination of aromatics or homolytic cleavage of carbon-hydrogen bonds with subsequent formation of the aliphatic chloride. In many cases chlorine atoms are present in the final product; on the other hand, in some processes (addition of an alcohol or amine to phosgene to produce, for example, polycarbonate and polyurethane plastics) no chlorine atoms are present in the final product. In addition, most of the processes involve generation of hydrogen chloride (HCl) as a co-product, via dehydrohalogenation or free radical reaction of chlorine with aliphatic hydrogen (Figures 1 and 2).

Crude products of these reactions vary in overall yield and purity, and as with virtually all industrial chemical processes, purification of the final product is required prior to sale or further internal use. Purification can involve separation of a mixture of saleable products – in many cases a spectrum of useful products results from a single reaction treatment – or separation of saleable products from the inevitable formation of high-molecular-weight by-products. For most organics and some inorganics that purification step involves distillation.

Generally, high-molecular-weight by-products are not saleable as themselves. In some cases they are thermally oxidized, with HCl, carbon monoxide (CO) and carbon dioxide (CO₂) as products of this oxidation. HCl is recovered and reused as an integral part of the process. In some cases they are viewed as wastes to be destroyed, usually by hazardous waste combustion, though HCl recycling is common.

■ Figure 1. General process overview

1.2 Co-product hydrogen chloride

Hydrogen chloride (HCl) is handled in one or more of the following ways. It can simply be neutralized and discharged as salt (sodium chloride). However, in some processes HCl can constitute a large amount of the effective use of input chlorine, so neutralization and discharge carries with it a large opportunity cost in the loss of potential raw material.

HCl can be recovered, hydrated and then sold as the commercial product muriatic (hydrochloric) acid or used for pH adjustment in chloralkali cells. Thus, there is some recycling of HCl electrolytically to chlorine. In the United States of America, muriatic acid, arising as a by-product of vinyl chloride production, has been analysed for polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) and found to contain about 20 pg I-TEQ/L range (0.004 g I-TEQ/yr for United States commercial production) (Carroll et al. 1997).¹

HCl can also be dried, oxidized catalytically and, in the presence of organic raw material, reacted as elemental chlorine to generate more of the desired product. The process by which this is accomplished is called oxychlorination and constitutes a means of in-process recovery of a valuable chlorine feedstock.

1.3 Direct chlorination

Free radical addition of chlorine to aliphatic hydrocarbons, typically methane, and direct electrophilic addition of a halogen to an alkene are well known from basic organic chemistry. As utilized in industry, the former is catalysed by light and the latter is typically a low-temperature operation catalysed by ferric chloride (FeCl₃) (OxyVinyls website). In the former, a free radical mechanism is desired. On the other hand, in the latter, unproductive side reactions result from free radicals, which can be inhibited with low concentrations of oxygen.

There is little if any potential for formation of by-product persistent organic pollutants in direct chlorination processes of pure aliphatic hydrocarbons. Aromatic feedstocks can also be chlorinated directly under mediation of a Lewis acid catalyst. The presence of aromatic chlorides as products of the process leaves open the possibility for generation of persistent organic pollutants under some conditions.

1.4 Oxychlorination

In oxychlorination, an organic such as ethylene reacts with dry HCl and either air or pure oxygen in a heterogeneous catalytic reaction (Figure 3). An example is the reaction involving HCl, oxygen and ethylene to form ethylene dichloride and water.



While there are many different commercial oxychlorination processes, in each case the reaction is carried out in the vapour phase over a modified Deacon catalyst. Unlike the Deacon process (which uses air or oxygen to oxidize HCl to chlorine (Cl₂) and H₂O under heat and catalysis) oxychlorination of ethylene occurs readily at temperatures well below those required for HCl oxidation per se. The catalyst typically contains cupric chloride (CuCl₂) as the primary active ingredient, impregnated on a porous support such as alumina, and may also contain numerous other additives.

The oxychlorination reaction generates heat and thus requires cooling for temperature control, which is essential for efficient production of ethylene dichloride. While there is an effective minimum temperature for the reactions, excessively high reactor temperatures lead to more by-products, mainly through increased ethylene oxidation to carbon oxides and increased ethylene dichloride cracking. Cracking of ethylene

dichloride yields vinyl chloride monomer and subsequent oxychlorination and cracking steps can lead progressively to higher-molecular-weight by-products with higher levels of chlorine substitution. Excessive temperatures (>300°C) can also deactivate the catalyst through increased sublimation of CuCl_2 . There is a strong commercial incentive to avoid those reaction conditions (overheating) that have the potential to lead to the production of polychlorinated by-products.

There are two types of catalyst systems used in oxychlorination: fixed bed and fluid bed. Both can be considered best available techniques (European Commission 2003).

Use of certain feedstocks in an oxychlorination process may lead to higher formation of persistent organic pollutants. For example, oxychlorination of heavy ends on a vinyl chloride plant can give considerable yields of PCDD/PCDF (UK Environment Agency 1997).

■ **Figure 2. C_1 and C_2 processes** (Wiley Interscience 2000)

■ Figure 3. Oxychlorination flow diagram

Source: Vinnolit website.

1.4.1 Fixed bed oxychlorination

Fixed bed reactors resemble multitube heat exchangers, with the catalyst packed in vertical tubes held in a tubesheet at top and bottom. Uniform packing of the catalyst within the tubes is important to ensure uniform pressure drop, flow and residence time through each tube. Reaction heat is removed by generating steam on the shell side of the reactor, or by flowing some other heat transfer fluid through it.

Temperature control in these reactions is important. The tendency to develop hot spots in a fixed bed can be minimized by packing the reactor tubes with active catalyst and inert diluent mixtures in proportions that vary along the length of the tubes, so that there is low catalyst activity at the inlet, but the activity steadily increases to a maximum at the outlet.

Alternatively, tubes can be packed with catalyst formulated to have an activity gradient along the length of the tubes. Multiple reactors in series can also be used in fixed bed oxychlorination, providing a similar activity gradient. Using pure oxygen as feed instead of air permits lower temperature and therefore lowers the formation of chlorinated by-products; however, this must be balanced against the cost of energy expended in producing pure oxygen. Staging the air or oxygen feed and grading the catalyst activity flatten the temperature profile and allow improved temperature control (OxyVinyls website).

1.4.2 Fluid bed oxychlorination

Fluid bed oxychlorination reactors are typically vertical cylindrical vessels equipped with a support grid and feed sparger system designed to provide good fluidization and feed distribution. They contain internal cooling coils for heat removal, and use either internal or external cyclones to minimize catalyst carry-over. Fluidization of the catalyst assures intimate contact between feed and product vapours, catalyst and heat transfer surfaces, and results in a uniform temperature within the reactor. Reaction heat is removed by

generating steam within the cooling coils or by passing some other heat transfer medium through them.

Operating temperature of 220°C – 245°C and gauge pressure of 150–500 kPa (22–73 psig) are typical for oxychlorination with a fluid bed reactor. Fixed bed oxychlorination generally operates at higher temperatures (230°C – 300°C) and gauge pressures of 150–1,400 kPa (22–203 psig). Chlorinated by-products of ethylene oxychlorination typically include 1,1,2-trichloroethane, chloroform, carbon tetrachloride, ethyl chloride, chloral, 2-chloroethanol, all of the chloroethylene congeners, and higher-boiling compounds (OxyVinyls website).

1.5 Main product isolation

Another common facet of these processes is the need to purify products that will either be sold or used in subsequent process steps. In virtually all cases, organic reaction products will be distilled. Fractional distillation separates streams of desired products and also separates desired products from unwanted high-molecular-weight materials called heavy ends or tars.

In the European Union the Integrated Pollution Prevention and Control (IPPC) Directive requires the use of best available techniques in generating a plant permit. To facilitate this, best available techniques reference documents (BREFs) are produced under the Directive by the European IPPC Bureau. Several of these are relevant to the application of best available techniques to processes using chlorination: for example, the BREF relating to large volume organic chemical processes, produced under the IPPC Directive, contains discussion of distillation (European Commission 2003).

Distillation is a standard engineering unit operation. It is based on sequential vaporization and condensation of liquid in a column, which typically includes packing or trays in order to maximize its internal surface area. Vapour that reaches the top of the column is enriched in the lowest-boiling material present in the distillation mixture.

Design and operation of distillation units are well understood, both in separations theory and in practice. For non-azeotroping materials with widely separated boiling points – for example, vinyl chloride and PCDD/PCDF – virtually complete separations can be accomplished in a well-designed and operated column (ChEResources website).

Desired materials are isolated and transported as liquids. For materials with boiling points above ambient temperature (e.g. ethylene dichloride) closed but not pressurized containers are used. For materials with boiling point below ambient temperature (e.g. vinyl chloride, chlorine) pressurized containers are used.

Some product isolations will not lend themselves to distillation. In principle, similarly useful and rigorous techniques (e.g. recrystallization) may be devised for specific materials. To the extent that those practices can demonstrate a similar result, such as isolation of by-products into a separate stream, these may, in some circumstances, also qualify as best available techniques.

1.6 By-product destruction

Undesired materials, including heavy ends, are usually destroyed in thermal processes, with or without oxygen. Figure 4 shows a prototypical heavy ends destruction train with HCl recovery.

Environmentally sound management of by-product and waste streams from chemical operations is critical to preventing the release of chemicals listed in Annex C into the environment. This management includes both effective and high-performance destruction of waste within a process and effective end-of-pipe methods to prevent release. Such destruction and end-of-pipe systems for the chemical and other industries are usually well defined by regulation, and should be monitored closely by operators and authorities.

Air, water and solid emissions from these processes can be analysed for chemicals listed in Annex C and treated appropriately. Further information is available in the European Union BREFs on large-volume organic chemical processes and on treatment of water and gas outputs from the chemical sector. A basic review of the technology of air, water and solids treatment is found in the cross-cutting considerations section (III.C) of the present guidelines.

In general, best available techniques for airstreams can involve recovery and recycling of HCl, combustion of trace volatiles, scrubbing of incinerator output streams with water, alkaline solutions or dry alkali, and addition of activated carbon and baghouses for removal of particulate. These may be used alone or in combination. Treatment of water streams can involve stripping and recovery (condensation or absorption) of volatile materials from water.

Subsequent biological purification of water streams with removal of solids is done in a dedicated water treatment system. Best available techniques for both streams will be considered in the granting of permits for facilities combusting heavy ends.

■ Figure 4. By-product destruction

1.7 Summary: What organic processes have in common

Figure 5 summarizes generically many of the processes described, including chlorination of organic or inorganic raw materials, purification of the products, separation of streams

for recycle (HCl, medium boilers), destruction of by-products (organic high boilers) and sale of products (low boilers, HCl, end products).

The United States Environmental Protection Agency notes: "Four major mechanisms have been postulated for the formation of halogenated dioxins and furans in the manufacture of halogenated organic chemicals: (1) direct halogenation of dioxins or furans...; (2) reaction of an ortho halogen with a phenate; (3) loss of the halogen (e.g., chlorine or bromine) from a halogenated phenate to form halogenated furans...; and (4) reactions between ortho- and meta-substituted halogens" (EPA 1997).

Mechanism (1) assumes a preformed PCDD or PCDF ring structure, possibly unhalogenated. Mechanisms 2–4 describe reactions of aromatic halides or halogenated phenols. A number of factors influence the amount of PCDD and PCDF that may be formed in a given manufacturing process, including temperature, pH, catalyst, and reaction kinetics (EPA 1997). The influence of these factors may be modulated by the specific chemistry: for example, the presence of aromatic or aliphatic organic materials.

Similarly, Fiedler et al. (2000) note that the likelihood of PCDD/PCDF generation in chemical processes to manufacture chlorine-containing materials generally decreases in the order chlorophenols > chlorobenzenes > aliphatic chlorides > inorganic chlorides. This may also be modulated by other reaction conditions. Total production will be affected both by propensity (ease) of formation and volume throughput so a large-volume process such as chlorine production may give a larger mass flow than a high-concentration/higher-yielding but smaller-volume process.

■ Figure 5. Block diagram of generic organic process

1.8 Inorganic chemical processes

Chlorine is used in generating inorganics whether it remains in the final product (NaOCl, ClO₂, FeCl₃, AlCl₃, ZnCl₂, etc.) or is simply used in the process (TiO₂, Si). These inorganic compounds may be used either stoichiometrically (NaOCl, ClO₂) or as catalysts (FeCl₃, AlCl₃, ZnCl₂, etc.). There are two inorganic chemical manufacturing processes identified with some production of chemicals listed in Annex C: chloride process manufacture of titanium dioxide (TiO₂) by certain manufacturers and production of anhydrous magnesium chloride (MgCl₂), an intermediate in the manufacture of magnesium metal. Other metal carbochlorination processes for purification of ore may involve similar conditions.

1.8.1 Chlorine and sodium/potassium hydroxide

Chlorine and either sodium or potassium hydroxide are produced by electrolysis of aqueous solutions of sodium or potassium chloride respectively. There are numerous technologies associated with this process, and while a full treatment of the process is beyond the scope of this guidance, an overview is provided in many general references (European Commission 2001, Appendix 1; Wiley Interscience 2000).

It is known anecdotally, and confirmed by reports of releases of persistent organic pollutants from modern chloralkali facilities, that there is the possibility of dioxin and furan generation at some point in the chloralkali process.

The use of graphite electrodes in this process is known to be a source of chemicals listed in Annex C. This process is generally considered obsolete in modern facilities (see subsection 4.2.2 below). With respect to other sources in the process, full mechanistic understanding of formation is lacking; however, it is believed that contact of elemental chlorine with preformed furan-like structures in organic gaskets and seals could be a source (see subsection 2.2). Even with modern processes PCDD/PCDF have been measured in releases and are formed in the process.

1.8.2 Titanium dioxide

There are two processes for manufacture of titanium dioxide (TiO₂): the chloride process and the sulphate process. They present an interesting case study: the chloride process produces much less waste but can be a source of persistent organic pollutants. The sulphate process involves much more waste in other categories, which is a problem as titanium dioxide is a high-volume chemical.

The production of titanium dioxide on the basis of the sulphate process gives rise to high amounts of contaminated spent acids of different concentrations. In the past those spent acids could not be recycled and used in other production processes. Methods for reuse and recycling of spent acids have been developed during the last decades and are currently standard operation for titanium dioxide production in industrialized countries.

The chloride process has grown in use over the past thirty years as an alternative for the sulphate route with its high amounts of spent acids. The chlorine route is a relatively compact process, giving the opportunity to recycle process materials directly without side products and with better product properties and considerably lower generation of

waste. TiO_2 ore, such as rutile or ilmenite – containing other metal oxides – is chlorinated under high temperature to produce titanium tetrachloride (TiCl_4), a stable, distillable liquid. Other metal halides are removed after cooling. TiCl_4 is then purified and oxidized with O_2 , liberating chlorine, which is recycled in the process. This oxidation process is thermodynamically favoured at temperatures above 600°C . A generalized overview of the chloride process is shown in Figure 6 and a more complete description of the competing sulphate process is found in subsection 3.1 below.

■ **Figure 6. Chloride process for manufacturing titanium dioxide**

1.8.3 Anhydrous magnesium chloride

Magnesium chloride (MgCl_2) can be produced by the reaction of magnesium oxide (MgO) and coke with elemental chlorine at $700\text{--}800^\circ\text{C}$. Details of this process and releases from it are presented in section VI.B (iii) of the present guidelines (magnesium production).

2. Potential sources of chemicals listed in Annex C

Central to formation of the basic structure of PCDD, PCDF, polychlorinated biphenyls (PCB) and hexachlorobenzene (HCB) is the presence or generation of aromatic materials. Those materials must, at some point, be chlorinated. UNEP 2003 notes that for chemical processes, generation of PCDD/PCDF may be favoured in processes that utilize, alone or together, elemental chlorine, elevated temperature, alkaline conditions and a source of free radicals.

For formation of PCDD/PCDF a source of oxygen or non-chlorinated dioxin/furan or related structures must be present. While it is difficult to imagine situations where PCDD/PCDF are generated without any possibility of generating PCB or HCB, PCDD/PCDF are favoured as by-products in processes where chlorinated phenols are a substrate or phenols are reacted with chlorine, especially if treated with alkali (see

subsections 4.2.3, 4.2.4 and 4.2.5 below). Combustion is a likely source of all of these materials; formation of by-products is dependent upon the exact technology employed in combustion processes, especially those involving uncontrolled combustion. Carbochlorination reactions (e.g. MgO to MgCl₂) may also be a source (see subsection 1.8 above).

HCB may be formed preferentially in similar kinds of reactions to those named above if oxygen or oxygenated materials are excluded. Electrolysis reactions with graphite electrodes fall into this category. A similar result may be obtained where chlorinated aliphatic rings are present and dehydrohalogenation can occur, as in reactions with hexachlorocyclohexane as a starting material.

In some cases, the source of aromatic carbon may be adventitious. Benzene as an impurity in raw materials of almost any chlorination reaction could result in HCB as a by-product even where it would not be expected from the chemistry of the desired reaction. Some patent work refers to reduction of aromatics in feed streams to other chemical synthesis as a means of reducing inadvertent manufacture of by-product persistent organic pollutants (see subsection 4.2.8). Finally, if HCB is a raw material for a process, carry-over of this material into final product will cause contamination (see subsection 4.2.5).

Many national inventories of emission estimates exist for PCDD/PCDF and PCB. For PCDD/PCDF, inventories typically involve unintentional generation. This is covered in the UNEP Toolkit (UNEP 2003). For PCB, inventories, if they exist, are mainly of legacy product still in use, waste in storage or recent production. Very few data on inadvertent generation of PCB exist.

It is important to note that there are sources of all of these by-products that are not related to chemical processes, but their release can only be prevented by installing high-performance technologies, closing the cycles and installing internal and external control of by-product and waste streams and the emissions connected with their destruction.

For HCB, both a product and a by-product, the situation is similar to that for PCB; however, some inventories of HCB as a by-product exist. The worldwide peak production and releases of HCB occurred in the late 1970s and early 1980s. Production was about 10,000 tons per year from 1978 to 1981 (Rippen and Frank 1986) of which 80% is believed to have been in Europe. A major input into the environment was its use as a pesticide, mainly as a fungicide for seeds of onions and sorghum and for crops such as wheat, barley, oats and rye, and as a fungicide to control bunt in wheat.

Since then, due to several regulations and bans, the production and releases have declined significantly. Bailey (2001) published a review of HCB sources and emissions worldwide in the mid-1990s. The total worldwide emission for that period was estimated at 10–90 tons per year. In the 1990s the contribution of different sources to the total emissions worldwide was as follows: fuel combustion 3.7%; iron and steel industry 0.3%; non-ferrous metal industry 36%; organic chemical industry 5.8%; other solvent use 0.004%; waste incineration 26%; and pesticide use 28%. The distribution in Europe, the United States and Canada showed considerable differences.

An extensive recent review of publications on HCB emissions was compiled as a Euro Chlor Science Dossier (Barber, Sweetman and Jones 2005). The dossier provides quite an exhaustive overview of all relevant published information up to 2004. It gives details on the production and releases in different periods, in different geographies and for different uses, and also deals with secondary and historical sources. A shorter version of this dossier was published in the peer-reviewed literature (Barber et al. 2005).

2.1 Oxychlorination process

The presence of heat, elemental chlorine, copper chloride catalyst and organic material makes the oxychlorination process a potential source of chemicals listed in Annex C, especially PCDD/PCDF and HCB. Aromatics may be generated in high-temperature processes and may also be present in feed materials, including HCl or air. Conditions in an oxychlorination reactor are in some ways similar to conditions in the areas of an incinerator downstream of the combustion zone, but may or may not contain similar amounts of soot-like elemental carbon or polycyclic aromatic hydrocarbons, which may contribute to de novo formation of PCDF (Lenoir et al. 2001; OxyVinyls website). Chemicals listed in Annex C created in this process, however, can be virtually completely removed from product and isolated in high-boiling materials (heavy ends) as a result of the distillation process.

Some chemicals listed in Annex C will adhere to particles of catalyst. In the case of fixed bed systems, they can be a part of the spent catalyst that is removed from service. This material can be treated thermally to destroy adsorbed organics or placed in a secure landfill. In reactors, fluidized bed catalyst particles undergo size attrition and can become entrained in the vapour stream. These particles eventually show up in solid waste or in the biological solids removed at the end of water treatment.

2.1.1 Acetylene process for vinyl chloride

Use of the balanced process for production of ethylene dichloride, and subsequent cracking to vinyl chloride, has, over the past fifty years, largely – but not entirely – superseded production of vinyl chloride via the acetylene route. In the acetylene process, calcium oxide and coke or coal are heated together at about 2,000°C to produce calcium carbide (CaC₂). When CaC₂ is reacted with water, acetylene is produced. Vinyl chloride results from a mercury catalyst-mediated addition of HCl to acetylene. Limited testing of effluents in the vinyl chloride process shows few if any chemicals listed in Annex C. The process to produce calcium carbide is uncharacterized; however, recent increases in capacity for this process may warrant further study.

2.1.2 Chlorinated solvents

Because the process to generate trichloroethylene, perchloroethylene and carbon tetrachloride involves chlorination, oxychlorination and pyrolysis, by-product will include chemicals listed in Annex C. These materials can be separated from final product by distillation and isolated in a fraction known as heavy ends. Many years ago, heavy ends material was commonly landfilled; however, since the 1970s, hazardous waste incineration, or thermal destruction with recovery and reuse of HCl, is by far the more common treatment.

There are a few examples of large extant stocks of HCB-containing material resulting from early solvent manufacture or more recent poor manufacturing practice. Annex II of this section is a case study of a Czech factory (IPEN 2006a). Included in the Euro Chlor dossier is a description of a long-standing situation in Australia (Barber, Sweetman and Jones 2005). It should be noted that neither of these case studies represents either best available techniques or best environmental practices; in fact, they are examples of the opposite.

2.2 Other process contact with elemental chlorine

There is anecdotal evidence that contact of elemental chlorine with organic process equipment (seals, gaskets, fibreglass equipment) that may contain aromatics, polycyclic aromatic hydrocarbons or elemental carbon can give rise to chemicals listed in Annex C, usually PCDF. In certain processes where high-boiling material or condensate is separated from manufactured elemental chlorine and not recycled in the process, chemicals listed in Annex C can be found in solid or liquid effluent.

2.3 Titanium dioxide, chlorine process

The presence of coke, chlorine, metals and elevated temperature may give rise to PCDD and PCDF analogous to those generated in oxychlorination. PCDD/PCDF, if formed, are expected to partition into stream(s) containing residual coke. If the residual coke is used for energy production, the potential content of PCDD/PCDF must be considered.

The emission from the chlorination process into atmosphere contains traces of $TiCl_4$, Cl_2 , HCl, CO and COS, even after the $TiCl_4$ condensation. $TiCl_4$, Cl_2 and HCl are eliminated by an acid off-gas washing in several steps. The wash liquors are recycled in the process or recovered and partly sold as pure hydrochloric acid (28%).

2.4 By-product destruction

There are three types of treatment commonly in use for wastes, especially heavy ends: hazardous waste combustion, thermal oxidation and catalytic oxidation. Some detail on each is presented in the chapter on ethylene dichloride and vinyl chloride in European Commission 2003. When heavy ends are burnt some chemicals listed in Annex C are generated, as in any hazardous waste combustion. The European IPPC Bureau is in the process of generating a BREF on waste combustion processes; however, there are legal requirements and best available technologies are already in use in the United States, the European Union and Japan, among others. Alternatives to the incineration of municipal solid waste, hazardous waste and sewage sludge that are presented in section V.A of the present guidelines (for example gas phase chemical reduction, base catalysed dechlorination and mechanochemical dehalogenation) may also be of use for certain types of by-product destruction. The Catoxid[®] process is a fluidized bed catalytic process for oxidation of organics. It generates a stream of HCl and CO_2 , which is sent in totality to the oxychlorination reactor for internal recycle (Randall 1994).

Alternatives to incineration described in this guidance document may also be of use for certain types of by-product destruction.

2.5 Products

Many products of these processes have been analysed for chemicals listed in Annex C, especially PCDD/PCDF. In general, products of the chloralkali-through-vinyl chloride chain are very low in such contamination; however, for these and other products the concentration of persistent organic pollutants may be a function of the efficiency of distillation or other purification.

IPEN (2006b) and references included therein contains reports of residual PCDD and PCDF in various products. PCDD/PCDF were also detected in five chlorinated chemicals, including triclosan, by Ni et al. (2005). HCB content of pesticides is described in Barber, Sweetman and Jones 2005 and references included therein. Chlorinated solvents prepared using modern techniques of purification have been tested for HCB and found to be in the low $\mu\text{g}/\text{kg}$ (parts per billion) range (<20 for trichloroethylene and <10 for perchloroethylene). Some similar information is also contained in UNEP 2003. Clearly, effective operation of the purification steps helps to ensure low levels of residual contaminants in products.

3. Alternative processes that avoid formation of chemicals listed in Annex C

3.1 General considerations

In many cases there are alternative processes by which desired chemicals can be manufactured. For processes where chemicals listed in Annex C are generated, there may be alternative processes that do not involve generation of such chemicals. Consistent with the Convention, the guidance on alternatives in this document, and good business practice, a thorough review of alternative processes and technologies should be conducted before building new or substantially modifying production facilities.

3.2 Titanium dioxide, sulphate process

For TiO_2 , there is an alternative commercial process utilizing sulphuric acid instead of chlorine.

In the sulphate process for TiO_2 ore is dried, ground and classified to ensure efficient sulphation by agitation with concentrated sulphuric acid in a batch or continuous exothermic digestion reaction. Controlled conditions maximize conversion of TiO_2 to water-soluble titanyl sulphate using the minimum acid. The resultant dry, green-brown cake of metal sulphates is dissolved in water or weak acid, and the solution is treated to ensure that only ferrous-state iron is present. The solution temperature is reduced to avoid premature hydrolysis and clarified by settling and chemical flocculation. The clear solution is then further cooled to crystallize coarse ferrous sulphate heptahydrate (known as copperas, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), which is separated from the process and sold as a by-product.

The insoluble “mud” is washed to recover titanyl sulphate liquor. That liquid is filtered to remove final insoluble impurities, then evaporated to a precise composition. Hydrolysis to produce a suspension (“pulp”) consisting predominantly of clusters of colloidal hydrous titanium oxide follows.

Precipitation is carefully controlled to achieve the necessary particle size, usually employing a seeding or nucleating technique. The pulp is then separated from the mother liquor and extensively washed to remove residual traces of metallic impurities, using chelating agents if necessary. The washed pulp is treated with chemicals, which adjust the physical texture and act as catalysts in the calcination step. This process can produce either anatase or rutile crystal forms, depending on the additives used prior to calcination (Millennium Chemical Corporation website).

The sulphate process requires 2.4–3.5 tons of concentrated H_2SO_4 per ton of TiO_2 , depending on the used raw material. Sulphuric acid is discharged from the process as sulphate, especially as iron(II) sulphate, or as free sulphuric acid in the spent acid. The total volume of spent acid caused by this process amounts to approximately 6–9 tons per ton of pigment. The recovery of the sulphuric acid from the used acid is divided into two processes:

- Recovery of the free acid by evaporation;
- Thermal decomposition of the sulphates and H_2SO_4 production on the basis of sulphur dioxide.

The spent acid is concentrated by evaporation to approximately 70%, where iron sulphate has a minimum solubility. Then the acid is cooled. After crystallization of the salts they are separated from the acid by filtration. The almost salt-free acid can be recycled directly or after a further concentration. Alternatively it can be used for other chemical processes or be decomposed to SO_2 .

The separated sulphates, strongly loaded with sulphuric acid, are thermally decomposed in flowing bed reactors at temperatures of 800°C – $1,000^\circ\text{C}$ (under the addition of sulphur, coal or oil as fuel) to sulphur dioxide and iron oxide. After cleaning, the obtained sulphur dioxide is processed to virgin sulphuric acid. The residual iron oxide can be reused in the cement industry.

The chloride process does not generate spent acids, and this means far less waste generation. There is, however, the possibility of some generation of chemicals listed in Annex C, specifically highly chlorinated furans (EPA 2006). Waste generation in the sulphate process, including of sulphuric acid and other mineral waste, is much higher but is not known to involve chemicals listed in Annex C. Trading elimination of small amounts of such chemicals for generation of large quantities of other waste materials may not be the optimal environmental approach. Best available techniques can be plant specific and viewed on a case-by-case basis.

4. Primary and secondary measures

4.1 Production approaches reducing emission of chemicals listed in Annex C

It is beyond the scope of this basic guidance to provide detailed comment on chemical plant and process design. However, responsible operation requires the recognition that chemical processes, while necessary for modern life, carry risks. To mitigate those risks to the greatest extent, processes must be designed to state-of-the-art safety and environmental standards as outlined, for example, in the European Union BREFs and comparable regulations in the United States and Japan. Experienced engineers must be engaged in the design of specific chemical processes.

Acceptable design must take into account the potential for side products and wastes, and make provisions for their safe handling or destruction. It must recognize that if the process carries the potential for generation of chemicals listed in Annex C, the four streams being emitted from a facility – air, water, solids and product – also carry that potential. Modern process design takes into account that potential, measures its reality, controls for it and includes operations to reduce or eliminate emission of those materials, commensurate with the requirements of the Convention. Modern safety management includes extensive training for operators and sufficient analytical and control instrumentation so that the facility as a whole operates to responsible standards.

The main demands for modern and safe chemical production can be stated as:

- Application of best available techniques, including high-performance technologies, in the design and construction of installations;
- Efficient closed cycles for the control of side products and destruction of wastes and emissions;
- Effective management of side products and handling of wastes;
- Dedicated facilities for destruction of wastes and emissions under the responsibility of the enterprise itself and with external control;
- Commitment to a standard of 0.1 ng I-TEQ/m³ for air emissions in destruction of any side products, wastes and emissions;²
- Development of a clearly defined regime for internal and external monitoring of key operating parameters.

4.2 Primary measures

4.2.1 Distillation and internal recycling of by-products

Distillation is used primarily to produce product of purity appropriate to downstream processing. As an example, vinyl chloride is manufactured via oxychlorination and purified by distillation. Rigorous distillation is used due to the potential for disruption of subsequent polymerization process by impurities. Unsaturated materials that might act as co-monomers competing in the polymerization and saturated or aromatic materials susceptible to free radical reactions other than polymerization can negatively impact polymerization reaction kinetics.

Distillation and high purity are important for good production. Distillation systems can be designed to effect separation of materials of closely or widely separated boiling points. The boiling points of chemical products of direct chlorination and the boiling points of competing impurities allow for their practical separation. Their boiling points are also sufficiently different from those of the chemicals listed in Annex C, however, that virtually complete separation can be accomplished. European Commission 2003 notes that purified ethylene dichloride does not contain significant amounts of PCDD/PCDF.

Destruction of chlorinated by-product materials allows for HCl to be harvested and reused (Vinnolit website). This is deemed to have greater impact because small changes in generation of persistent organic pollutants upstream of distillation are not reflected in the quality of desired products after distillation.

Distillation is a means of separating desired product from inadvertent by-products used across the chemical production industry from commodities to pesticides. Adapting the design and operation of the distillation apparatus is, in principle, relatively straightforward. Residual by-product contained in commercial product can be minimized by appropriate design and operation of the distillation apparatus. Effecting more complete separation for materials with boiling points that are not so widely separated as, for example, those of vinyl chloride and the various lower-molecular-weight by-products is for the most part a matter of correct design and construction and operation cost. Differences in concentration of residual chemicals listed in Annex C in commercial product may be due to differences in local regulation of products.

4.2.2 Elimination of carbon electrodes for chloralkali production

Older technology in the manufacture of chlorine and caustic soda utilized graphite anodes. Residues found from cells so constructed contained significant amounts of PCDD and especially PCDF (UNEP 2003). This problem was eliminated in much of the world following the invention of the coated titanium anode by H.B. Beer in 1965 and subsequent substitution for graphite in these processes (European Commission 2001). To the extent that the technology is still employed, the use of graphite electrodes is not a best available technique.

4.2.3 Elimination of alkali treatment of 1,2,4,5-tetrachlorophenol for the manufacture of 2,4,5-trichlorophenol

Manufacture of 2,4,5-trichlorophenol was accomplished by alkali treatment of 1,2,4,5-tetrachlorobenzene. This chlorinated phenol, in the presence of excess alkali, could generate significant amounts of by-product tetrachlorodibenzo-*p*-dioxins (TCDD). This process is not a best available technique.

4.2.4 Elimination of phenol route to chloranil

This process is described in UNEP 2003. Chloranil (2,3,5,6-tetrachloro-2,5-cyclohexadiene-1,4-dione) is the precursor for production of dioxazine dyes. When prepared by chlorination of phenol or aniline via elemental chlorine, significant amounts of PCDD/PCDF are generated as by-products. This process is not a best available technique. Chlorination of hydroquinone by HCl generates much cleaner product.

4.2.5 Modified production of pentachlorophenol and sodium pentachlorophenate

The following processes are also described in UNEP 2003. Three routes to pentachlorophenol are known commercially: chlorination of phenol by Cl₂ over a catalyst, hydrolysis of HCB with sodium hydroxide and thermolysis of HCB. The most common route today is the first. Sodium pentachlorophenate can be produced via hydrolysis of HCB or, more commonly, by treatment of pentachlorophenol by sodium hydroxide.

For both products, careful control of reaction conditions (e.g. temperature, chlorine feed rate and purity of catalyst) leads to significant reductions of PCDD microcontaminants. In the United States, emission of these materials was reduced from about 3–4 mg I-TEQ/kg in the mid- to late 1980s to about 1 mg I-TEQ/kg in the years since 1988 (EPA 2001).

Facilities utilizing products manufactured in the processes named above should also examine the need for secondary measures of their own, especially waste disposal practices using best available techniques.

4.2.6 Use of hydrogen in oxychlorination

Oxychlorination process feed purity can be a factor in by-product formation, although the problem usually is only with the low levels of acetylene, which are normally present in HCl from the ethylene dichloride cracking process. Acetylene fed to the oxychlorination reactor could in principle be converted to highly chlorinated C₂ products, and chlorinated C₂ products could give rise to chlorinated aromatics via cyclotrimerization (OxyVinyls website, Oxychlorination Technology and Hydrogenation Technology pages). Selective hydrogenation of this acetylene to ethylene and ethane in a reactor prior to the oxychlorination reaction is widely used as a measure to avoid by-product synthesis, especially of polychlorinated aliphatics (see Figure 2).

4.2.7 Catalyst maintenance and temperature uniformity control

Fluidized bed reactors tend to have better temperature control and more uniform performance, although the previously mentioned attrition of catalyst particles can allow for carry-over into other streams within the facility. For fixed bed oxychlorination catalysts, appropriate packing and maintenance can reduce hot spots and can reduce fouling of the catalyst bed, loss of productivity and the potential for generation of high-molecular-weight products. Catalyst beds are changed on a regular basis to maintain efficiency.

4.2.8 Reduction in aromatic hydrocarbons in feeds to oxychlorination processes

Two patents specify pretreatment of air or HCl reagents used in oxychlorination to remove aromatics, presumably precursors to various persistent organic pollutants (Cowfer, Johnston and Popiel 1998, 2001). This patented technology is proprietary and as such may not be appropriate for any required implementation of best available techniques, but indicates another primary approach.

Feeds to oxychlorinators should be controlled to minimize or eliminate feed of higher organics and aromatics that could lead to high formation of Annex C compounds. Because raw heavy ends from ethylene dichloride or solvent streams may contain these compounds, heavy ends should be suitably treated prior to use in solvent production.

4.3 Secondary measures: Best available techniques for waste treatment practices

The purpose of distillation or other purification steps is to separate desired product from by-products, and to concentrate chemicals listed in Annex C in the by-product stream. There are a number of processes that are capable of treating by-product streams, many of which are described in section V.A of the present guidelines. Alternatives to incineration described in this section may also be appropriate to the task of destruction of chemicals listed in Annex C in this context.

5. Summary of measures

Measures for the reduction of chemicals listed in Annex C arising from certain chemical production processes might be summarized as follows:

- Modify processes to reduce generation of chemicals listed in Annex C;
- Incorporate steps that treat impurities in raw materials, and use rigorous operational maintenance;
- Purify products by distillation where physical properties allow;
- Internally recycle inadvertently generated high-molecular-weight by-products as an integral part of the process;
- Manage wastes appropriately taking full account of the potential release of chemicals listed in Annex C to air, water and land and avoid any inadvertent formation.

6. Performance standards and measures

6.1 Performance standards

Performance standards can be set locally in individual plant permits, and will vary. By-product PCDD/PCDF emission is mentioned in the Charter of the European Council of Vinyl Manufacturers, and reflected in the OSPAR (Oslo and Paris Convention for the Protection of the Marine Environment of the North-East Atlantic) process via Decision 98/4 and adoption of best available techniques via PARCOM (Paris Commission) Recommendation 96/2. That standard is 1 g I-TEQ/ton annual oxychlorination capacity release to water. Air emission limits in the Charter of the European Council of Vinyl Manufacturers are 0.1 ng I-TEQ/Nm³ (ECVM website). This limit corresponds to the European Union regulatory limit for emissions of PCDD/PCDF to air from incinerators.

In the European Union, requirements for the chemical industry are based on the Council Directive 69/61/EC on integrated pollution prevention and control. Four BREFs on best available techniques in the large-volume and speciality organic and inorganic chemical industries describe comprehensive requirements for environmentally sound operation of all chemical industry installations, including standards for emissions of PCDD/PCDF (European Commission 2001, 2003, 2006a, 2006b). For any combustion installation or part of it in the chemical industry within the European Union a limit value requirement of 0.1 ng I-TEQ/Nm³ is the basis for its operation.

Air emissions from combustors in Japan are regulated according to size and whether they are new or retrofitted. Large new incinerators must achieve emission limits below 0.1 ng I-TEQ/Nm³. Water emissions from these processes are limited to 10 pg I-TEQ/L effluent. Limits in other regions or countries will typically be congruent with hazardous waste combustor regulations in local areas.

In the United States as well as in other regions, regulations based on maximum achievable control technology (MACT) have been proposed to control HCB and other hazardous air pollutant emissions from incinerators, medical waste incinerators, cement kilns, and lightweight aggregate kilns that burn hazardous wastes.

The United States Environmental Protection Agency (EPA) regulates the maximum allowable concentrations of HCB as a contaminant in certain pesticides. The established microcontaminant level for HCB in certain pesticides is in the order of 40–50 parts per million. As noted in Bailey 2001, because of process improvements, actual HCB concentrations in pesticide products may be significantly lower.

In Canada, as in many countries, HCB is a prohibited substance. Canadian law prohibits the manufacture, use, sale or import of HCB. However, these restrictions do not apply to HCB that is:

- An incidental by-product of the manufacturing process of a product and that is present in the product in a concentration not exceeding 20 parts per billion; or
- Contained in a control product (pesticides, herbicides, etc.) within the meaning of Section 2 of the Canadian Pest Control Products Act.

6.2 Performance measures

These may include analytical chemistry on emission streams and, in some areas, reporting of persistent organic pollutants to a pollutant release and transfer registry, such as the Toxics Release Inventory in the United States (EPA 2006; CCC website).

■ Annex I. Synthesis of commodity chemicals

| Chemical | Process | Process use | Co-products |
|--------------------------------------|--|-------------|--------------------------------|
| Chlorine, caustic soda | $\text{NaCl} + \text{H}_2\text{O} \rightarrow \text{Cl}_2 + \text{NaOH} + \text{H}_2$ | More common | |
| | See European Commission 2001, 2003 | | |
| Organics | | | |
| Allyl chloride | Direct chlorination of propylene >300°C | More common | HCl |
| | Pyrolysis of 1,2-dichloropropane | Less common | Chlorinated olefins, HCl |
| Chloranil dye | See UNEP 2003 | | |
| Chloroprene (2-chloro-1,3-butadiene) | $\text{C}_2\text{H}_2 + \text{CuCl}/\text{NH}_4\text{Cl} \rightarrow \text{vinyl acetylene} + \text{HCl} \rightarrow \text{chloroprene}$ | Less common | |
| | Vapour phase: butadiene + $\text{Cl}_2 \rightarrow$ 1,4- & 3,4-dichloro; isomerized (Cu catalyst) to 3,4-dichloro; HCl via NaOH; distilled to separate low-boiling mono-Cl's; 3,4-di; 1,4-di; heavies | More common | NaCl; overchlorinated products |
| Chlorinated benzenes | Vapour phase: benzene + chlorine + HCl | Less common | Mixed product |
| | Liquid phase: $\text{Cl}_2/\text{FeCl}_3$ to yield mix; controlled by amount of chlorinating agent (monos); some other specialized processes for certain isomers; high-Cl materials can precipitate. Purified by distillation and crystallization; separations difficult | More common | HCl |
| Epichlorohydrin | Allyl chloride + HOCl (chlorine water) \rightarrow glycerol chlorohydrins + $\text{NaOH}/(\text{CaOH})_2 \rightarrow$ epichlorohydrin | More common | Hydrolysed product; polymers |
| | Steam stripped then distilled | | |
| | Also: propylene + O_2 (Pd catalyst) \rightarrow allyl acetate \rightarrow allyl alcohol + $\text{Cl}_2 \rightarrow$ allyl chloride | | |
| Isocyanurate disinfectants | Isocyanuric acid + NaOH + Cl_2 | | |
| Phosgene | $\text{CO} + \text{Cl}_2$ used virtually immediately to produce polycarbonate and polyurethane | | |
| Chlorinated phenols | Lesser chlorinated phenols; phenol + Cl_2 ; various Lewis acid catalysts; FeCl_3 , ZnCl_2 | More common | |
| Pentachlorophenol (PCP) | Phenol + Cl_2 ; AlCl_3 as main industrial catalyst; 100°C – 180°C | More common | HCl |
| | Hexachlorobenzene (HCB) + NaOH | Less common | NaCl |

| Chemical | Process | Process use | Co-products |
|--|---|-------------|---------------------------|
| Sodium pentachlorophenate | PCP + NaOH | More common | NaCl |
| | HCb + NaOH | Less common | NaCl |
| Vinylidene chloride (ViCl ₂) | 1,1,2-trichloroethane + NaOH or Ca(OH) ₂ ; can also be a co-product of high-temperature chlorination of C ₂ materials | More common | NaCl or CaCl ₂ |
| Vinyl chloride (VCM) | Acetylene + HCl → vinyl chloride; Hg catalyst | Less common | |
| | Ethylene + Cl ₂ → EDC (direct; Fe catalyst); HCl + O ₂ + ethylene → EDC (oxychlor; Cu catalyst) | More common | |
| | See European Commission 2001, 2003 | | |
| C₁ products | | | |
| Methyl chloride | CH ₄ + Cl ₂ via heat or light | More common | |
| | CH ₃ OH + HCl → CH ₃ Cl | More common | |
| Other chlorinated methanes | CH ₃ Cl + Cl ₂ heat or light → CH ₂ Cl ₂ , CHCl ₃ , CCl ₄ | More common | |
| | CS ₂ + Cl ₂ → S ₂ Cl ₂ + CCl ₄ | Less common | |
| | CS ₂ + S ₂ Cl ₂ → S + CCl ₄ | | |
| C₂ products | | | |
| Chlorinated ethanes | | | |
| 1,1-di | VC + HCl/FeCl ₃ | More common | |
| 1,2-di (EDC) | Ethylene + Cl ₂ → EDC (Fe cat) (direct chlorination) | More common | |
| | Ethylene + HCl + O ₂ (Cu cat) → EDC (oxychlorination) | | |
| 1,1,1-tri | 1,1-di + Cl ₂ (photochemical) | More common | HCl |
| | 1,1,2-tri → 1,1,1-tri | More common | |
| | Ethane + Cl ₂ | Less common | |
| 1,1,2-tri | VC + Cl ₂ | More common | |
| | EDC + Cl ₂ | More common | HCl |
| 1,1,1,2-tetra, 1,1,2,2-tetra | EDC + Cl ₂ (can include oxychlor) | More common | HCl |
| | C ₂ H ₂ + Cl ₂ | | |
| | C ₂ H ₄ + Cl ₂ | More common | HCl |
| 1,1,1,2,2-penta | TCE + Cl ₂ → penta | | |

| Chemical | Process | Process use | Co-products |
|---|--|-------------|-------------------------|
| Chlorinated ethylenes | | | |
| Trichloroethylene (TCE) and perchloroethylene (PCE) | $\text{EDC} + \text{Cl}_2 \rightarrow \text{TCE} + \text{PCE}$ | More common | HCl |
| | $\text{EDC} + \text{Cl}_2 \rightarrow \text{PCE} + \text{CCl}_4$ | More common | HCl |
| | $2 \text{CCl}_4 \rightarrow \text{PCE}$ | More common | |
| | $\text{EDC} + \text{Cl}_2 + \text{O}_2 \rightarrow \text{PCE/TCE}$ | More common | |
| | Tetrachloroethanes + heat \rightarrow TCE | More common | HCl |
| | Pentachloroethane + heat \rightarrow PCE | Less common | HCl |
| Inorganics | | | |
| HCl | By-product; salt + sulphuric acid; hydrogen + chlorine; recovery from combustion of chlorinated organics | More common | |
| TiO_2 | $\text{C}, \text{Cl}_2, \text{TiO}_2 \text{ ore} \rightarrow \text{TiCl}_4 + \text{O}_2 \rightarrow \text{TiO}_2$ | More common | Cl_2 , recycle |
| | $\text{TiO}_2 \text{ ore} + \text{H}_2\text{SO}_4 \rightarrow \text{Ti}(\text{SO}_4)_2 \rightarrow \text{TiO}_2$ | Less common | sulphates |
| FeCl_3 | Iron or iron oxide + HCl \rightarrow FeCl_3 | | |
| Hypochlorites | $\text{Na}: 2\text{NaOH} + \text{Cl}_2 \rightarrow \text{NaOCl}$ | | NaCl |
| | $\text{Ca}: \text{Ca}(\text{OH})_2 + 2\text{Cl}_2 \rightarrow \text{Ca}(\text{OCl})_2$ also via NaOCl used as aid in chloride removal; recovered, then dried | | CaCl_2 |
| ZnCl_2 | $\text{Zn} + \text{HCl} \rightarrow \text{ZnCl}_2$ | | |
| ClO_2 | Generated from HClO_2 or NaClO_3 | | |

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Notes

¹ For information on toxicity measurement see section I.C, subsection 3 of the present guidelines.

² 1 ng (nanogram) = 1×10^{-12} kilogram (1×10^{-9} gram); Nm³ = normal cubic metre, dry gas volume measured at 0°C and 101.3 kPa. For information on toxicity measurement see section I.C, subsection 3 of the present guidelines.



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UNEP/SSC/BATBEP/2008/11

Section I-IV
Section VA
Section VB
Section VC
Section VD
Section VA
Section VB
Section VC
Section VD
Section VE
Section VF
Section VG
Section VH
Section VI
Section VII
Section VIII
Section IX
Section X