

Section VI.F.

Guidance by source category: Annex C, Part III Source Categories

Chemical production processes

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Best Available Techniques-Best Environmental Practices (BAT-BEP) for Chemical Production Processes

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1.0 Process Description

1.1 Introduction to Organic Chemical Processes. This paper focuses on processes for the manufacture of large-volume industrial chemicals which could theoretically give rise to by-product POPs. Chlorination processes are used in synthesis of hundreds of industrial and specialty chemicals.¹ Chlorine chemistry is also 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 by-product POPs.^{2,3}

Many of the general principles developed here can also be applied to the much larger number of manufacturing processes used to produce a wide range of fine (low-volume specialty) chemicals, including pesticides and pharmaceuticals. Production of such chemicals depends 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 Appendix A.¹ It is beyond the scope of this paper to attempt to define BAT/BEP 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 by BAT/BEP to reduce the formation and particularly the release of by-product POPs.

Figure 1. General Process overview

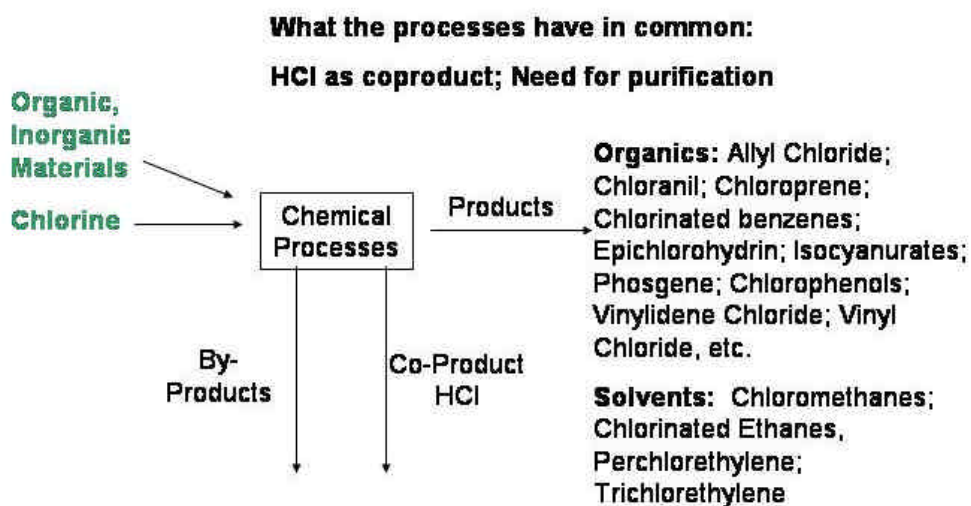
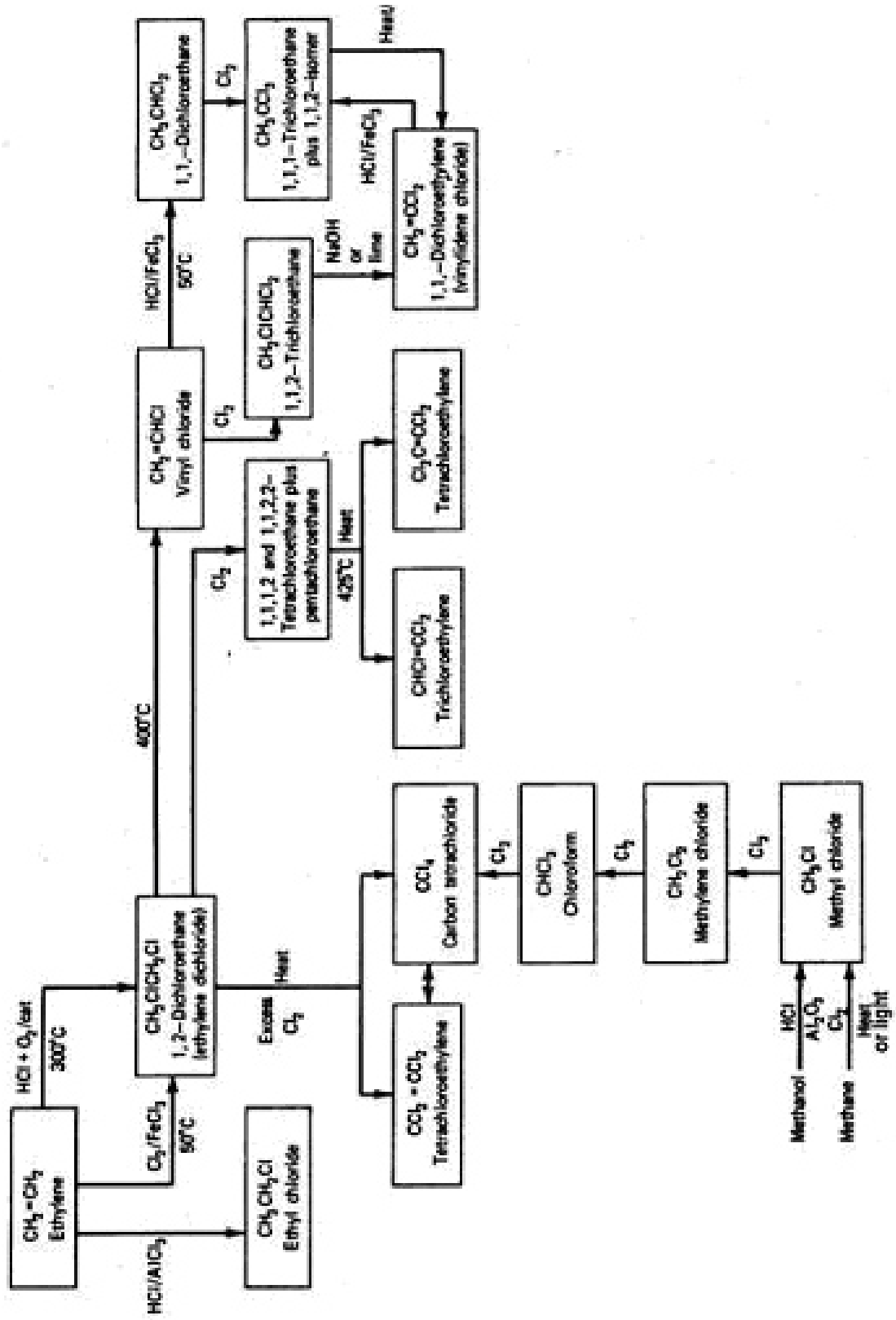


Figure 2. C₁ and C₂ processes.¹



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 HCl as a co-product, via dehydrohalogenation or free radical reaction of chlorine with aliphatic hydrogen (Figure 1).

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 salable products—in many cases a spectrum of useful products results from a single reaction treatment—or separation of salable products from the inevitable formation of high molecular weight side products. For most organics and some inorganics that purification step involves distillation.

Generally, high molecular weight side products are not salable as themselves. In some cases they are thermally oxidized, with HCl, CO and 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, still, HCl recycling is common.

1.2 Co-Product 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. Muriatic acid in the US has been analyzed for PCDD/F and found to contain ca. 20 pg I-TEQ/L range (0.004 g I-TEQ/yr for US production).⁴

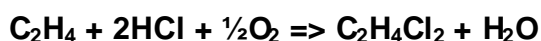
HCl can also be dried, oxidized catalytically and in the presence of organic raw material, reacted as elemental chlorine to generate more of the desired product. The process by which this is accomplished is called oxychlorination and often constitutes a valuable means of in-process recycling to avoid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

light and the latter is typically a low-temperature operation catalyzed by FeCl_3 .⁵ 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 byproduct POPs in direct chlorination processes of 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 POPs generation 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. An example is the reaction involving HCl, oxygen and ethylene to form ethylene dichloride (EDC) and water.



While there are many different commercial oxychlorination processes, in each case the reaction is carried out in the vapor phase over a modified Deacon catalyst. Unlike the Deacon process (which oxidizes HCl and O_2 to Cl_2 and H_2O 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 (CuCl_2) 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 EDC. While there is an effective minimum temperature for the reactions, excessively higher reactor temperatures lead to more by-products, mainly through increased ethylene oxidation to carbon oxides and increased EDC cracking. Cracking of EDC yields vinyl chloride monomer (VCM) and subsequent oxychlorination and cracking steps can lead progressively to higher molecular weight by-products with higher levels of chlorine substitution. Excessive temperatures ($>300^\circ\text{C}$) 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 BAT.⁶

1.4.1 Fixed Bed Oxychlorination. Fixed bed reactors resemble multi-tube heat exchangers, with the catalyst packed in vertical tubes held in a tubesheet at top and bottom. Uniform packing of catalyst within the tubes is important to ensure uniform pressure drop, flow, and residence time through each tube. Reaction heat is removed

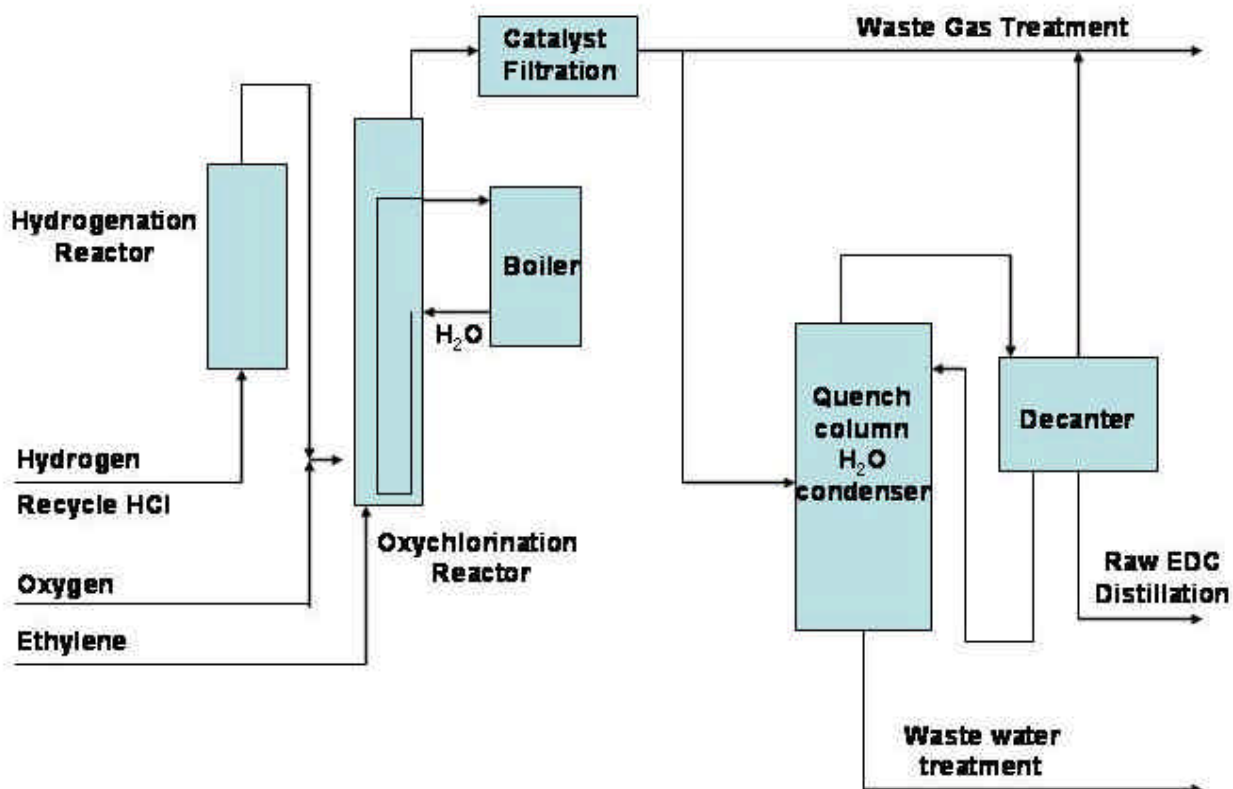
by generating steam on the shell side of the reactor, or by flowing some other heat transfer fluid through it.

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. Staging the air or oxygen feed and grading the catalyst activity flatten the temperature profile and allow improved temperature control.⁷

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 carryover. Fluidization of the catalyst assures intimate contact between feed and product vapors, 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 220-245°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 (230-300°C) and gauge pressures of 150-1400 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.

Figure 3. Oxychlorination Flow Diagram ⁸

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 desired product 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 (BAT) in generating a plant permit. To facilitate this, BAT Reference Documents (BREFs) are produced under the Directive by the European Integrated Pollution Prevention and Control Bureau (EIPPCB). Several of these are relevant to the application of BAT to processes using chlorination. For example, the BREF relating to Large Volume Chemical Processes produced under the IPPC Directive contains discussion of distillation.⁶

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 so as to maximize its internal surface area. Vapor 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 is well-understood both in separations theory and in practice. For non-azeotroping materials with widely separated boiling points—for example, vinyl chloride and PCDD/F--virtually complete separations can be accomplished in a well-designed and operated column.⁹

Desired materials are isolated and transported as liquids. For materials with boiling points above ambient temperature (example: EDC) closed but not pressurized containers are used. For materials with boiling point below ambient temperature (example: VCM, chlorine) pressurized containers are used.

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

When there are air, water and solid emissions from this process, these streams can be analyzed and treated for by-product POPs contamination. Under the IPPC Directive, BREFs for waste combustion and treatment of water and gas outputs from these kinds of processes are being developed, although treatment systems are well-defined by regulation in many countries.

In general, BAT for air streams can involve recovery and recycle of HCl, combustion of trace volatiles, scrubbing of incinerator output streams with water, alkaline solutions or dry alkali, 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. BAT for both streams will be considered in the granting of permits for facilities combusting heavy ends.

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 side-products (Organic High Boilers) and sale of products (Low Boilers, HCl, End Products).

Figure 4. By-Product Destruction

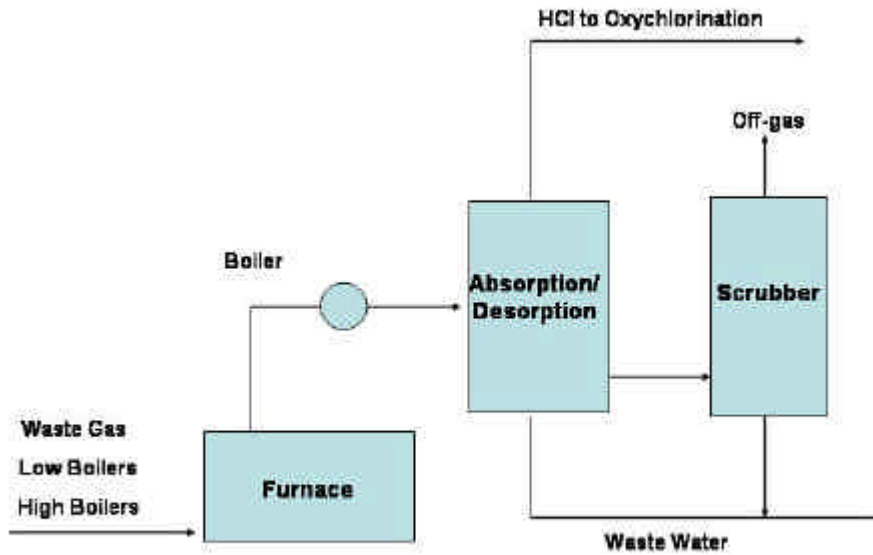
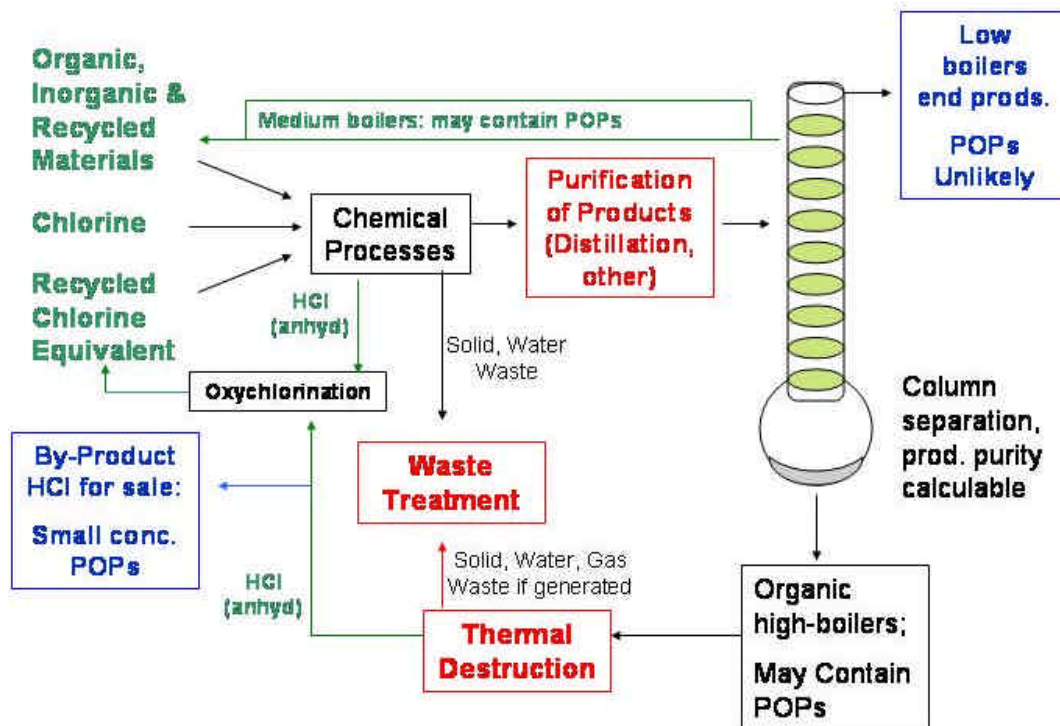


Figure 5. Block Diagram of Generic Organic Process

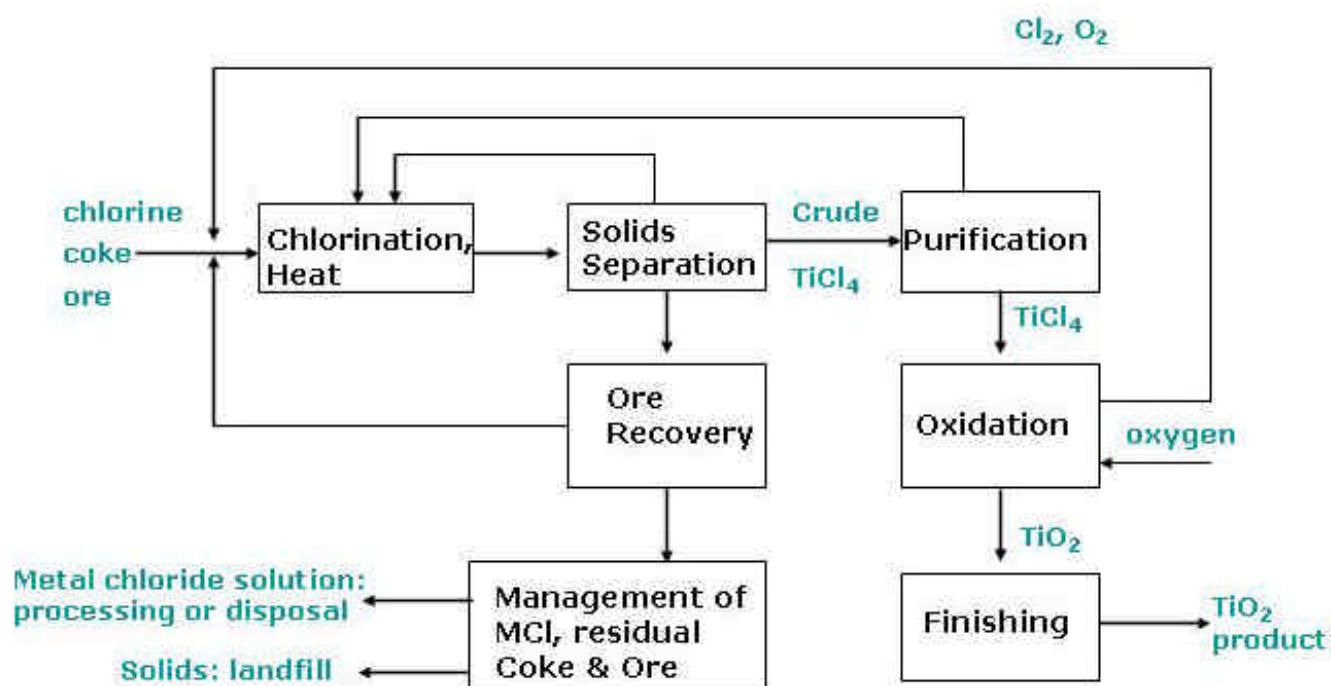


1.8 Introduction to Inorganic Chemical Processes. Chlorine is used in generating inorganics whether it remains in the final product (NaOCl, ClO₂, FeCl₃, AlCl₃, ZnCl₂, etc.) or is simply used in the process (TiO₂, Si). These inorganic compounds may be used either stoichiometrically (NaOCl, ClO₂) or as catalysts (FeCl₃, AlCl₃, ZnCl₂, etc). Thus far, the only inorganic chemical manufacturing process identified with production of by-product POPs is manufacture of TiO₂ by the chloride process; however, other metal carbochlorination processes for purification of ore may involve similar conditions to that of TiO₂ processing.

1.9 Titanium Dioxide. There are two processes for manufacture of TiO₂: the chloride process and the sulfate process. They present an interesting case study: the former produces much less waste but under some circumstances can give rise to POPs. The latter involves much more non-POPs waste.

The chloride process has grown in use over the past thirty years as a result of its relative compactness, recycling of process materials, better product properties and considerably lower generation of waste. TiO₂ ore such as rutile or ilmenite -- containing other metal oxides--is chlorinated under high temperature to produce TiCl₄, a stable, distillable liquid. Other metal halides are removed after cooling. TiCl₄ is then purified and oxidized with O₂, liberating chlorine, which is recycled in the process. This oxidation process is thermodynamically favored at temperatures above 600^o C. A generalized overview of the chloride process is shown in Figure 6 and a more complete description of the competing sulfate process is found in Section 3.1

Figure 6. Chloride Process for Manufacturing Titanium Dioxide.



2.0 Potential Sources of Unintentionally Produced POPs.

2.1 Oxychlorination Process. The presence of heat, elemental chlorine, copper chloride catalyst and two-carbon organic material capable, in principle, of cyclotrimerization (acetylene, chloroacetylenes, ethylene, chlorinated ethylenes) to aromatics makes the oxychlorination process a potential source of by-product POPs. Aromatics may also be present in feed materials, including air. Conditions in an oxychlorination reactor are in some ways similar to conditions in the cooler areas of an incinerator.^{10,11} By-product POPs created in this process, however, are virtually completely isolated in high-boiling materials (heavy ends) rather than product as a result of the distillation process.

Some by-product POPs 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 vapor 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 EDC, and subsequent cracking to vinyl chloride has, over the past 50 years, largely—but not entirely--superseded production of vinyl chloride via the acetylene route. In the acetylene process, calcium oxide and carbon are strongly heated together to produce calcium carbide. When CaC_2 is reacted with water, acetylene is produced. Vinyl chloride results from catalyst-mediated addition of HCl to acetylene. Due to the decreasing use of this process in the days of well-defined analytical procedures for detection of POPs, little is known of POPs generation and concentration in materials and wastes.

2.2 Other Process Contact with Elemental Chlorine. There is anecdotal evidence that contact of elemental chlorine with organic process equipment (seals, gaskets, fiberglass equipment) can give rise to by-product POPs, usually furans. In certain processes where high boiling material or condensate is separated from manufactured elemental chlorine and not recycled in the process, by-product POPs can be found in solid or liquid effluent.

2.3 Titanium Dioxide. The presence of coke, chlorine, metals and elevated temperature may give rise to dioxins and furans analogous to those generated in oxychlorination. PCDD/F, if formed, are expected to partition into stream(s) containing residual coke.

2.4 By-Product Destruction. There are three types of waste treatment: Hazardous Waste Combustion, Thermal Oxidation and Catalytic Oxidation, and some detail on each is presented in the EDC/VCM Chapter of the EIPPCB BREF on Large Volume Organics.⁶ When heavy ends are burned, some by-product POPs are generated as in any hazardous waste combustion. EIPPCB is in the process of generating a BREF on

waste combustion processes; however, there are legal requirements and best available technologies already in use in the US, the EU and Japan among others.

The Catoxid^{®12} process is a fluidized-bed catalytic process for oxidation of organics. It generates an HCl and CO₂ stream that is sent in totality to the oxychlorination reactor for internal recycle.

2.5 Products. Many products of these processes have been analyzed for by-product POPs, especially PCDD/F. In general, products of the chloralkali-through-vinyl chloride chain are very low in such contamination; however, for these and other products the POPs concentration may be a function of the efficiency of distillation or other purification.

3.0 Alternate Processes to Chlorination.

3.1 Titanium Dioxide, Sulfate Process. For TiO₂, there is an alternate commercial process utilizing sulfuric acid instead of chlorine.

In the sulfate process for TiO₂ ore is dried, ground, and classified to ensure efficient sulfation by agitation with concentrated sulfuric acid in a batch or continuous exothermic digestion reaction. Controlled conditions maximize conversion of TiO₂ to water-soluble titanyl sulfate using the minimum acid. The resultant dry, green-brown cake of metal sulfates is dissolved in water or weak acid, and the solution 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 sulfate heptahydrate (known as "copperas", FeSO₄·7H₂O) which is separated from the process and sold as a by-product.

The insoluble "mud" is washed to recover titanyl sulfate 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 additives used prior to calcination.¹³

Waste generation is far less in the chloride process, but the chloride process may give rise to small amounts of by-product POPs. Waste generation in the sulfate process, including sulfuric acid and other mineral waste can be 10-20 times higher, but is not known to involve by-product POPs. Trading elimination of small amounts of by-product

POPs for generation of large quantities of other waste materials may not be the optimal environmental approach. BAT can be plant specific and viewed on a case-by-case basis.

4.0 Primary and Secondary Measures

4.1 Primary Measures of Greater Impact

4.1.1 Distillation and Internal Recycling of By-products. Distillation is used primarily to produce product of a purity appropriate to downstream processing. As an example, VCM 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 unintended POPs, however, that virtually complete separation can be accomplished. The Large Volume Organic BREF notes that purified EDC does not contain significant amounts of PCDD/F.⁶

Destruction of chlorinated by-product materials allows for HCl to be harvested and reused.¹⁴ This is deemed “greater impact” because small changes in POPs generation upstream of distillation are not reflected in the quality of desired products after distillation.

Distillation as a means of separating desired product from inadvertent side products is used across the chemical production industry from commodities to pesticides. Adapting the design and operation of distillation apparatus is, in principle, relatively straightforward. Residual side product contained in commercial product can be minimized by appropriate design and operation. 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 side products is for the most part a matter of correct design and construction and operation cost. Differences in concentration of residual by-product POPs in commercial product may be due to differences in local regulation of products.

4.1.2 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.² This problem was eliminated following the invention of the coated

titanium anode by H. B. Beer in 1965 and subsequent substitution for graphite in these processes.¹⁵ The use of graphite electrodes does not constitute BAT.

4.1.3 Elimination of Alkali Treatment of 1,2,4,5-Tetrachlorophenol and 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 side-product TCDD. This process does not constitute BAT.

4.1.4 Elimination of Phenol Route to Chloranil. This process is described in the Toolkit.² 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/F are generated as by-products. This process does not constitute BAT. Chlorination of hydroquinone by HCl generates much cleaner product.

4.1.5 Modified Production of Pentachlorophenol (PCP) and Sodium Pentachlorophenate. The following processes are also described in the Toolkit.² Three routes to PCP are known commercially. Chlorination of phenol by Cl₂ over a catalyst, hydrolysis of hexachlorobenzene (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 PCP 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 dioxin microcontaminants. In the US, emission of these materials was reduced from ca 3-4 mg I-TEQ/kg in the mid- to late-1980s to ca 1 mg I-TEQ/kg in the years since 1988.³

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

4.2 Primary Measures of Lesser Impact

4.2.1 Use of Hydrogen in Oxychlorination. Oxychlorination process feed purity can contribute to by-product formation, although the problem usually is only with the low levels of acetylene which are normally present in HCl from the EDC cracking process. Acetylene fed to the oxychlorination reactor could be converted to highly chlorinated C₂ products, and chlorinated C₂ products can give rise to chlorinated aromatics via cyclotrimerization.^{11,16} Selective hydrogenation of this acetylene to ethylene and ethane in a reactor prior to the oxychlorination reaction is widely used as a preventive measure (See Figure 2)

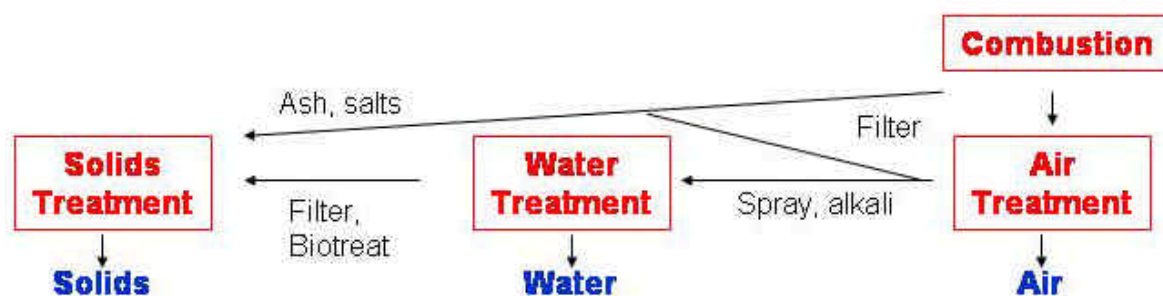
4.2.2 Catalyst Maintenance and Temperature Uniformity Control. Fluidized-bed reactors tend to have better temperature control, and more uniform performance, although the previously mentioned attrition of catalyst particles can allow for carryover into other streams within the facility. For fixed-bed oxychlorination catalysts appropriate packing and maintenance can reduce hot spots and potentially can both 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.

4.2.3 Reduction in Aromatic Hydrocarbons in Feeds to Oxychlorination Processes. Two patents specify pretreatment of air¹⁷ or HCl¹⁸ reagents used in oxychlorination to remove aromatics, presumably precursors to various POPs. This technology, being patented, is proprietary and as such is probably not appropriate for BAT but indicates another primary approach.

4.3 Secondary Measures

4.3.1 BAT for Waste Disposal Practices. Since all or nearly all POPs by-products are isolated in the by-product stream, practice of BAT in destruction of these by-products, including the combustion step, is critical for POPs minimization. Combustion technology has been developed that discriminates against generation of POPs. In addition to prevention of formation, treatment of gases prior to release reduces emissions of POPs.

Figure 7. Schematic of Downstream Treatment of Combustion Products.



In the US, Europe and Japan there are specified technologies for treatment of flue gas, waste water and waste solids from combustion processes. For flue gas they involve, among others, rapid cooling or neutralization, addition of activated carbon and removal of solids via properly designed baghouses or electrostatic precipitators. For waste water, they involve, among other processes, neutralization, settling ponds and biological treatment. Waste solids may be deposited in a secure landfill or in some cases used as filler in products such as asphalt or concrete.

Development of BREFs by the EU or BAT under the Stockholm Convention on Hazardous Waste Combustion and downstream treatment of gas, liquid and solid

wastes will be useful here as the processes are fairly well-known and generic. When these techniques are practiced, emission of by-product POPs is virtually eliminated.

5.0 Summary of Measures. Modify processes to reduce generation of by-product POPs. Incorporate steps that treat impurities in raw materials, and use rigorous operational maintenance. Purify products by distillation. Internally recycle inadvertently generated high molecular weight side-products as an integral part of the process.

6.0 Performance Standards. Performance standards can be set locally in individual plant permits, and will vary. By-product PCDD/F emission is mentioned in the ECVM Charter, and reflected in the OSPAR process via Decision 98/4 and adoption of BAT via PARCOM Recommendation 96/2. That standard is 1 µg TEQ/ton oxychlorination capacity release to water. Air emission limits in the ECVM Charter are 0.1 ng TEQ/Nm.^{3,19} This limit corresponds to the EU regulatory limit for emissions of PCDD/F to air from incinerators. Limits in other regions/countries will typically be congruent with hazardous waste combustor regulations in local areas.

7.0 Performance Measures. These may include: analytical chemistry on emission streams; in some areas, reporting of POPs to a Pollutant Release and Transfer Registry (PRTR), such as the Toxics Release Inventory in the US.^{20,21}

Appendix A: Synthesis of commodity chemicals

Chemical	Process	Process Use	Co-Products
Chlorine, Caustic soda	$\text{NaCl} + \text{H}_2\text{O} \Rightarrow \text{Cl}_2 + \text{NaOH} + \text{H}_2$ See EIPPCB BREF, Expert Group presentation	More Common	
Organics			
Allyl chloride	Direct chlorination of propylene >300 deg C;	More Common	HCl
	Pyrolysis of 1,2-dichloropropane	Less Common	Chlorinated olefins, HCl
Chloranil dye	See toolkit		
Chloroprene (2-chloro-1,3-butadiene)	$\text{C}_2\text{H}_2 + \text{CuCl}/\text{NH}_4\text{Cl} \Rightarrow \text{vinyl acetylene} + \text{HCl} \Rightarrow \text{chloroprene}$ Vapor 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	Less Common More Common	NaCl; overchlorinated products
Chlorinated benzenes	Vapor 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) ==> glycerol chlorohydrins + NaOH/(CaOH) ₂ ==>epichlorohydrin;	More Common	Hydrolyzed product; polymers
	Steam stripped then distilled. Also: propylene +O ₂ , (Pd catalyst) ==> allyl acetate==>allyl alcohol + Cl ₂ ==> allyl chloride		
Isocyanurate disinfectants	Isocyanuric acid + NaOH + Cl ₂		
Phosgene	CO + 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;100-180 deg C;	More Common	HCl
	Hexachlorobenzene (HCB)+NaOH	Less Common	NaCl
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 coproduct 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) See EU BREF, Expert Group Presentation	More Common	
C₁ Products			
Methyl Chloride	CH ₄ + Cl ₂ via heat or light CH ₃ OH + HCl ==> CH ₃ Cl	More Common More Common	
Other Chlorinated Methanes	CH ₃ Cl + Cl ₂ heat or light ==> CH ₂ Cl ₂ , CHCl ₃ , CCl ₄ CS ₂ + Cl ₂ ==>S ₂ Cl ₂ + CCl ₄ CS ₂ + S ₂ Cl ₂ ==> S + CCl ₄	More Common Less Common	
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) Ethylene + HCl + O ₂ (Cu cat) ==>EDC (oxychlorination)	More Common	
1,1,1-Tri	1,1-Di + Cl ₂ (Photochemical) 1,1,2-Tri ==>==>1,1,1-Tri Ethane + Cl ₂	More Common More Common Less Common	HCl

1,1,2-Tri	VC + Cl ₂ EDC + Cl ₂	More Common 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		
Chlorinated Ethylenes Trichloroethylene (TCE) and Perchloroethylene (PCE)			
	EDC + Cl ₂ ==> TCE + PCE	More Common	HCl
	EDC + Cl ₂ ==> PCE + CCl ₄	More Common	HCl
	2 CCl ₄ ==> PCE	More Common	
	EDC + Cl ₂ + O ₂ ==> PCE/TCE	More Common	
	Tetrachloroethanes + Heat ==> TCE	More Common	HCl
	Pentachloroethane + Heat ==> PCE	Less Common	HCl
Inorganics			
HCl	Byproduct; salt +sulfuric acid; hydrogen +chlorine; Recovery from combustion of chlorinated organics	More Common	
TiO ₂	C, Cl ₂ , TiO ₂ Ore ==> TiCl ₄ + O ₂ ==> TiO ₂	More Common	Cl ₂ , recycle
	TiO ₂ Ore + H ₂ SO ₄ ==> Ti(SO ₄) ₂ ==> TiO ₂	Less Common	sulfates
FeCl ₃	Iron or iron oxide + HCl ==> FeCl ₃		
Hypochlorites	Na: 2NaOH + Cl ₂ ==> NaOCl		NaCl

	Ca: $\text{Ca(OH)}_2 + 2\text{Cl}_2 \Rightarrow \text{Ca(OCl)}_2$ 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		

[Appendix B: Chlorine Product Tree, adapted from World Chlorine Council Sustainable Development Report \(chlorinetree.pdf, appended\)](#)

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