EUROPEAN COMMISSION

Integrated Pollution Prevention and Control

**Reference Document on
Best Available Techniques in
Common Waste Water and Waste Gas
Treatment / Management Systems in
the Chemical Sector**

February 2003

EXECUTIVE SUMMARY

INTRODUCTION

The BREF (Best Available Techniques reference document) on waste water and waste gas treatment and management in the chemical sector reflects an information exchange carried out under Article 16(2) of Council Directive 96/61/EC. This Executive Summary – which is intended to be read in conjunction with the BREF Preface's explanations of objectives, usage and legal terms – describes the main findings, the principal BAT conclusions and the associated emission levels. It can be read and understood as a stand-alone document but, as a summary, it does not present all the complexities of the full BREF text. It is therefore not intended as a substitute for the full BREF text as a tool in BAT decision making.

Waste water and waste gas handling has been identified as a horizontal issue for the chemical sector as it is described in Annex I, 4 of the Directive. It means that the term "Best Available Techniques (BAT)" is assessed in this document for the entire chemical sector, independently of the particular production process(es) and the kind or size of the chemical enterprise(s) involved. It also means that the term BAT needs to include, apart from treatment technologies, a management strategy to achieve optimal waste prevention or control.

Thus the scope of the document comprises:

- the application of environmental management systems and tools
- the application of the treatment technology for waste water and waste gas as it is commonly used or applicable in the chemical sector, including the treatment technology for waste water sludge, as long as it is operated on the chemical industry site
- the identification of or conclusion on best available techniques based on the two preceding items, resulting in a strategy of optimum pollution reduction and, under appropriate conditions, in BAT-associated emission levels at the discharge point to the environment.

Only commonly applied or applicable techniques for the chemical industry are dealt with in this document, leaving process-specific techniques or process-integrated techniques (i.e. non-treatment techniques) to the vertical process BREFs. Though restricted to the chemical industry, it is recognised that the document might also contain valuable information for other sectors (e.g. the refinery sector).

GENERAL ISSUES (CHAPTER 1)

Discharges to air and water are the main environmental impacts caused by releases from chemical installations.

The main sources of **waste water** in the chemical industry are:

- chemical syntheses
- waste gas treatment systems
- conditioning of utility water
- bleed from boiler feed water systems
- blowdown from cooling cycles
- backwashing of filters and ion exchangers
- landfill leachates
- rainwater from contaminated areas, etc.,

their main impact being characterised by:

- hydraulic load
- content of pollutant substances (expressed as load or concentration)
- effect or hazardous potential on the receiving water body, expressed as surrogate or sum parameters
- effect on organisms in the receiving water body, expressed as toxicity data.

Waste gas emissions appear as:

- ducted emissions, which are the only emissions that can be treated
- diffuse emissions
- fugitive emissions.

The main air pollutants are:

- VOCs
- sulphur compounds (SO_2, SO_3, H_2S, CS_2, COS)
- nitrogen compounds (NO_x, N_2O, NH_3, HCN)
- halogen compounds (Cl_2, Br_2, HF, HCl, HBr)
- incomplete combustion compounds (CO, C_xH_y)
- particulate matter.

MANAGEMENT SYSTEMS AND TOOLS (CHAPTER 2)

Environmental management is a strategy for dealing with waste releases (or their prevention) from (chemical) industry activities, taking local conditions into account, thereby improving the integrated performance of a chemical site. It enables the operator to:

- gain insight into the pollution-generating mechanisms of the production processes
- make balanced decisions about environmental measures
- avoid temporary solutions and no-return investments
- act adequately and proactively on new environmental developments.

An **environmental management system** (Section 2.1) normally follows a continuous loop process, the various steps supported by a number of management and engineering tools (Section 2.2), which are roughly categorised as:

- **inventory tools** providing, as a starting point, detailed and transparent information for the necessary decisions on waste prevention, minimisation and control. They include:
  - site inventory, giving detailed information on the location, the production processes and the respective plants, the existing sewerage system, etc.
  - stream (waste water and waste gas) inventory, giving detailed information on the waste streams (amount, pollutant content, their variability, etc.), their sources, quantification, evaluation and validation of the causes of emissions, ending in a ranking of the various streams to identify options and a priority listing for future improvements. A Whole Effluent Assessment and an assessment of the reduction of water usage and waste water discharge are also parts of a stream inventory
  - energy and material flow analysis, which aims to improve the operating efficiency of processes (as regards consumption of energy, raw material, waste release)

- **operational tools** for turning environmental management decisions into action. They include:
  - monitoring and regular maintenance
  - setting and regular review of internal targets or programmes for continuous environmental improvement
  - choice of treatment options and collection systems, based on the result of, e.g., inventory tools, and their implementation
  - quality control methods, used as 'trouble shooters' when an existing treatment process runs out of control or cannot fulfil set requirements. Such methods are, e.g., cause-effect diagram, Pareto analysis, flow diagram or statistical process control
- **strategic tools**, comprising the organisation and operation of waste handling on the entire chemical site in an integrated manner, evaluating environmental and economic options. They include:
  - risk assessment as a common methodology to calculate human and ecological risk as a result of activities of production processes
  - benchmarking as a process of comparison of the achievements of one plant or site with those of others
  - life cycle assessment as a process of comparison of the potential environmental effects of different ways of operating
- **safety and emergency tools**, necessary in the case of unplanned events such as accidents, fires or spillages.

TREATMENT TECHNIQUES (CHAPTER 3)

The techniques identified by the Technical Working Group and described in this document are those that are common in the chemical sector as a whole. They are introduced in a logical order, which follows the pollutant path.

The described <u>WASTE WATER</u> treatment techniques are:

- **separation or clarification techniques**, which are mainly used in combination with other operations, either as a first step (to protect other treatment facilities against damage, clogging or fouling by solids) or a final clarification step (to remove solids or oil formed during a preceding treatment operation):
  - grit separation
  - sedimentation
  - air flotation
  - filtration
  - microfiltration / ultrafiltration
  - oil-water separation

- **physico-chemical treatment techniques** for non-biodegradable waste water, mainly used for inorganic or hardly biodegradable (or inhibitory) organic contaminants, often as a pretreatment upstream of a biological (central) waste water treatment plant:
  - precipitation/sedimentation/filtration
  - crystallisation
  - chemical oxidation
  - wet air oxidation
  - super-critical water oxidation
  - chemical reduction
  - hydrolysis
  - nanofiltration / reverse osmosis
  - adsorption
  - ion exchange

- extraction
- distillation / rectification
- evaporation
- stripping
- incineration

- **biological treatment techniques** for biodegradable waste water:
  - anaerobic digestion processes, such as anaerobic contact process, UASB process, fixed-bed process, expanded-bed process, biological removal of sulphur compounds and heavy metals
  - aerobic digestion processes, such as complete-mix activated sludge process, membrane bioreactor process, trickling filter process, expanded-bed process, biofilter fixed-bed process
  - nitrification / denitrification
  - central biological waste water treatment.

The described <u>WASTE WATER SLUDGE</u> treatment techniques can be seen as single options or as a combination of single options. The following list is by no means intended to indicate a ranking. The availability (or non-availability) of a disposal route, however, can be a strong driver, at least at a local level, in the choice of an appropriate waste water control technique. The described waste water sludge treatment techniques are:

- preliminary operations
- sludge thickening operations
- sludge stabilisation
- sludge conditioning
- sludge dewatering techniques
- drying operations
- thermal sludge oxidation
- landfilling of sludge on site.

The described <u>WASTE GAS</u> treatment techniques cannot simply be classified as recovery or abatement techniques. Whether contaminants are recovered depends on the application of additional separation stages. Some of the techniques can be used as individual final operations, others only as a pretreatment or final polishing step. Most waste gas control techniques require further downstream treatment for either waste water or waste gas generated during the treatment process. The techniques are:

- **for VOC and inorganic compounds**:
  - membrane separation
  - condensation
  - adsorption
  - wet scrubbing
  - biofiltration
  - bioscrubbing
  - biotrickling
  - thermal oxidation
  - catalytic oxidation
  - flaring

- **for particulate matter**:
  - separator
  - cyclone
  - electrostatic precipitator
  - wet dust scrubber
  - fabric filter
  - catalytic filtration
  - two-stage dust filter
  - absolute filter (HEPA filter)
  - high-efficiency air filter (HEAF)
  - mist filter

- **for gaseous pollutants in combustion exhaust gases**:
  - dry sorbent injection
  - semi-dry sorbent injection
  - wet sorbent injection
  - selective non-catalytic reduction of NO_x (SNCR)
  - selective catalytic reduction of NO_x (SCR).

CONCLUSIONS ON BEST AVAILABLE TECHNIQUES (CHAPTER 4)

The chemical industry covers a wide range of enterprises: at one end the one-process-few-products small enterprises with one or few waste release sources and, at the other, the multi-production-mix enterprises with many complex waste streams. Although there are probably no two chemical sites that are totally comparable in production range and mix, environmental situation and the quantity and quality of their waste emissions is it possible to describe BAT for waste water and waste gas treatment for the chemical sector as a whole.

The implementation of BAT in new plants is not normally a problem. In most cases it makes economic sense to plan production processes and their waste releases to minimise emissions and material consumption. With existing sites, however, the implementation of BAT is not generally an easy task, because of the existing infrastructure and local circumstances. Nevertheless, this document does not distinguish between BAT for new and existing installations. Such a distinction would not help to improve the environmental situation of industrial sites towards adopting BAT and it would not reflect the commitment of the chemical industry to continuous improvement of environmental conditions.

❑ **Management**

As the detailed description of environmental management in Chapter 2 indicates, the prerequisite of good environmental performance is an Environmental Management System (EMS). In the final analysis, the proper and consistent execution of a recognised EMS will lead to the optimum environmental performance of a chemical industry site, thus achieving BAT.

On this premise, it is BAT to implement and adhere to an EMS that could include:

- implementation of a transparent hierarchy of personnel responsibility, the persons in charge reporting directly to the top management level
- preparation and publication of an annual environmental performance report
- setting internal (site- or company-specific) environmental targets, reviewing them regularly and publishing them in the annual report
- holding a regular audit to secure compliance with the principles of EMS
- regular monitoring of performance and progress towards the achievement of EMS policy

- practising risk assessment on a continuous basis to identify hazards
- practising benchmarking on a continuous basis and challenging the processes (production and waste treatment) on their water and energy consumption, waste generation and cross-media effects
- implementation of an adequate training programme for staff and instructions for contractors working on the site on Health, Safety and Environment (HSE) and emergency issues
- application of good maintenance practices.

It is further BAT to implement a waste water / waste gas management system (or waste water / waste gas assessment), as a subsystem to the EMS, using an appropriate combination of:

- site inventory and stream inventory
- checking and identifying the most relevant emission sources for each medium and listing them according to their pollutant load
- checking the receiving media (air and water) and their tolerance of the emissions, using the results to determine the extent to which stronger treatment requirements are needed or if the emissions can be accepted at all
- performing assessment of toxicity, persistence and potential bioaccumulation of waste water to be discharged into a receiving water body and sharing the results with the competent authorities
- checking and identifying relevant water-consuming processes and listing them according to their water usage
- pursuing options for improvement, focusing on streams with higher concentrations and loads, their hazard potential and impact on the receiving water body [1]
- assessing the most effective options by comparing overall removal efficiencies, overall balance of cross-media effects, technical, organisational and economic feasibility etc.

Further BAT are to:

- assess impact on the environment and the effects on treatment facilities when planning new activities or alterations to existing activities
- practise emission reduction at source
- link production data with the data on emission loads to compare the actual and calculated releases
- treat contaminated waste streams at source in preference to dispersion and subsequent central treatment, unless there are good reasons against it
- use quality control methods to assess the treatment and/or production processes and/or prevent them running out of control
- apply good manufacturing practice (GMP) for equipment cleaning to reduce emissions to water and to air
- implement facilities / procedures to enable timely detection of a deviation that could affect the downstream treatment facilities, so as to avoid an upset of those treatment facilities
- install an efficient central warning system that will give notice of failures and malfunctions to all concerned
- implement a monitoring programme in all waste treatment facilities to check that they are operating properly
- put in place strategies for dealing with fire-fighting water and spillages
- put in place a pollution incident response plan
- allocate costs of waste water and waste gas treatment associated with production.

Process-integrated measures are not within the scope of the document, but they are an important means of optimizing environmental performance of production processes. Thus, it is BAT to:

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[1] One Member State wants a more precise definition of 'streams with higher concentration' that includes values for loads and/or concentrations. A split view is reported. Further details are given in Chapter 4.

- use process-integrated measures in preference to end-of-pipe techniques when there is a choice
- assess existing production installations for options of retrofitting process-integrated measures and implement them when feasible or at latest when the installation undergoes major alterations.

❑ **Waste Water**

An adequate <u>WASTE WATER COLLECTION SYSTEM</u> plays an essential role in effective waste water reduction and/or treatment. It ducts the waste water streams to their appropriate treatment device and prevents mixing of contaminated and uncontaminated waste water. Thus, BAT is to:

- segregate process water from uncontaminated rainwater and other uncontaminated water releases. If existing sites do not yet operate water segregation, it can be installed – at least partially – when major alterations are made to the site
- segregate process water according to its contamination load
- install a roof over areas of potential contamination wherever feasible
- install separate drainage for areas of contamination risk, including a sump to catch leakage or spillage losses
- use overground sewers for process water inside the industrial site between the points of waste water generation and the final treatment device(s). If climatic conditions do not allow overground sewers (temperatures significantly below 0 °C), systems in accessible underground ducts are a suitable replacement. Many chemical industry sites are still provided with underground sewers and the immediate construction of new sewer systems is normally not viable, but work can be done in stages when major alterations to production plants or the sewer system are planned
- install retention capacity for failure events and fire-fighting water in the light of a risk assessment.

<u>WASTE WATER TREATMENT</u> in the chemical sector follows at least four different strategies:

- central final treatment in a biological WWTP on site
- central final treatment in a municipal WWTP
- central final treatment of inorganic waste water in a chemical-mechanical WWTP
- decentralised treatment(s).

None of these four is preferred to the others, as long as an equivalent emission level is guaranteed for the protection of the environment as a whole and provided this does not lead to higher levels of pollution in the environment [Article 2(6) of the Directive].

It is assumed at this stage that the appropriate effluent management decisions have been made, the impact on the receiving water body has been assessed, all practical options for prevention and reduction of waste water have been exploited and all safety measures have been taken into account, i.e. from this point on, only end-of-pipe solutions are considered.

For **rainwater**, it is BAT to:

- duct uncontaminated rainwater directly to a receiving water, by-passing the waste water sewerage system
- treat rainwater from contaminated areas before discharging it into a receiving water.

In some cases the use of rainwater as process water to reduce fresh water consumption may be environmentally beneficial.

Appropriate treatment facilities are:

- grit chamber
- retention pond
- sedimentation tank
- sand filter.

It is BAT to remove **oil and/or hydrocarbons** when they appear as large slugs or where they are incompatible with other systems, with the aim of maximising recovery, by applying an appropriate combination of:

- oil/water separation by cyclone, microfiltration or API (American Petroleum Institute) separator, when large slugs of free oil or hydrocarbons can be expected, otherwise the parallel plate interceptor and the corrugated plate interceptor are alternatives
- microfiltration, granular media filtration or gas flotation
- biological treatment.

BAT-associated emission levels	
Parameter	**Concentration [a] [mg/l]**
total hydrocarbon content [b]	0.05-1.5
BOD_5	2-20
COD	30-125
[a] monthly average [b] There is disagreement on the analytical methods to assess hydrocarbons which could not be solved within the TWG.	

It is BAT to break and/or remove **emulsions** at source.

For **suspended solids (TSS)** (TSS that include heavy metal compounds or activated sludge need other measures), it is BAT to remove them from waste water streams when they could cause damage or failure to downstream facilities or before they are discharged into a receiving water. Common techniques are:

- sedimentation / air flotation to catch the main TSS load
- mechanical filtration for further solids reduction
- microfiltration or ultrafiltration when solid-free waste water is required.

Techniques that enable recovery of substances are preferred.

It is further BAT to

- control odour and noise by covering or closing the equipment and ducting the exhaust air to further waste gas treatment if necessary
- dispose of the sludge, either by handing it to a licensed contractor or by treating it on site (see section on sludge treatment).

As **heavy metals** are chemical elements that cannot be destroyed, recovery and re-use are the only ways to prevent them being released into the environment. Any other option causes them to be transferred between the different media: waste water, waste air and landfilling.

Thus, for heavy metals, it is BAT to do **all** of the following:

- segregate waste water containing heavy metal compounds as far as possible and
- treat the segregated waste water streams at source before mixing with other streams and
- use techniques that enable recovery as widely as possible and
- facilitate further elimination of heavy metals in a final WWTP as a polishing step, with subsequent treatment of sludge, if necessary.

The appropriate techniques are:

- precipitation / sedimentation (or air flotation instead) / filtration (or microfiltration or ultrafiltration instead)
- crystallisation
- ion exchange
- nanofiltration (or reverse osmosis instead).

Because the emission levels that can be achieved by these control techniques are strongly dependent on the source process from which the heavy metals are released, the TWG found themselves unable to identify BAT-associated emission levels that would be valid for the chemical sector as a whole. It was recommended that this subject be dealt with in the appropriate process BREFs.

The **inorganic salt (and/or acid) content** of waste water can influence both the biosphere of a receiving water, e.g. small rivers when they are confronted with high salt loads, and the operation of sewerage systems, e.g. corrosion of pipes, valves and pumps or malfunction of downstream biological treatment. In the case of one or both of these possibilities, it is BAT to control the inorganic salt content, preferably at source and preferably with control techniques that enable recovery. Appropriate treatment techniques (not including techniques for treating heavy metals or ammonium salts) are:

- evaporation
- ion exchange
- reverse osmosis
- biological sulphate removal (used only for sulphate, but when heavy metals are present, they are also removed).

Pollutants unsuitable for biological treatment are, e.g. recalcitrant TOC and/or toxic substances that inhibit the biological process. Thus their discharge into a biological treatment plant needs to be prevented. It is not possible to forecast which contaminants are inhibitors for

biological processes in a WWTP, because this depends on the adaptation to special contaminants of the micro-organisms working in the particular plant. Thus, it is BAT to avoid the introduction of waste water components into biological treatment systems when they could cause a malfunction of such systems and to treat tributary waste water streams with relevant non-biodegradable part by adequate techniques.[2]

- choice 1: techniques that enable substance recovery:
  - nanofiltration or reverse osmosis
  - adsorption
  - extraction
  - distillation / rectification
  - evaporation
  - stripping
- choice 2: abatement techniques without need of additional fuel, when recovery is not feasible:
  - chemical oxidation, but care must be taken with chlorine-containing agents
  - chemical reduction
  - chemical hydrolysis
- choice 3: abatement techniques entailing considerable energy consumption, when there is no other choice to abate toxicity or inhibitory effects or when the process can be operated on a self-sustaining basis:
  - wet air oxidation (low-pressure or high-pressure variant)
  - waste water incineration
- in cases where water supply and consumption is an environmental issue, techniques requiring considerable amounts of cooling water or wet scrubber systems for exhaust air treatment need to be assessed, such as:
  - extraction
  - distillation / rectification
  - evaporation
  - stripping.

Biodegradable waste water can be treated in biological control systems, either as tributary streams in specially designed (pre)treatment systems, e.g. anaerobic or aerobic high load systems, or as mixed waste water in a central biological waste water treatment plant, or as a polishing step behind the central waste water treatment plant. Thus, it is BAT to remove biodegradable substances by using an appropriate biological treatment system (or an appropriate combination of them), such as:

- biological pretreatment to relieve the final central biological waste water treatment plant from high biodegradable load (or as a final polishing step). Appropriate techniques are:
  - anaerobic contact process
  - upflow anaerobic sludge blanket process
  - anaerobic and aerobic fixed-bed process
  - anaerobic expanded-bed process
  - complete-mix activated sludge process
  - membrane bioreactor
  - trickling (percolating) filter
  - biofilter fixed-bed process
- nitrification / denitrification when the waste water contains a relevant nitrogen load
- central biological treatment, avoiding the introduction of non-biodegradable waste water pollutants, when they can cause malfunction of the treatment system and when the plant is not suitable to treat them. In general the BAT-associated emission level for BOD after central biological treatment is < 20 mg/l. In the case of activated sludge a typical application is a low-loaded biological stage with a daily COD load of ≤ 0.25 kg/kg sludge.

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[2]   One Member States insists on a more close definition of the criterion 'relevant non-biodegradable part'. A split view is reported. Details in Chapter 4.

BAT-associated emission levels for the final discharge into a receiving water body [3]:		
Parameter [a]	Performance rates [%]	Emission levels [mg/l] [b]
TSS		10-20 [c]
COD	76-96 [d]	30–250
total inorganic N [e]		5-25
total P		0.5-1.5 [f]
AOX		

[a] for BOD see preceding section on central biological treatment
[b] daily average, exception TSS
[c] monthly average
[d] low performance rates for low contaminant concentrations
[e] sum of NH_4-N, NO_2-N and NO_3-N (a more recommendable parameter would be total N. Because of the lack of information on total N, total inorganic N is used here)
[f] lower range from nutrient feed in biological WWTP, upper range from production processes

❑ **Waste Water Sludge**

When waste water sludge is handled on the chemical industry site it is BAT to use one or several of the following options (without preference):

- preliminary operations
- sludge thickening operations
- sludge stabilisation
- sludge conditioning
- sludge dewatering techniques
- drying operations
- thermal sludge oxidation
- landfilling of sludge on site.

Off-site treatment is not taken into account because it is not within the scope of the document. This is by no means a BAT conclusion against off-site treatment by third-party contractors.

❑ **Waste Gas**

WASTE GAS COLLECTION SYSTEMS are installed to route gaseous emissions to treatment systems. They consist of the emission source enclosure, vents and pipes. It is BAT to:

- minimise the gas flow rate to the control unit by encasing the emission sources as far as feasible
- prevent explosion risk by:
  - installing a flammability detector inside the collection system when the risk of occurrence of a flammable mixture is significant
  - keeping the gas mixture securely below the lower explosion limit or above the higher explosion limit
- install appropriate equipment to prevent the ignition of flammable gas-oxygen mixtures or minimise its effects.

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[3]   One Member State insists on also including BAT-associated emission levels for AOX and heavy metals at the final discharge point. A split view is reported. Details of the state of discussion are given in Chapter 4.

The sources of waste gases are distinguished in this document as:

- low-temperature sources, such as production processes, handling of chemicals, work-up of products
- high-temperature sources, such as combustion processes, which include facilities such as boilers, power plants, process incinerators and thermal and catalytic oxidisers.

Low-temperature sources

Pollutants to be controlled in waste gases released from low-temperature sources (production process gases) are dust (particulate matter), VOCs and inorganic compounds (HCl, SO_2, NO_x etc.).

It is BAT to remove **dust/particulate matter** from waste gas streams, either as final treatment or as pretreatment to protect downstream facilities, using material recovery whenever it is feasible. The energy and water consumption of treatment techniques needs to be borne in mind. Appropriate control techniques are:

- pretreatment techniques with potential recovery:
  - separator
  - cyclone
  - mist filter (also as polishing filter for aerosols and droplets)
- final treatment techniques
  - wet scrubber
  - electrostatic precipitator
  - fabric filter
  - various high efficiency filters, dependent on kind of particulate matter.

It is BAT to remove **VOCs** from waste gas streams. The control technique to apply depends strongly on the process from which they are released and the degree of hazard they represent.

- choice 1: techniques to recover raw material and/or solvents, often applied as pretreatment to recover the main VOC load before downstream abatement facilities or to protect downstream facilities as a safety issue. Appropriate techniques are:
  - wet scrubbing
  - condensation
  - membrane separation
  - adsorption

  or combinations thereof:
  -condensation / adsorption
  -membrane separation / condensation

- choice 2: abatement techniques when recovery is not feasible, giving preference to low-energy techniques

- choice 3: combustion techniques (thermal or catalytic oxidation), when other equally efficient techniques are not available.

When combustion techniques are applied, it is BAT to implement combustion exhaust gas treatment when considerable amounts of exhaust gas contaminants are to be expected.
It is further BAT to use flaring only to dispose safely of surplus combustible gases from, e.g. maintenance events, upset systems or remote vents not connected to abatement systems.

For **other compounds than VOCs**, it is BAT to remove these pollutants, applying the appropriate technique:

- wet scrubbing (water, acidic or alkaline solution) for hydrogen halides, Cl_2, SO_2, H_2S, NH_3
- scrubbing with non-aqueous solvent for CS_2, COS
- adsorption for CS_2, COS, Hg
- biological gas treatment for NH_3, H_2S, CS_2
- incineration for H_2S, CS_2, COS, HCN, CO
- SNCR or SCR for NO_x.

When feasible, recovery techniques are preferred to abatement techniques, e.g.:

- recovery of hydrogen chloride when using water as scrubbing medium in the first scrubbing stage to produce a solution of hydrochloric acid
- recovery of NH_3.

The TWG has not been able to come to a conclusion on BAT-associated emission levels for waste gases from production processes that would apply to the chemical industry as a whole. BAT-associated emission levels for process gases are strongly dependent on the actual production process and it was recommended to deal with this subject in the appropriate process BREFs.

High-temperature sources

Pollutants to be controlled in waste gases from high-temperature processes (combustion exhaust gases) are dust (particulate matter), halogen compounds, carbon monoxides, sulphur oxides, NO_x and possibly dioxins.

It is BAT to remove **dust / particulate matter** by the implementation of one of the following:

- electrostatic precipitator
- bag filter (after heat exchanger at 120-150 °C)
- catalytic filter (comparable conditions as bag filter)
- wet scrubbing.

It is BAT to recover **HCl, HF and SO₂** by using two stage wet scrubbing or to remove them by dry, semi-dry or wet sorption injection, although wet scrubbing is normally the most efficient technique for abatement as well as for recovery.

For **NO_x**, it is BAT to implement SCR instead of SCNR (at least for larger installations) because it has better removal efficiency and environmental performance. For existing installations which operate SNCR devices, the time to consider changing might be when major alterations are planned for the incineration plant. Although SCR is BAT in the general sense, there are individual cases (typically smaller installations) where SNCR is the technically and economically best solution. Other measures need to be assessed for their ability to deliver greater overall improvement than retrofitting SNCR.

| BAT-associated emission levels of combustion exhaust gas treatment ||
Parameter	Emission levels [mg/Nm^3] [1]
dust	<5-15
HCl	<10
HF	<1
SO$_2$	<40-150 [2]
NO$_x$ (gas boilers/heaters)	20-150 [3]
NO$_x$ (liquid boilers/heaters)	55-300 [3]
NH$_3$ [4]	<5 [5]
dioxins	0.1 ng/Nm^3 TEQ
[1] ½ hourly average, reference oxygen content 3 % [2] lower range for gaseous fuel, upper range for liquid fuel [3] higher value for small installations using SNCR [4] NH$_3$ slip with SCR [5] value for new catalysts, but higher NH$_3$ emissions occur as the catalyst ages	

CONCLUDING REMARKS AND RECOMMENDATIONS (CHAPTER 6)

There were four split views expressed by one Member State following the second TWG meeting.

1. they expressed the opinion that the statements on BAT for waste water and waste gas management are partly too general and they refer to examples for streams with higher concentrations and loads (as mentioned in Section 2.2.2.3.1).
2. they expressed a view that the criterion 'relevant non-biodegradable part' needs to be more closely defined by giving a set of indicative values for recalcitrant TOC to waste water streams.
3. they insist on naming BAT-associated emission levels for heavy metals based on the examples given in Annex 7.6.4. In their view, when following the strategy of prevention, pretreatment and central treatment as outlined above (see section on heavy metals), it is possible to name BAT-associated emission values for heavy metals which are valid for many chemical sites. They further state that the values are influenced by the portion of productions relevant to heavy metals and hence are dependent on the production mix, which can cause higher values in special cases, especially in fine chemicals production. With regard to releases into public sewerage systems, the effect of the WWTP would have to be taken into account in so far as it would be ensured that the heavy metals are not shifted to other media.

   The TWG did not follow this request, stating that it would not be useful to name BAT-associated emission levels which are influenced by particular combinations of waste water streams on individual production sites, resulting in values which might or might not be valid in real-life cases. A split view is therefore recorded.

4. they insist on naming BAT-associated emission levels for AOX based on the examples given in Annex 7.6.2. They state that BAT-associated emission levels can be given, although the emission values for AOX are strongly influenced by the portion and kind of chlororganic syntheses on a chemical site, when waste water treatment is operated according to the BAT-conclusions given above (see section on pollutants unsuitable for biological treatment).
   The TWG did not follow this request. The examples presented (see Annex 7.6.2) were interpreted as consisting of different statistical data sets which did not allow naming BAT-associated emission levels. It was even mentioned that one of the lowest AOX emission levles reported as examples represented poor performance, whereas the highest emission level within the data set came from a site with very good performance. Under these conditions the TWG saw it to be unsuitable to give BAT-associated emission levels for AOX. A split view is therefore recorded.

The exchange of information itself has been considerably less than complete. It is difficult to understand why this should have been so, given the chemical industry's past efforts and achievements in the management of waste water and waste gas releases. Equally difficult was the exchange of information with a number of Member States.

As to reviewing the BREF, the recommendation is to fill the existing gaps. The review should wait until all the vertical BREFs in the chemical sector are finalised. For such a review to make sense, however, it will be necessary to focus more on the information that is useful for a permit writer. Further detail can be found in Chapter 6.

The EC is launching and supporting, through its RTD programmes, a series of projects dealing with clean technologies, emerging effluent treatment and recycling technologies and management strategies. Potentially these projects could provide a useful contribution to future BREF reviews. Readers are therefore invited to inform the EIPPCB of any research results which are relevant to the scope of this document (see also the preface of this document).

PREFACE

1. Status of this document

Unless otherwise stated, references to "the Directive" in this document means the Council Directive 96/61/EC on integrated pollution prevention and control. As the Directive applies without prejudice to Community provisions on health and safety at the workplace, so does this document.

This document forms part of a series presenting the results of an exchange of information between EU Member States and industries concerned on best available technique (BAT), associated monitoring and developments in them. It is published by the European Commission pursuant to Article 16(2) of the Directive, and must therefore be taken into account in accordance with Annex IV of the Directive when determining "best available techniques".

2. Relevant legal obligations of the IPPC Directive and the definition of BAT

In order to help the reader understand the legal context in which this document has been drafted, some of the most relevant provisions of the IPPC Directive, including the definition of the term "best available techniques", are described in this preface. This description is inevitably incomplete and is given for information only. It has no legal value and does not in any way alter or prejudice the actual provisions of the Directive.

The purpose of the Directive is to achieve integrated prevention and control of pollution arising from the activities listed in its Annex I, leading to a high level of protection of the environment as a whole. The legal basis of the Directive relates to environmental protection. Its implementation should also take account of other Community objectives such as the competitiveness of the Community's industry thereby contributing to sustainable development.

More specifically, it provides for a permitting system for certain categories of industrial installations requiring both operators and regulators to take an integrated, overall look at the polluting and consuming potential of the installation. The overall aim of such an integrated approach must be to improve the management and control of industrial processes so as to ensure a high level of protection for the environment as a whole. Central to this approach is the general principle given in Article 3 that operators should take all appropriate preventative measures against pollution, in particular through the application of best available techniques enabling them to improve their environmental performance.

The term "best available techniques" is defined in Article 2(11) of the Directive as "the most effective and advanced stage in the development of activities and their methods of operation which indicate the practical suitability of particular techniques for providing in principle the basis for emission limit values designed to prevent and, where that is not practicable, generally to reduce emissions and the impact on the environment as a whole." Article 2(11) goes on to clarify further this definition as follows:

"techniques" includes both the technology used and the way in which the installation is designed, built, maintained, operated and decommissioned;

"available" techniques are those developed on a scale which allows implementation in the relevant industrial sector, under economically and technically viable conditions, taking into consideration the costs and advantages, whether or not the techniques are used or produced inside the Member State in question, as long as they are reasonably accessible to the operator;

"best" means most effective in achieving a high general level of protection of the environment as a whole.

Furthermore, Annex IV of the Directive contains a list of "considerations to be taken into account generally or in specific cases when determining best available techniques ... bearing in mind the likely costs and benefits of a measure and the principles of precaution and prevention". These considerations include the information published by the Commission pursuant to Article 16(2).

Competent authorities responsible for issuing permits are required to take account of the general principles set out in Article 3 when determining the conditions of the permit. These conditions must include emission limit values, supplemented or replaced where appropriate by equivalent parameters or technical measures. According to Article 9(4) of the Directive, these emission limit values, equivalent parameters and technical measures must, without prejudice to compliance with environmental quality standards, be based on the best available techniques, without prescribing the use of any technique or specific technology, but taking into account the technical characteristics of the installation concerned, its geographical location and the local environmental conditions. In all circumstances, the conditions of the permit must include provisions on the minimisation of long-distance or transboundary pollution and must ensure a high level of protection for the environment as a whole.

Member States have the obligation, according to Article 11 of the Directive, to ensure that competent authorities follow or are informed of developments in best available techniques.

3. Objective of this Document

Article 16(2) of the Directive requires the Commission to organise "an exchange of information between Member States and the industries concerned on best available techniques, associated monitoring and developments in them", and to publish the results of the exchange.

The purpose of the information exchange is given in recital 25 of the Directive, which states that "the development and exchange of information at Community level about best available techniques will help to redress the technological imbalances in the Community, will promote the world-wide dissemination of limit values and techniques used in the Community and will help the Member States in the efficient implementation of this Directive."

The Commission (Environment DG) established an information exchange forum (IEF) to assist the work under Article 16(2) and a number of technical working groups have been established under the umbrella of the IEF. Both IEF and the technical working groups include representation from Member States and industry as required in Article 16(2).

The aim of this series of documents is to reflect accurately the exchange of information which has taken place as required by Article 16(2) and to provide reference information for the permitting authority to take into account when determining permit conditions. By providing relevant information concerning best available techniques, these documents should act as valuable tools to drive environmental performance.

4. Information Sources

This document represents a summary of information collected from a number of sources, including in particular the expertise of the groups established to assist the Commission in its work, and verified by the Commission services. All contributions are gratefully acknowledged.

5. How to understand and use this document

The information provided in this document is intended to be used as an input to the determination of BAT in specific cases. When determining BAT and setting BAT-based permit conditions, account should always be taken of the overall goal to achieve a high level of protection for the environment as a whole.

The rest of this section describes the type of information that is provided in each section of the document.

Chapter 1 provides a general description of waste water and waste gas, including general information on management and treatment systems.

Chapter 2 describes environmental and effluent management and appropriate tools to implement them.

Chapter 3 provides a description of treatment techniques for waste water and waste gas that are common in the chemical sector. The techniques include recovery and abatement processes. Chapters 2 and 3 are the core of this Reference Document to provide the necessary information to come to the BAT conclusions of Chapter 4.

Chapter 4 presents the techniques and the associated emission levels that are considered to be compatible with BAT in a general sense. In finding the most suitable treatment techniques for specific situations, the term 'techniques' in the context of this horizontal document embraces more than just technology; it also includes management strategies. The purpose is thus to provide general indications regarding the emission and consumption levels that can be considered as an appropriate reference point to assist in the determination of BAT-based permit conditions or for the establishment of general binding rules under Article 9(8). It should be stressed, however, that this document does not propose emission limit values. The determination of appropriate permit conditions will involve taking account of local, site-specific factors such as the technical characteristics of the installation concerned, its geographical location and the local environmental conditions. In the case of existing installations, the economic and technical viability of upgrading them also needs to be taken into account. Even the single objective of ensuring a high level of protection for the environment as a whole will often involve making trade-off judgements between different types of environmental impact, and these judgements will often be influenced by local considerations.

Although an attempt is made to address some of these issues, it is not possible for them to be considered fully in this document. The techniques and levels presented in Chapter 4 will therefore not necessarily be appropriate for all installations. On the other hand, the obligation to ensure a high level of environmental protection including the minimisation of long-distance or transboundary pollution implies that permit conditions cannot be set on the basis of purely local considerations. It is therefore of the utmost importance that the information contained in this document is fully taken into account by permitting authorities.

Since the best available techniques change over time, this document will be reviewed and updated as appropriate. All comments and suggestions should be made to the European IPPC Bureau at the Institute for Prospective Technological Studies at the following address:

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Reference Document on Best Available Techniques in Common Waste Water and Waste Gas Treatment / Management Systems in the Chemical Sector

List of figures

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SCOPE

This horizontal BAT Reference Document (BREF), entitled "Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector" (CWW), covers the entire chemical sector and is intended as support and guidance to a regulator reaching a decision on a permit relating to aqueous and/or gaseous releases from chemical installations. It is one of a series of BREFs relating to the chemical industry, all of which are designed to be read together. They are:

- Chlor-Alkali Manufacture
- Large Volume Organic Chemicals (LVOC)
- Large Volume Inorganic Chemicals (LVIC)
- Polymers
- Organic Fine Chemicals (OFC)
- Speciality Inorganic Chemicals (SIC)

and the horizontal BREFs

- Industrial Cooling Systems
- Emissions from Storage of Bulk or Dangerous Materials
- Monitoring Systems
- Economic and Cross-media Issues.

The refinery industry also sees this BREF as relevant to the refinery sector.

Since there are numerous options for waste water and/or waste gas treatment in the chemical industry, this document must restrict itself to those techniques that are 'commonly' used or applicable in the sector. Even with this restriction the BREF can deal with only some of the techniques used. This means that treatment methods applied at only one site and/or designed only for one special production process are not covered by this document. They fall within the scope of appropriate vertical documents. On the other hand, treatment techniques that have not yet been operated in the chemical industry, but that are successfully in use in other sectors, are covered when they are expected to be usefully applicable.

Process-integrated techniques are touched on in this document when they can be used in several processes, or when their application is generally acknowledged. Typically site-specific or process-specific issues concerning waste water / waste gas treatment are not covered here but are considered in a general approach explaining how to deal with specific conditions.

Another main topic in this Reference Document is waste water and waste gas management as part of operational management. Management means the adaption of local conditions (such as production specifics, legislation, local environmental situation, availability and quality of raw material and/or auxiliaries and climate issues) to the economically and ecologically efficient running of an industry site as a whole. The task of this document is to describe the approach or approaches to making management decisions to minimise the overall environmental impact of waste water and waste gas emissions.

The term 'impact on the environment' as used throughout this BREF includes, e.g.:

- resource consumption such as water from natural water bodies, energy, raw material, chemical substances, etc.; this is of greater significance when limited resources are involved, e.g. water under unfavourable climatic conditions or non-renewable energy
- emissions to water and/or air, including noise and odour
- generation of waste
- emissions arising from events such as start-up / shutdown.

The organisation of the disposal of sludge or solid residues from waste water and waste gas treatment is part of the operator's decision for a chemical site. Since there are sites that are equipped with appropriate treatment facilities for waste water sludge, its treatment is dealt with in this document. The treatment of waste apart from waste water sludge is within the scope of other vertical documents for other sectors of Annex 1 of the Directive. This BREF, however, will not anticipate the BREF on waste incineration, which is still to be written.

To avoid as far as possible duplication of work and overlap of topics with the relevant vertical and horizontal BREFs, boundaries need to be drawn. As an example, the boundary between the vertical chemical BREFs and this horizontal document is explained for the waste water part by Figure I, with a comparable situation for the waste gas part.
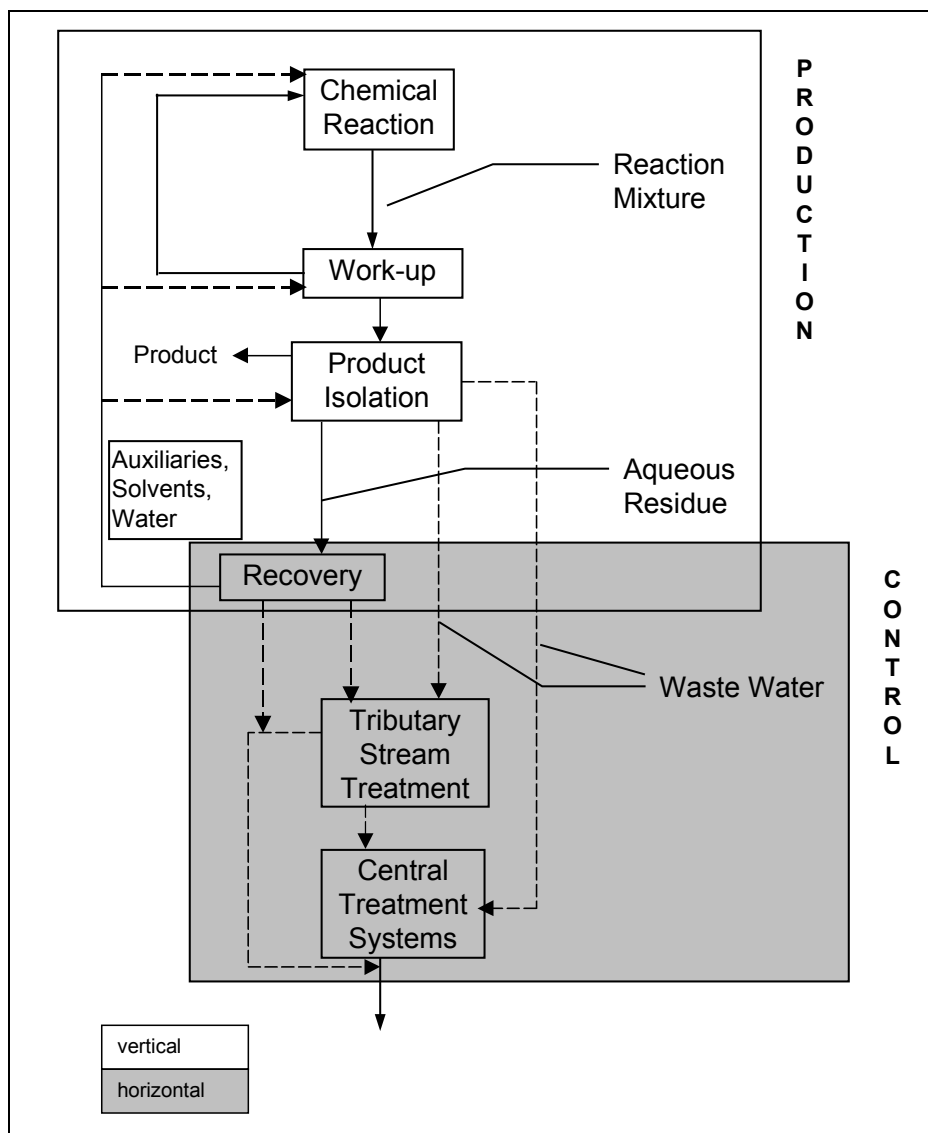
Figure I: Borderline between Relevance to Production and Control, or between Vertical and Horizontal BREF

Thus, the scope of this horizontal Reference Document comprises:

- the presentation of environmental management concerning waste water and waste gas and how to apply it to a site in the most advantageous way for the environment
- the description of generally applicable process-integrated measures (i.e. applicable with an identical purpose in distinct production processes)
- the description of treatment techniques applied to waste water and waste gas with regard to their impact on the environment, their treatment efficiency/performance, their limitations and advantages, and their costs
- the description of treatment techniques for waste water sludge, as far as they are operated on chemical sites
- based on the information given above, the description of schemes with options to ensure that waste water and waste gas treatment techniques and/or combinations thereof contribute to the application of BAT to the operation of a chemical site as a whole.

Illustrative examples naming achievable performance data to support the BAT conclusion are not meant to imply that the stated values can be achieved with each individual application under all working conditions, but that recommendations or proposals given are generally valid.

The document is particularly valid for the chemical sector. It is, however, recognised by the TWG that the items described - management systems and tools, waste water and waste gas treatment techniques - contain valuable information for other sectors too. But the application of this information by other sectors needs careful assessment in each case.

1   GENERAL DESCRIPTION

General scientific laws such as chemical and/or physical equilibrium make the occurrence of waste inevitable during chemical processes (syntheses), so that unwanted by-products have to be expelled. The character and scale of these emissions are highly variable and depend on the composition of raw materials, products, intermediates, auxiliaries, process conditions, etc.

The waste occurring during these processes can be divided into:

- waste water
- waste gas
- liquid and solid residues.

Liquid (non-aqueous) and solid residues originating from chemical production and product handling are to be dealt with separately – usually in vertical BREFs – and are not the subject of this document.

Chapter 1 gives an overview of the general aspects of:

- waste water and waste gas
- environmental management
- treatment technology
- environmental impact of waste water and waste gas treatment,

without going into specifics.

1.1 Waste Water and Waste Gas in the Chemical Industry

1.1.1 Waste Water

From the qualitative point of view, the majority of waste water in the chemical industry does not usually originate directly from chemical reaction steps. Though waste water can arise directly from reactions, e.g. as condensate or reaction water, the aqueous discharges from subsequent physico-chemical work-up of synthesis mixtures are generally greater. Products and/or intermediates from each synthesis or each synthesis stage are isolated and purified by operations such as filtration and centrifugation from aqueous reaction solutions, or by work-up of reaction mixtures via, e.g., extraction or distillation.

Such waste water streams arising in direct association with chemical syntheses – 'process water' – are, for example:

- mother liquors
- washing water from purification of products
- vapour condensates
- quench water
- waste water from exhaust air / flue gas clean-up
- waste water from equipment cleaning
- waste water from vacuum generation.

Tributary waste water streams from other on-site sources, such as:

- scrubbing of exhaust gases from incineration and combustion
- conditioning of utility water
- bleed from boiler feed water systems (probably containing corrosion inhibitors, biocides, scale)
- blowdown from cooling cycles
- back-washing of filters
- laboratory and pilot-scale plants
- workshops
- sanitation waste water collection
- collection of rainwater from contaminated areas
- landfill leachates,

contribute to the overall water pollution as well. So waste water generally contains as contaminants almost every compound present or arising during the reaction, such as:

- non-reacted starting material
- production residues
- auxiliaries, to the extent that they are not recovered from the aqueous discharges
- intermediate compounds
- unwanted by-products.

If syntheses are carried out using organic solvents and other auxiliaries, these regularly make up the majority of the organic pollutant load emitted to the waste water treatment facilities. On the other hand, by-products and starting compounds can often be responsible for the poorly biodegradable part of the total waste water load.

The majority of process waste water (70–90 %) consists of tributary streams with a low pollution level [cww/tm/82], e.g.:

- cleaning water
- waste water from vacuum generation
- washing water from exhaust air clean-up
- waste water originating from equipment such as product pumps.

Tributary streams such as mother liquors, initial aqueous discharges, blowdown from cleaning cycles and vapour condensates make up the remaining 10–30 % [cww/tm/82].

When considering pollution loads, the ratio is reversed. The more highly concentrated tributary waste water streams (10–30 % of the total waste water) generally contain up to 90 % of the relevant contaminant loads [cww/tm/82].

The consequences of contaminants of complex waste water streams, however, are not sufficiently expressed by their loads or concentrations. The impact of hazardous and toxic contaminants with concentrations close to the detection limit can be significant in contrast to high concentrations of non-toxic substances. Thus, waste water from chemical industry sites might show toxic effects. Alternatively, synergetic effects of different individual streams, having no toxic effects themselves, might be observed when they are mixed together either in the sewerage system or in the receiving water.

Waste water and its impact on the environment are normally characterised by:

- the content and emission of pollutants, expressed by load and/or concentration of single substances, such as NH_4^+-ions, NO_3^--ions, NO_2^--ions, PO_4^{3-}-ions, each of the heavy metals, inorganic acids and salts, oil
- the effect and/or hazardous potential on the receiving water body, expressed by surrogate or sum parameters such as TSS, BOD, COD, AOX/EOX, VOX, pH, conductivity and temperature
- the effect on organisms in the receiving water, expressed by toxicity data such as acute toxicity, chronic toxicity or mutagenity
- properties such as hydraulic load.

1.1.2 Waste Gas

Waste gas streams can roughly be divided into ducted and non-ducted (diffuse, fugitive) emissions. Only ducted emissions can be treated. As far as diffuse and fugitive emissions are concerned the objective of waste gas management is their prevention and/or minimisation (e.g. by capturing them in a ducted system).

Waste gas and exhaust air emissions in the chemical industry are:

- ducted emissions, such as:
  - process emissions released through a vent pipe by the process equipment and inherent to the running of the plant
  - flue gases from energy-providing units, such as process furnaces, steam boilers, combined heat and power units, gas turbines, gas engines
  - waste gases from emission control equipment, such as filters, incinerators or adsorbers, likely to contain unabated pollutants or pollutants generated in the abatement system
  - tail gases from reaction vessels and condensers
  - waste gases from catalyst regeneration
  - waste gases from solvent regeneration
  - waste gases from vents from storage and handling (transfers, loading and unloading) of products, raw materials and intermediates
  - waste gases from purge vents or pre-heating equipment, which are used only on start-up or shutdown operations
  - discharges from safety relief devices (e.g. safety vents, safety valves)
  - exhaust from general ventilation system
  - exhaust from vents from captured diffuse and/or fugitive sources, e.g. diffuse sources installed within an enclosure or building.

- diffuse emissions (see Glossary), arising from point, linear, surface or volume sources under normal operating circumstances [cww/tm/158]:
  - process emissions from the process equipment and inherent to the running of the plant, released from a large surface or through openings, etc.
  - non-ducted emissions (e.g. working losses and breathing losses, when not captured and ducted) from storage equipment and during handling operations (e.g. filling of drums, trucks or containers)
  - non-routine emissions, resulting from operations other than the routine processing of the facility, including emissions during start-up or shutdown, and during maintenance
  - emissions from flares
  - secondary emissions, resulting from the handling or disposal of waste (e.g. volatile material from sewers, waste water handling facilities or cooling water).

- fugitive emissions (see Glossary), such as:
  - equipment leaks from pump and compressor seals, valves, flanges, connectors and other piping items, or other equipment items, such as drain or vent plugs or seals.

The main air pollutants from chemical processes and energy supply are:

- carbon dioxide
- sulphur oxides (SO_2, SO_3) and other sulphur compounds (H_2S, CS_2, COS)
- nitrogen oxides (NO_x, N_2O) and other nitrogen compounds (NH_3, HCN)
- halogens and their compounds (Cl_2, Br_2, HF, HCl, HBr)
- incomplete combustion compounds, such as CO and C_xH_y
- volatile organic compounds (VOC) and organosilicon compounds, which might encompass compounds with carcinogenic potential
- particulate matter (such as dust, soot, alkali, heavy metals) with possible carcinogenic properties.

1.2 Environmental Management with Regard to Waste Water and Waste Gas

Environmental management as part of the overall management system is becoming increasingly important. It includes the organisational structure, responsibilities, practices, procedures, processes and resources to develop, implement, achieve, review and monitor the environmental policy of the industrial company. With regard to waste water and waste gas it sets the rules for the involvement in concept finding, planning, evaluation, design, construction, operation and maintenance of a chemical site, i.e. a strategy to meet all objectives connected with waste water and/or waste gas. It gives assistance to, e.g.:

- consideration of possible environmental impact when planning new production lines, or planning enlargement of existing lines
- decisions on the planned production process
- decisions on the implementation of process-integrated measures
- decisions on the production path
- decisions on the choice of the discharge path
- decision on the implementation of central or decentralised treatment or control
- decisions on the method for minimising contamination
- decisions on the creation of an appropriate infrastructure, or the alteration of an existing one, for the purposes of improving waste water and/or waste gas quality
- evaluation of the cross-media effects of the different treatment strategies
- decisions on the prevention of fugitive emissions by replacing or modifying older equipment which tends to have a high leakage rate
- decisions on the implementation of a Leak Detection and Repair (LDAR) programme.

As can be seen from the few examples above, the rationale of environmental management has much to do with decision making between several options in light of the particular situation. And it has – of course – to do with economics and competitiveness. The main question environmental management helps to answer is: How can one operate a complex site and manage its demands for a supply of resources and discharge of waste with the least possible impact on the environment as a whole, with the highest economic efficiency and without any loss of product quality? Answering this question is one of the issues in Chapter 4 on BAT conclusions.

To keep the environmental impact caused by waste water and/or waste gas to a minimum, an overall and integrated environmental strategy should be developed by operators. It is important for this strategy to reflect the following items:

- Water is increasingly becoming a valuable resource, and recycling of treated effluent water, when possible and necessary in special situations, is of increasing importance. Thus, the purpose of effluent treatment is to achieve recycling or water recovery, as well as to improve discharge quality. The result of such an overall waste water strategy might be, in the final analysis, site-specific, applicable only to this particular situation. The approach to this result, however, normally follows the pathway described in Chapters 2 and 4.

- Though air is not a diminishing resource, its purity is essential for life (with key issues such as climate change and ozone layer depletion) so that more efforts have to be taken to avoid the release of pollutants to the atmosphere and recycle them instead to the production process or use them elsewhere on the site.

- In contrast to waste water, there are substantial components of waste gas – namely non-ducted waste gas – that are not susceptible to treatment. They have to be dealt with by prevention techniques. The management of fugitive emissions relates to detection, quantification methods, equipment selection, housekeeping and preventive maintenance measures.

- When planning and designing a production process, the first aim should be the prevention of waste to be discharged to the environment. Selecting clean technologies and clean raw materials supports this aim.

- When planning and designing a waste gas treatment system, deciding whether to use techniques with or without water consumption (e.g. wet scrubbing, biofiltration, refrigeration through water cooling) is a major issue, most of all for regions with a shortage of water.

- If – as is usually the case – complete prevention of waste is not practicable, the next step is minimisation, not only of volume, but also of impact caused by hazardous substances that might be replaced in the production process.

- If all measures for minimisation are taken, the next step is controlling the inevitable discharge by implementing the most effective treatment system possible, so as to minimise the total environmental impact. The choice of this treatment system is based on an evaluation of:
  - its control efficiency
  - its energy needs
  - its space requirement
  - the possible generation of waste gases or waste water, waste and noise
  - its consumption of resources
  - its capital costs
  - its interference with other units and safety issues
  - its maintenance requirements.

- The quality of the receiving medium into which the industrial site is going to discharge its waste may be such as to impose special and more stringent requirements of the waste water and/or waste gas quality.

Planning of action is only one part of environmental management. The next and more important step is a process of continuous improvement of a given situation, i.e. all the different stages and steps have to be done and redone repeatedly over time. This is usually supported by company policy on environmental issues for all their sites and by Member State legislation.

The basis for environmental management – or waste water and waste gas management – applied to waste control is that the introduction of pollutants into final treatment systems not suitable for their removal should be avoided or at least minimised.

Opportunities to introduce or apply environmental management are different for new and existing plants. In new plants, preventive control measures, in-plant segregated waste stream treatment and/or process-integrated measures can be effectively taken into account in the design stage of the plant. For existing plants, retrofitting to existing installations and infrastructure may involve technical and organisational constraints and will generally be more expensive. However, the approach and principle – but probably not the result – of environmental management as proposed in this document are basically the same for new and existing plants.

A detailed description of environmental management systems and tools to implement them is given in Chapter 2.

1.3 Treatment Technology

The different sources of emissions (aqueous and/or gaseous) and the variety of the contaminants and their load make the implementation of a more or less – according to the complexity of the production – complex system of handling techniques (prevention and/or control), based on management decisions, inevitable for the operation of a chemical industry site. Such a handling system consists of:

- process-integrated measures, such as water re-use, water saving and pollution prevention
- end-of-pipe treatment (individual and/or central facilities).

How the kinds of handling techniques fit within the scope of this document is illustrated in Figure 1.1 for waste water and in Figure 1.2 for waste gas. The vertical bars signify the boundaries of this horizontal BREF.
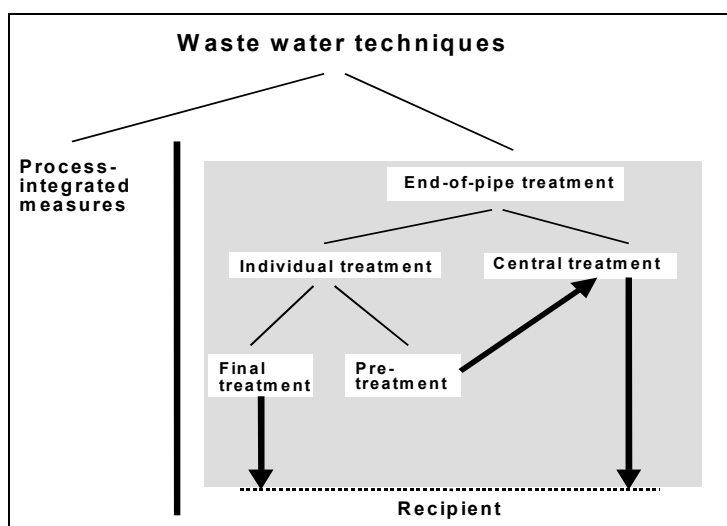
Figure 1.1: Waste Water Handling Techniques

The arrows in Figure 1.1 symbolise the waste water flow. This illustration, however, does not suggest that pretreatment facilities must always exist if a central treatment facility is used.
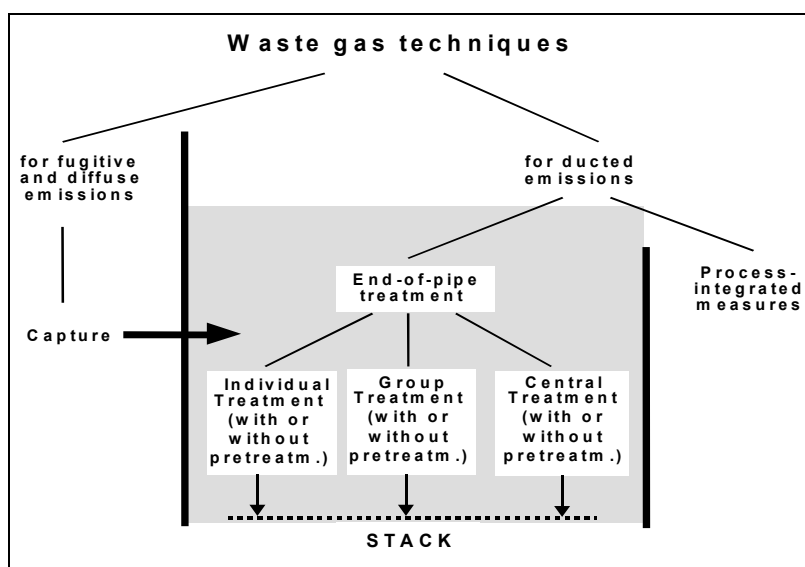
Figure 1.2: Waste Gas Handling Techniques

Figure 1.2 shows that fugitive and diffuse emissions are outside of the scope of this document. When fugitive and diffuse emissions can be captured, they enter the area of treatment techniques for ducted emissions.

1.3.1 Process-Integrated Measures

Though, strictly speaking, process-integrated measures for waste prevention or reduction of the pollutant discharge via waste water and waste gas are part of the scope of vertical BREFs, they are nevertheless mentioned in this horizontal document as long as they are generally applicable in chemical production processes. They are in any case items of good management practice and for consideration when implementing a waste water and waste gas management system on a site.

Advanced environmental protection is more and more shifting from end-of-pipe methods to process-integrated – or production-integrated – measures. Process-integrated measures are a source of significant environmental improvement in both new and existing plants. They are intended to reduce – or even avoid – the production of residues directly at source before they become a discharge. Often these 'process improvements' help to decrease costs for additional treatment measures, as well as increase economic efficiency by increasing production yield and/or decreasing input of raw material. Disposal costs and the limitations of end-of-pipe treatment can influence this shift toward process-integrated measures. Although the prevention of waste, and thus the implementation of process-integrated measures, is becoming increasingly significant, waste treatment techniques will remain essential contributors to the control of emissions into the environment, mainly when process-integrated measures are not feasible for existing production.

Proper process-integrated environmental protection uses all possible physical, chemical, biological and engineering techniques for the prevention, reduction and recycling of residues. Examples are:

- new synthesis pathways
- use of purer or even different feedstock and process agents
- use of purer or different fuels
- optimisation of process steps
- improved plant technology, process control and reaction sequence
- technical adaptations to the process
- improved use of catalysts and/or solvents
- recycling of auxiliaries (e.g. washing water, inert gases, solvents, catalysts)
- recycling of residues immediately during the process
- use of residues as raw material for other productions (product integration within and/or outside the location)
- use of residues for energy generation.

Obviously the development of completely new pathways for syntheses in existing plants will – mostly for economic reasons – remain an exception, and will be restricted to bulk products or products of high economic value. In practice, production-integrated environmental protection will progress continuously as the sum of many individual – and maybe tiny – improvements over time.

1.3.2 End-of-Pipe Techniques

End-of-pipe techniques are those that treat the waste stream arising from a process or storage unit, or an area – or part thereof – to reduce its pollutant content (see Figure 1.1 and Figure 1.2).

1.3.2.1 Waste Water Treatment

Since process-integrated measures are preferably implemented in newly built plants or production processes because of economic limitations due to high capital costs or retrofitting limitations (e.g. lack of space) in existing ones, the chemical industry and most other industrial sectors resort to end-of-pipe treatment techniques to reduce waste water and the pollutants it carries. They encompass pretreatment or final treatment of segregated waste water streams as well as the central treatment of collected waste water before discharge into a receiving water. The different waste water end-of-pipe treatment techniques and their applicability to control the main contaminants in the chemical industry are shown in Table 1.1.

Technique	TSS	BOD COD TOC	Refrac-tory COD	AOX EOX	N-total	NH$_4$-N (NH$_3$)	PO$_4$-P	Heavy metals	Phe-nols	Oil
Sedimentation	X	(X)[a]						(X)[j]		
Air flotation	X	X[b]						(X)[j]		X
Filtration	X	(X)[a]						(X)[j]		
MF / UF	(X)[c]	(X)[a]								
Oil separation		X								X
Precipitation							X	X		
Crystallisation							X	X		
Chemical oxidation		X	X	X						
Wet air oxidation		X	X	X					X	
SCWO		X	X	X					X	
Chemical reduction										
Chemical hydrolysis										
NF / RO		X	X	X				X		
Adsorption		X	X	X				X		
Ion exchange		(X)[d]						X		
Extraction		X	X	X						
Distillation / rectification		X	X	X						
Evaporation		(X)[e]						X		
Stripping		(X)[f]		X		X				
Incineration		X	X	(X)[g]		X		(X)[k]	X	X
Anaerobic biological		X		(X)[h]	(X)[h]			X[l]		
Aerobic biological		X		(X)[h]			X		X	
Nitri / denitrification					X	X				

[a] only solid
[b] undissolved organic content
[c] finely dispersed and low concentration
[d] ionic organic species
[e] non-volatile organic content
[f] volatile organic content
[g] special incinerator equipment required
[h] only biodegradable part
[j] undissolved heavy metal compounds
[k] transferred to ash or waste water originating from incinerator
[l] in combination with sulphate precipitated as sulphides

Table 1.1: Major Waste Water Contaminants and their Respective Treatment Techniques

Complex chemical production sites normally have an extensive system for the collection and treatment of process water. There are several approaches to waste water treatment, each of them having its advantages and disadvantages, depending on the situation:

- decentralised waste water treatment facilities, treating the aqueous effluent at source and discharging into a receiving water (i.e. no central waste water treatment facility on site)
- centralised waste water treatment, normally using a central Waste Water Treatment Plant (WWTP)
- central WWTP, with upstream tributary stream pretreatment at source
- waste water discharge into a municipal WWTP
- waste water discharge into a municipal WWTP with on-site pretreatment at source,

the last two bullet points being special situations of the two preceding bullet points respectively.

The advantages of decentralised waste water treatment or treatment at source (or the disadvantages of centralised waste water treatment) are:

- the operators of the several production installations show a more responsible attitude to the effluent when they are made directly responsible for the quality of their own waste water discharge
- more flexibility for works enlargement or for reacting to changing conditions
- facilities for treatment at source are tailor-made and thus normally show better performance
- in contrast to the central biological treatment there is no (or less) excess activated sludge to dispose of
- treatment performance of non-biological techniques is independent of biodegradability of waste water streams
- avoidance of dilution by mixing of different waste water streams, normally resulting in a higher treatment efficiency, etc.
- cost benefit ratio can be much better in tributary stream treatment than in central treatment.

Decentralised waste water treatment is a preferred option when tributary waste water streams with completely different properties are expected.

The main advantages of using a centralised WWTP (or the disadvantages of decentralised treatment facilities) are:

- making use of synergetic effects by mixed biodegradable waste water, i.e. effects that enable microbiological degradation of special contaminants in a mixture with others (or even in a dilution with other waste water streams) whereas the tributary stream alone has poor biodegradability
- making use of mixing effects, such as temperature or pH adjustment
- more effective use of chemicals (e.g. nutrients) and equipment, thus decreasing relative operating costs.

Waste water from chemical industry sites is also treated together with municipal waste water, either in common municipal WWTPs or in specially built plants for the combined treatment of municipal and industrial waste water. The joint treatment is frequently arranged in such a way that, because of its high initial organic loading and the tendency to decreasing degradation rates in diluted waste water, the industrial waste water initially undergoes a high performance (high load) step, and is subsequently joined by the municipal waste water in a second biological (low load) step.

Experience has shown that the joint treatment of municipal and chemical industry waste water generally has – at least as a first approximation – neither synergetic nor antagonistic effects on the receiving water [cww/tm/82] (a contrary example of a coordinated operation of a chemical and a municipal WWTP is described in Annex 7.1). The disposed pollutant loads are generally additive.

Advantages [cww/tm/82] of joint waste water treatment can be:

- the operational stability of joint biological treatment can be favourably influenced by:
    - improving the nutrient conditions
    - optimizing the waste water temperature and thus the degradation kinetics
    - equalizing the feed load, as long as the daily progress lines of the two waste water streams are correspondingly structured, or can be matched to one another
    - suppressing the toxic and inhibitory effects of waste water constituents by lowering the concentrations below the critical thresholds,
- the joint treatment of waste water and excess activated sludge can, in individual cases, realise savings in capital and operating costs.

Disadvantages can be:

- systems with mixed drainage and without appropriate buffer tanks for excess rain can suffer from hydraulic overload in the event of heavy rainfall, which might lead to increased pollutant discharge accompanied by loss of bacteria from the activated sludge compartment of the central WWTP [cww/tm/82]
- reduced cleaning performance due to production-related operation disturbances, which leads to increased water pollution because of insufficient treatment of both municipal and industrial waste water streams [cww/tm/82]
- quite a number of chemicals can, even at lower concentrations, hinder nitrification. If the nitrification step collapses, it might take several weeks to recover and ensure sufficient nitrogen elimination again. So, to minimise the risk for joint waste water treatment, it is crucial to study and monitor carefully the waste water streams coming from the industrial part for any inhibiting or disturbing factors [cww/tm/82]
- combined treatment of waste water streams from different origins bears the risk that persistent contaminants, such as heavy metals and non-biodegradable compounds, can escape control – and sometimes even detection – because of dilution. These contaminants discharge without degradation into a receiving water, adsorb onto the activated sludge or are stripped into the atmosphere during aeration. This would counteract the obligation to prevent or control these substances at source. This disadvantage affects all treatment actions on combined waste water streams
- combined treatment may result in sludge too contaminated for further usage or further treatment by, e.g., anaerobic digestion.

Another important aspect of the waste water system is the handling of rainwater and rinsing water. In a number of older chemical complexes in Europe, only one sewer system is present and rainwater, rinsing water, cooling water and process water are collected in this system and directed to the waste water treatment facilities. Especially during periods of heavy rainfall, this might lead to upsets of the WWTP and lead to increased discharges. Advanced chemical sites usually have a separate sewer system for the collection of uncontaminated rainwater and cooling water. Details are given in Section 3.3.4.4.

1.3.2.2 Waste Gas Treatment

Waste gas treatment techniques in general are concerned with the reduction of:

- particulate matter
- vapours of volatile liquid substances
- gaseous air contaminants.

Waste gas treatment normally takes place directly at source. Only rarely can waste gas streams with different characteristics be treated simultaneously in one central treatment unit. One main reason is that treatment units are normally specifically designed for a particular waste gas composition. Another important reason is that special attention must be paid to the release of toxic and hazardous components and their impact on the surroundings as well as on the safety of the plant. In the chemical industry, given the toxicity and/or hazardous characteristics of many components and the generally large volumes that are handled and processed, safety is a crucial issue.

A selection of techniques by pollutant is given in Table 1.2, and by waste gas flow rate in Table 1.3 [both cww/tm/70].

Technique	dry matter	wet matter	inorganic particulates	organic particulates	inorganic gaseous or vapourous components	organic gaseous or vapourous components	odour
Dust recovery and abatement							
Separator (pre)	x	x	x	x			
Cyclone (pre)	x	x	x	x			
Wet dust scrubber (FT)	x	x	x	x			
Electrostatic precipitator (FT)	x	x	x	x	(x)	(x)	
Fabric filter (incl. ceramic filter) (FT)	x		x	x			
Catalytic filtration (FT)	x	x	x	x		x	
Two-stage dust filter (pol)	x		x	x			
Absolute (HEAP) filter (pol)	x		x	x			
HEAF (pol)		x					
Mist filter (pre, pol)		x			(x)		
Gas recovery							
Membrane separation (pre)						x	
Condenser (pre)					(x)	x	
Cryocondensation (pre, FT)					(x)	x	(x)
Adsorption (FT)					x	x	x
Wet gas scrubber (water) (FT)	(x)	(x)	(x)	(x)	x	x	x
Wet gas scrubber (alkaline) (FT)	(x)	(x)	(x)	(x)	x	x	x
Wet gas scrubber (alkaline-oxidation) (FT)	(x)	(x)	(x)	(x)			x
Wet gas scrubber (acidic) (FT)	(x)	(x)	(x)	(x)	x	x	x
Gas abatement							
Biofiltration (FT)						x	x	x
Bioscrubbing (FT)					x	x	x
Biotrickling (FT)					x	x	x
Thermal oxidation (FT)				x		x	x
Catalytic oxidation (FT)						x	x
Flaring (FT)						x	x
Combustion gas treatment							
Dry alkali injection (FT)					x		
Semi-dry alkali injection (FT)					x		
Wet lime injection (FT)					x		
SNCR (FT)					x		
SCR (FT)					x	(x)	

x = primary application
(x) = secondary application
(pre): mainly as pretreatment facility
(FT): treatment technique used as final treatment technique
(pol): mainly as polishing technique after standard technique

Table 1.2: Selection of Techniques for Waste Gas Emission Reduction in Relation to the Pollutant to be removed

Technique	100 [Nm³/h]	1000 [Nm³/h]	10000 [Nm³/h]	100000 [Nm³/h]
Dust recovery and abatement				
Separator	x	x	xx	xx
Cyclone	x	xx	xx	x
Wet dust scrubber		x	xx	xx
Electrostatic precipitator (1-stage)			x	x
Fabric filter	x	x	xx	xx
Ceramic filter		xx	x	x
Catalytic filtration	x	x	x	
2-stage dust filter		x	x	
Absolute (HEAP) filter	x	x		
HEAF	xx	xx	x	
Mist filter		x	xx	xx
Gas recovery				
Membrane filtration				
Condenser	x	x	xx	x
Cryocondensation	x	x		
Adsorption	x	xx	xx	x
Wet gas scrubber (water)	x	x	xx	xx
Wet gas scrubber (alkaline)	x	x	xx	xx
Wet gas scrubber (alkaline-oxidation)	x	x	xx	x
Wet gas scrubber (acidic)	x	x	xx	xx
Gas abatement				
Biofiltration	x	xx	xx	xx
Bioscrubber	x	x	x	x
Biotrickling	x	x	x	x
Thermal oxidation		x	xx	
Catalytic oxidation		x	xx	
Combustion exhaust gas treatment				
Dry alkali injection			xx	x
Semi-dry alkali injection			x	xx
Wet lime injection		x	x	x
SNCR	x	x	x	x
SCR		x	xx	xx

x   =   application
xx   =   most common applications

Table 1.3: Selection of Techniques for Waste Gas Emission Reduction in Relation to Waste Gas Flow Rate

1.4 Environmental Impact of Waste Water and Waste Gas Treatment and their Interdependencies

Although waste water treatment systems generally reduce emissions to water, the operation of these systems has its own environmental effect. Especially relevant with regard to emissions to air from waste water treatment are those water streams which are polluted with volatile organic compounds (VOC) and volatile inorganic compounds (e.g. ammonia, hydrogen sulphide or hydrogen chloride). Whenever these water flows are in open connection to the atmosphere, (odorous) emissions of these components may occur. Special attention should be paid to aeration of biological waste water treatment basins, stirring operations, open buffer tanks, settling tanks and waste water stripping facilities. In all these cases, the emission of pollutants can be shifted from the water compartment to the air. Thus additional waste gas treatment can be necessary. Air emissions may also evolve from the mixing of water flows with different temperatures or the addition of acids or alkalis for pH-adjustment.

The potential impact of waste water treatment plants on the environmental compartments is briefly reviewed in Table 1.4 [cww/tm/84].

Environmental compartment	Potential effect/emission
Air	• Evaporation/formation of odour (e.g. H_2S, NH_3, mercaptans etc.). • Formation of aerosols. • Drift of potentially hazardous micro-organisms from the treatment plant. • VOC emissions (evaporating or stripped from the water). • If biogas is generated and not used as fuel for energy supply, it is normally flared, resulting in emissions to the air.
Water	• In principle, significant reduction of water emission. • When rainwater is treated together with process water, the treatment system might get overloaded in the event of heavy rain fall, which can cause additional pollutant emission because the treatment system cannot function properly.
Waste	• Waste water treatment sludge and scrubber solutions.
Other	• The central WWTP plant consumes energy. In some cases, biogas is generated and can be used as a source of energy.

Table 1.4: Potential Impact of Waste Water Treatment Facilities

Other relevant points of concern are the energy consumption and sludge generation of the waste water treatment techniques. The generation and handling of sludge (e.g. dewatering, incineration) account for a significant part of the energy requirement and the environmental impact of a WWTP. On the other hand, treatment systems with a beneficial energy balance do exist. In anaerobic biological waste water treatment units, for example, the gas generated by treatment (biogas) can be used as a fuel. Otherwise it needs to be flared, causing untreated discharges to the air.

What has been said about waste water treatment systems in the preceding paragraphs is also valid for waste gas treatment technologies. Their relevant environmental impacts are emissions to the water and air compartments. Wet scrubbing procedures, for example, mean that waste water has to be treated in a subsequent treatment step. Waste gas oxidation discharges a flue gas containing gaseous contaminants not present in the original input, that might require further waste gas treatment. As with waste water treatment, the operation of waste gas treatment facilities is connected with energy and water consumption, the latter being an essential issue under special climatic conditions. This is briefly reviewed in Table 1.5.

Environmental compartment	Potential effect / emission
Air	• In principle (and primarily), significant reduction of contaminant emissions. • Replacement of VOCs by flue gas contaminants, such as carbon oxides, hydrogen halides, sulphur dioxide, nitrogen oxides, dioxins, in the case of thermal/catalytic oxidation. • Emissions from flares.
Water	• Scrubbing/absorption processes transfer contaminants from air into water compartment. • Some treatment processes need excessive water (e.g. scrubbing, water-run condensation).
Waste	• Sludge from secondary treatment of waste water originating from waste gas treatment. • Residues from waste gas treatment facilities (e.g. separated solids, condensed liquid not recycled, spent adsorbent, spent catalyst).
Other	• Waste gas treatment facilities normally consume energy.

Table 1.5: Potential Impact of Waste Gas Treatment Facilities

In addition to flares and thermal/catalytic oxidisers, a large number of environmental and safety facilities can be found in the chemical industry. The main purpose of these facilities is to reduce the environmental impact or increase the safety of the plant operation. The facilities vary from very simple measures to complex treatment units.

In general, the overall effects of the environmental and safety facilities should be positive. That is the reason for installing them in the first place. However, because of fundamental conservation laws, most treatment technologies can have, in addition to their purging abilities, negative impacts on the environment. Examples of these cross-media effects are waste generated by filters, waste water generated by scrubbers and increased energy consumption because of the operation of treatment systems. It is hard to give an indication of the break-even point, where the positive effects outweigh the negative effects of a treatment measure, since this is strongly influenced by local conditions. As a rule of thumb one could say that local environmental quality and safety should have priority. Furthermore, it is generally considered preferable for pollutants to be in the most concentrated and controllable state. This offers the best opportunities for recycling, further treatment or controlled disposal.

To sum up, waste water and waste gas treatment, in addition to their individual impacts on the environment, affect each other in different ways:

- several waste water treatment techniques result in gaseous emissions, which need to be ducted to downstream waste gas treatment facilities, often entailing complex construction steps
- waste gas treatment technologies result in gaseous and/or aqueous releases, which need further waste gas and/or waste water treatment.

Each item (gaseous releases to waste gas treatment facilities or aqueous ones to waste water treatment facilities) can normally influence existing downstream facilities though in most cases they lead only to a low load increase. Contrary examples are wet scrubbing of exhaust gases or stripping of volatile material from WWTPs.

2   WASTE WATER/WASTE GAS MANAGEMENT

Chapter 2 adds detail to the general description in Chapter 1 and describes the aspects of waste water and waste gas management in the context of IPPC. It emphasises the significance of management in achieving a high level of protection of the environment as a whole when operating a chemical plant or site. Where possible, the joint approach to aqueous and gaseous emissions is maintained; references to the medium are only made when media-specific strategies or tools are involved.

This chapter describes environmental management as the interplay between management systems and management tools and is not strictly restricted to waste water and waste gas issues, but to the involvement with IPPC requirements. Otherwise it would not meet the objective of an integrated approach.

The implementation of an environmental management system at a given site depends on the environmental impact of the activities carried out there, and has to take into account the specific environmental situation at and around the site. This chapter presents the general schedule and the relevant tools to implement an environmental management system valid for chemical sites.

2.1 Environmental Management System (EMS)

As briefly mentioned in Chapter 1, the importance of environmental management, often referred to as 'Health, Safety and Environmental' (HSE) management, cannot be overestimated. It has many advantages, such as:

- improved insight into the environmental aspects of the company
- improved basis for decision making
- improved motivation of personnel
- additional opportunities for reducing operating costs and improving product quality
- improved environmental performance
- improved company image
- reduced liability, insurance costs, non-compliance
- increased attractiveness for employees, customers and investors
- improved relationship with authorities and environmental groups.

In general, an EMS consists of a loop of strategic items as shown in Figure 2.1 [cww/tm/132] These items are [cww/tm/132]:

- environmental policy, which means a public statement - approved and endorsed by the highest level of management - of the intentions, principles of action and objectives that govern the management of a company with respect to the environment
- organisation and structure to implement the company's environmental policy
- comprehensive register of applicable legislation and company standards
- regular sampling and monitoring programme with data collected in registers
- establishing an individual environmental programme for the site, on the basis of global, long-term targets, set at the highest achievable level, together with data from the register of environmental effects
- environmental auditing
- regular review and assessment of the suitability and effectiveness of the EMS, the result having influence on the environmental policy, thus closing and starting the loop again.
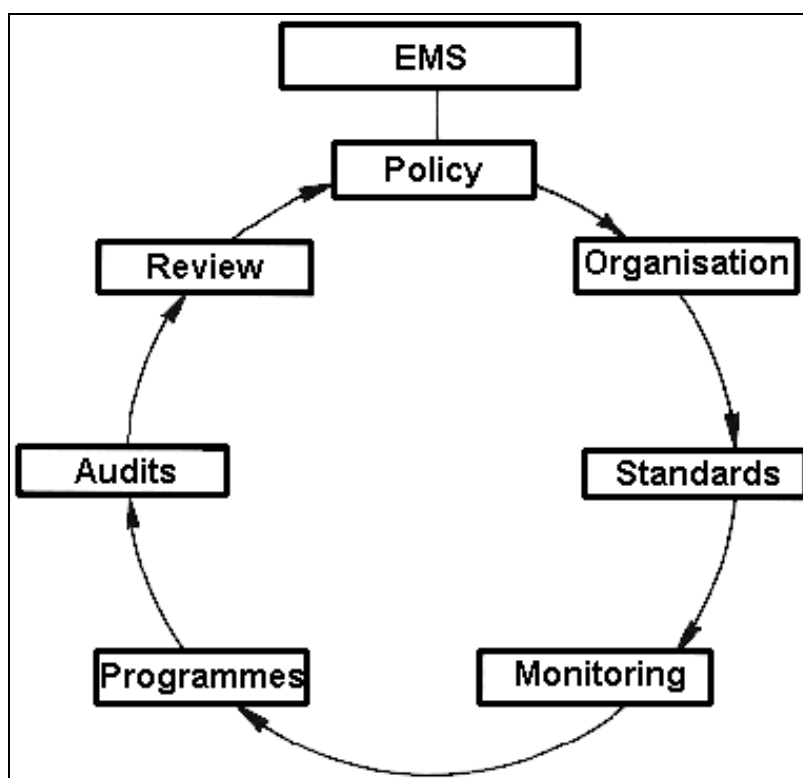
Figure 2.1: The Environmental Management System (EMS) Loop

This 'loop' signifies that EMS is not a once-through process but an iterative way of optimising the environmental situation or attitude of a company or a site of industrial activities.

There are accepted standards for an EMS, such as:

- ISO 9001 / 14001 (International Organisation for Standardisation)
- EMAS (European Commission, Council Regulation 761/2001 – Eco-Management and Audit Scheme), which took on board the requirements of ISO 14001
- Responsible Care® (Chemical Industry)
- ICC Business Charter for Sustainable Development (International Chamber of Commerce)
- CEFIC Guidelines for Protection of the Environment (European Chemical Industry Council).

It is not within the scope of this document to give a detailed overview of the entire EMS for a chemical site, therefore in the following the term 'EMS' is restricted to its involvement with waste water and waste gas management in the context of IPPC issues.

The EMS is an excellent item to improve the integrated environmental performance of an industrial site. It offers the management of a company the possibility to:

- gain insight into the pollution-generating mechanisms of the production processes
- make balanced decisions about environmental measures
- avoid temporary solutions and no-return investments
- act adequately and pro-actively on new environmental developments.

The EMS regularly follows the strategy of a cyclic process of:

- analysis or pollution characterisation / evaluation of the manufacturing processes to understand how pollution is generated, using tools that are detailed in Section 2.2.1.
- identification of the possibility of pollution reduction by measures such as:

-   consideration of environmental impact when planning new production lines or when planning enlargement of existing production lines
-   re-thinking on and re-designing the process technology, e.g. change to cleaner process technology, cleaner raw material and/or improved process equipment
-   process-integrated prevention measures
-   possibilities to recycle or recover waste content
-   options to improve emission collection and control, e.g. optimising releases by pretreatment
-   end-of-pipe measures
-   assessment of centralised vs decentralised end-of-pipe treatments;

- assessment of the most effective options, taking into consideration:
    -   environmental benefits and impact, such as overall removal efficiency, overall balance of cross-media effects
    -   technical, organisational and financial feasibility
    -   site-specific constraints and options (such as space requirements vs existing space limitations, quality of the receiving media)
    -   safety issues
    -   required resources and utilities;

- execution of the goal and monitoring its achievement according to an action plan, which contains items such as:
    -   schedule of action
    -   responsibility for action
    -   data to be assessed
    -   monitoring method and frequency
    -   guidelines on which the monitoring process and evaluation process are based,

    and which is followed by evaluation of the results.

The cycle is illustrated in Figure 2.2. Evaluation re-starts the whole cycle since – as stated above – the EMS is an iterative process.
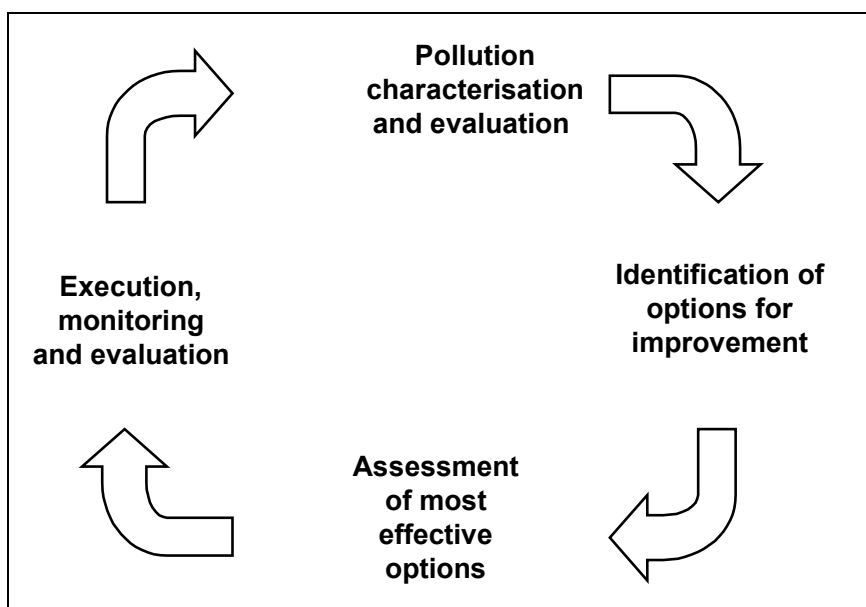
Figure 2.2: Strategy of a Site-Oriented EMS

Part of EMS is the environmental impact assessment at early planning stages of process development and/or new activities. It is to decide (using the cycle of Figure 2.2):

- what is – or might be – their impact?
- what becomes of wastes?
- can they be treated in existing facilities?
- are they toxic (acutely toxic) with regard to the receiving media or existing treatment facilities?
- can they – or must they – be avoided?

The operation of an EMS is a complex procedure because the cycle in Figure 2.2 needs to be followed for all individual process units with all relevant environmental aspects in respect of the result for the whole site. Figure 2.3 gives a rough impression of this complexity, noting that only some main environmental aspects – a plant orientated pollution treatment strategy – and two individual units are included. Steps 1 to 4 correspond with those in Figure 2.2.
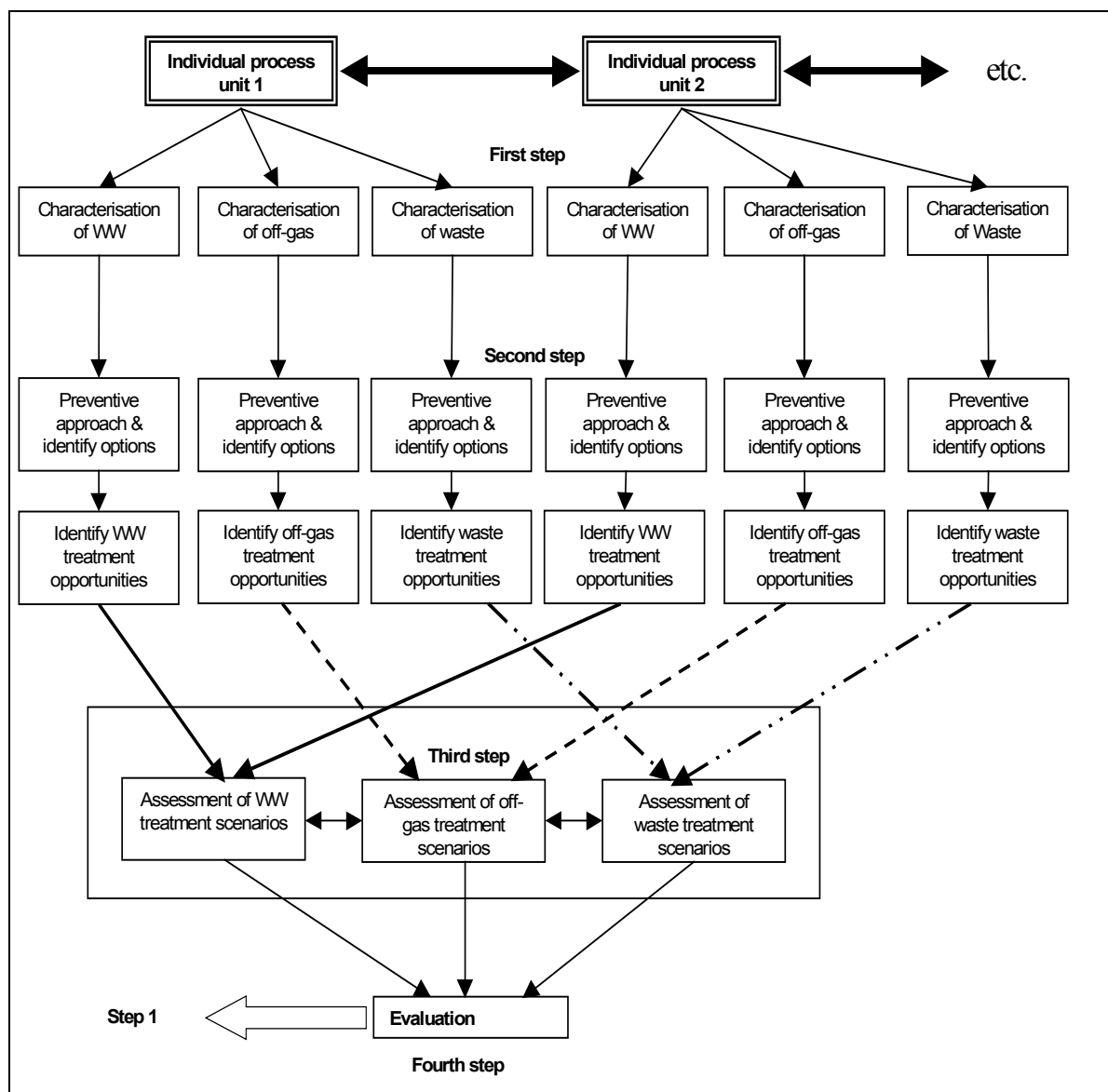
Figure 2.3: Complexity of a Site-Oriented EMS

The EMS is accomplished by expert judgement supported by management tools. The different kinds of tools are presented and explained in Section 2.2.

2.2 Management Tools

To operate an EMS around the loop of strategic items (see Figure 2.1), several kinds of (management and engineering) tools are used. These can be roughly categorised as:

- inventory tools, giving detailed information on the location, the production, the environmental circumstances, the emissions etc. of the chemical site and thereby helping to detect emissions that can be prevented or reduced
- operational tools, helping to decide upon planning, designing, installing, operating and improving pollution prevention and/or treatment facilities
- strategic tools, comprising the organisation and operation of release handling on the entire chemical industry site in an integrated manner
- safety or emergency tools, necessary for troubleshooting in the case of unplanned events.

2.2.1 Inventory Management Tools

To operate an industrial site in accordance with a good EMS, it is essential to have detailed and transparent information on:

- the site and its environmental circumstances
- the production processes
- pollutant characteristics of the individual production processes
- the characteristics of the emitted streams
- the local situation.

Without this knowledge it is not possible to develop a coherent, efficient and cost effective strategy to prevent or reduce emissions. Though it is often virtually impossible to quantify the emissions of each contaminant present in each emitted stream, a way can normally be found to reduce the necessary parameters (e.g. number of measurements) without relevant loss of information.

2.2.1.1 Site Inventory

A site inventory consists of information on:

- location (map, plot plan)
- climate, geography, quality of soil and groundwater, neighbourhood, receiving water
- size of the site (total area, built-up area, drained area, covered area)
- number of employees
- production units
- list of production plants comprising, for each one, data on:
    - classification of production plants according to the Directive, Annex I, 4. Chemical Industry, 4.1 – 4.6
    - typical production plant data,
- information on the production processes, for each process giving:
    - a brief description
    - simplified process scheme(s) with sources of waste streams
    - details of the chemical reactions (main and side reactions) and supporting operations
    - information on operating material, intermediate and final products
    - operating mode (continuous or batch process or campaign operation)
    - potential emergency situations (spills, leakages)
- sewerage system (sewer, WWTP, rainwater drainage).

2.2.1.2 Stream Inventory or Register

The compilation of relevant basic data on the composition and quantity of waste water and waste gas streams – each one individually – is done in a stream inventory or register (waste water register, waste gas register). The emitted streams are listed respective to their source, i.e the production process from which they originate. This is a key element in assessing their degree of contamination and the nature of the contaminants, as well as the reduction-at-source possibilities. The sources of waste water are listed in Section 1.1.1, those for waste gas in Section 1.1.2.

A stream register consists of:

- information about the chemical production process, such as:
    - chemical reaction formula including starting compounds, products and by-products
    - simplified process flow-sheet of the corresponding production unit, showing reactor, work-up and product isolation, and showing the exact origin of the various emission contributions,
- information about the emitted streams, such as:
    - components and their variability
    - relevant data on concentration and load of significant components and their variability (including monitoring method and frequency)
    - stream flow rate and its variability (e.g. pulse dose, continuous flow or batch-wise)
    - temperature
    - pH (for waste water)
    - conductivity (for waste water)
    - flammability (for waste gas)
    - explosion limits (lower explosion limit – LEL – and higher explosion limit – HEL)
    - reactivity (for waste gas)
    - relevant contaminants and/or parameters, such as:
        - ➢ COD/TOC, NH_4-, NO_3- and NO_2-N, phosphorus, heavy metals, halogenated hydrocarbons, persistent organic pollutants (POP) – when expected – and toxicity in waste water
        - ➢ chlorine, bromine, fluorine, hydrogen chloride, sulphur oxides (SO_x), hydrogen sulphide, mercaptans, carbon monoxide, nitrogen oxides (NO_x), particulate matter, heavy metals and their compounds, volatile organic compounds (VOC) in waste gas
    - data on biodegradability (for waste water) such as:
        - ➢ BOD-concentrations
        - ➢ results from modified Zahn-Wellens-Test
        - ➢ refractory COD/TOC loads
        - ➢ denitrification inhibition potential
    - presence of other substances (for waste gas), which may have an impact on the treatment system or may be safety topics, such as oxygen, nitrogen, water vapour, dust.

The purpose of a stream inventory is to identify the most relevant emission sources (for each medium, waste water and waste gas) and to allow a prioritisation of the emission reduction steps to be taken. Generally speaking, this is a four-step operation:

- listing of the sources
- evaluation of the causes of emissions from each source
- quantification of the amount of emission from each source
- validation of the results through a material balance.

An appropriate ranking of the distinctive tributary streams (i.e. individually for waste water and waste gas), corresponding to the characteristics and load of contaminants, is a decisive part of the inventory and an attractive basis for identification of further release reduction potential (see Section 2.2.1.3), the respective streams at the top of each ranking list being prime candidates for a most effective emission reduction.

On chemical sites, measures for the reduction of emissions are best realised for those chemical processes where an optimum ratio of environmental benefit to cost is achievable. For existing installations, non-optimum elimination rates for minor emitted streams not carrying a significant load might be tolerated, when efforts are instead concentrated on streams containing significant loads, thereby reducing overall emissions and environmental impact.

2.2.1.2.1 Whole Effluent Assessment (WEA)

Effluent discharges have largely been assessed and regulated on the basis of physical and chemical properties, such as COD, BOD, TSS, pH and concentrations of specific hazardous substances. These properties provide a sound basis for controlling effluents containing relatively few and well characterised contaminants with well defined and understood toxicological properties. It is, however, sometimes very difficult to assess the environmental significance of complex and variable effluents on the basis of their composition and physico-chemical properties.

Whole effluent assessment is a methodology to evaluate complex waste water streams and is additional to the use of surrogate and sum parameters such as COD, AOX or EOX. The aim is to assess the possible hazardous character of effluents, which would be insufficiently controlled when relying only on the chemical indications provided by those sum parameters or by limits set on individual chemicals. Whole effluent assessment provides an additional and perhaps even more direct means of assessing the potential impact of effluents on the aquatic environment and is likely to play an increasing part in the regulation of discharges, supplementing and perhaps replacing the traditional measures of effluent quality in environmental monitoring and risk assessment. Co-operation and mutual understanding between regulator and discharger will be essential to ensure appropriate and suitable control of complex effluent discharges.

Biological test methods, bioassay methods, are used for whole effluent toxicity assessment, e.g. fish, algae, bacteria and crustaceans bioassays. Their advantage over chemical analyses of single substances is that the toxic properties of the water samples are determined in an integrated manner and interactive effects, which may occur in the presence of several pollutants, are directly accounted for. With biological test methods the environmental significance of a complex effluent can be determined. This is usually quicker and cheaper than extensive chemical characterisation and thereby simplifies regulation. They cover a range of substances and produce results that can be interpreted fairly easily. In addition, they allow conclusions to be drawn on the efficiency of waste water treatment plants in eliminating toxic substances.

The choice of bioassay methods and the choice of experimental design depends on the application, i.e. whether results are to be used for hazard assessment, monitoring or compliance. Bioassay methods for different applications will have different requirements.

There is a lot of experience of acute toxicity measurements and there are two procedures commonly used for the evaluation of toxicity data:

- EC_x/LC_x approach using statistical data analysis where at least five data pairs of concentration / response between 0 and 100 % response are needed
- LID (Lowest Ineffective Dilution) approach resulting in the dilution of the original waste water stream until no effects are observed, i.e. equivalent to 1/NOEC. It does not need a concentration / response relationship and thus the whole test procedure is simpler, but no statistical evaluation and confidence limits are available.

Whole effluent assessment (WEA) provides information on effluents by using a range of chemical, physical and/or biological methods to examine their potential for biological effects. The methodology of WEA is aimed at determining possible adverse effects of effluents and addresses basically the same effect parameters, which are used in a substance-orientated approach:

- acute toxicity
- mutagenicity, or (preferably) genotoxicity
- chronic toxicity
- bioaccumulation
- persistence, or (bio)degradability.

Chemicals which are persistent (P), toxic (T) and/or liable to bioaccumulation (B) are of specific concern to the aquatic environment. The chemical-orientated approach focuses on measuring hazardous substances that have been selected and prioritised using the P-T-B criteria. A well-designed WEA programme can provide environmental management with integrated measures with regard to complex effluents. The advantages of using biological effect parameters are:

- WEA considers all waste water compounds regardless of their origin and detectability by chemical analysis. The compounds do not necessarily need to be identified. By-products and metabolites are assessed as well
- toxic effects on aquatic organisms are directly displayed; combined effects are also considered
- the sources of hazardous effluents (production steps or hot-spots) inside industrial areas can be identified in many cases (backtracking)
- the effort required to perform tests in WEA is comparable with a comprehensive analysis of single substances in a complex effluent.

The advantages mentioned above are more or less scientific ones, but WEA may also support everyday production practices:

- a combination of direct and indirect measures of a range of potential effects can be used by environmental management, particularly when effluents contain substances which are poorly understood with respect to their persistence, bioaccumulation and toxicity
- whereas toxicity results can be readily applied, e.g. in dilution calculations, bioaccumulation and persistence of an effluent are not indicative of effects by themselves, they rather relate to a chronic exposure assessment
- it provides information on potential risks for the environment, delivering proactive information to operators and regulators
- with specific techniques, it can be used to identify hazardous components in the effluent and aid operators to reduce the discharge of such components.

The application of WEA faces challenges addressed by the scientific community. They include:

- a continuous focus on the toxicity component of P-T-B in combination with a lack of agreement on standardised tests for bioaccumulation and persistence
- WEA itself generally does not take into account the protection of sediment and the pathways of food chain exposure, which can be examined, however, in a broader ecological risk assessment process
- it is important to communicate the results of WEA testing in the context of temporal and spatial effluent sampling, applied test methods, the assumptions made and the statistical analyses applied to the data. Further agreement and international standardisation on such issues are required.

Generally, WEA can be used as a tool within an EMS to give detailed information on the pollutant characteristics of an effluent. As noted in Section 2.2.1, it is virtually impossible to quantify the emissions of each contaminant present in an effluent stream. However, a well-designed WEA programme can provide operators with integrated measures of effluent quality. WEA can be one of the measures used in an effluent stream register as described in Section 2.2.1.2.

Potential applications of WEA include:

- Regulations or guidance on effluent toxicity
  Some jurisdictions set numerical toxicity criteria in discharge permits, while others use toxicity data as a planning and assessment tool. Establishing toxicity criteria ensures consistent evaluation of effluents: enforcement or management action is usually taken only when the effluent repeatedly fails the toxicity criteria. Alternatively, less formal approaches to using toxicity data can reduce uncertainties about the risks of effluent discharge by complementing conventional chemical effluent data. In addition to toxicity data, evaluations of persistence and bioaccumulation can be used in the same way. [4]

- Ranking the environmental risk of discharges to an aquatic system
  WEA can be used to evaluate relative risks posed by multiple dischargers with the objective of prioritising attention where it is needed.

- Toxicity identification / reduction evaluations (TIE/TRE)
  TIE / TRE are used to determine why an effluent is toxic and what can be done to reduce that toxicity to an acceptable level (see http://www.setac.org/wettre.html). TRE can be defined as a site-specific study conducted in a step-wise procedure [5] designed to:

  - identify the agent causing effluent toxicity
  - isolate the source of toxicity
  - evaluate the effectiveness of toxicity control options and
  - confirm the reduction in effluent toxicity.

  TIE are defined as a set of procedures that identify the specific agent responsible for effluent toxicity (and that might be a subset of tools used in TRE). Reduction of toxicity to an acceptable level may be accomplished through the identification and control of the source of the toxicity or identification and implementation of a treatment strategy that reduces toxicity to an acceptable degree. TIE/TRE can range from very simple to highly complex means and they provide a logical process for operators to address a significant toxicity issue. TRE can guide the efforts of treatment engineers to focus on the minimisation of costs for effluent improvements. This kind of study, however, needs to be done by experienced personnel with good laboratory support (chemical and toxicity capabilities). By convention, TIE/TREs evaluate "toxicity", but elements of both persistence and bioaccumulation could be an addition to the process (e.g. PIE/PRE or BIE/BRE).

- Prioritisation of waste treatment measures
  Identification/reduction evaluations (as described above) can be used to predict the effectiveness of various waste treatment measures and rank their contribution to a reduction of effluent hazards. For example, toxicity test data can give an integrated measure of proposed waste treatment improvements (e.g. toxicity testing of effluents from pilot-scale treatment plants). This kind of information helps decision-makers to get the most value for their investment in waste (water) treatment.

- Judging effectiveness of treatment improvements
  Once a facility has upgraded its waste (water) treatment system, toxicity and other testing of the effluent over a period of operation can be used to evaluate the improvements to waste treatment over time. A comparative study on the toxicity of different effluents showed that treatment improvements using conventional approaches do not guarantee the absence of acute toxicity [6].

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[4] Approaches described in: de Maagd, R.G.-J. 2000. Bioaccumulation tests applied in whole effluent toxicity testing. Env. Toxicol. & Chem. 19(1): 25-35.

[5] USEPA. 1991. Technical support document for water quality based toxics control. Washington DC: Office of Water. EPA/505/2-90-001.

[6] Tonkes, M., P.J. F. de Graaf and J. Graansma. 1999. Assessment of complex industrial effluents in the Netherlands using a whole effluent toxicity (or wet) approach. Water Science and Technology 39 (10-11): 55.

- Backtracking of effects observed in receiving environments
  If environmental conditions in the receiving environment show negative impacts, WEA (often at a range of concentrations to match dilution in the receiving environment) can be used to try to establish cause and effect. For example, the hypothesis that poor benthic community quality was caused by an effluent discharge could be tested using carefully designed WEA. In addition, methods for effluent assessment can be used to evaluate receiving environment quality, allowing direct comparison between the two.

- Site-specific hazard/risk assessment
  The environmental risk posed by an effluent could be predicted or assessed using a risk assessment approach, where one of the likely methods to assess biological effects would be WEA [7]. It would be important to attempt field validation of any biological effects by linking WEA data with measured biological effects in aquatic communities [8].

As demonstrated in the examples above, WEA might be used to support decisions on BAT in a number of practical ways. Each jurisdiction can decide which combination of applications will suit its effluent control policies and practices. Whether strictly emission-based or combined with a water quality-based approach, WEA supports most approaches to effluent discharge management.

WEA is widely used, both within and outside the EU. One of the main differences between the approaches used by each country is the combination and types of tests that are used (toxicity/genotoxicity, persistence and/or bioaccumulation). In the EU, WEA implementation in a regulatory context is largely at the research and development stage, but the examples below show a range of uses of or approaches to WEA:

- Germany routinely uses acute toxicity and genotoxicity as ecotoxicological standards for effluents of several different industrial sectors [cww/tm/130] and there is also a WEA research and development programme (e.g. development of fish egg tests).
- For the past six years, Ireland has had mandatory emission limit values in terms of Toxic Units (TUs) for effluents discharged to waters from Integrated Pollution Control industries. The TU limits range from 5 to 10 and they are stipulated in the published BATNEEC guidance documents [cww/tm/95] for the various sectors. In addition, industries discharging to a municipal WWTP may also be required to carry out a combination of toxicity and respirometry tests.
- In Sweden, effluent characterisation (including WEA) is used to assess whether the effluent treatment for a particular operation is adequate. This is usually done as a check on new production units (in-process and end-of-pipe installations) that have been on-line for some time as part of the permitting process. This approach, however, can be used at any time to assess the need for further installations.
- The UK is presently phasing in Direct Toxicity Assessement (DTA) for effluent discharge [9], having conducted extensive research and development and a demonstration programme.
- The Netherlands is in the final stages of a WEA research and development phase, which will weight (geno)toxicity, persistence and bioaccumulation equally. WEA will be implemented in a regulatory context by 2005.

On a broader European scale, OSPAR (Oslo and Paris Convention for the Protection of the Marine Environment of the North East Atlantic) took up the issue of ecotoxicological evalution of waste water as a means of assessing effluent quality through the Point and Diffuse Sources Group (PDS) in 1994. In November 1999, the German Federal Environmental Agency drafted a

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[7]   Chapman, P.M. 2000. Whole effluent toxicity testing- usefulness, level of protection, and risk assessment. Env. Toxicol. & Chem. 19(1):3-13

[8]   Grothe, D.R., K.L. Dickson and D.K. Reed-Judkins (eds). 1996. Whole effluent toxicity testing: an evaluation of methods and prediction of receiving system impacts. Society of Environmental Toxicology and Chemistry. Pensacola. FL. USA.

[9]   Boumphrey, R., Tinsley, D., Forrow, D. and R. Moxon. 1999. Whole Effluent Assessment in the UK. OSPAR Workshop on Whole Effluent Assessment, Lelystad, Netherlands, 28-29 October, 1999.

background document on the use of WEA in waste water evaluation [cww/tm/130]. An Intersessional Expert Group (IEG) was formed in 1999 specifically to develop WEA within the context of OSPAR's Hazardous Substances Strategy (OSPAR, 2000, http://www.ospar.org). The OSPAR-IEG examined the use of WEA for different industries (to date, pulp and paper and pharmaceutical manufacturing industries). In addition, the IEG has undertaken a review of test methods for persistence and bioaccumulation and also for genotoxicity and endocrine disruption (both in preparation).

In conclusion, WEA is a useful tool for integrated pollution prevention and control, but will complement traditional chemical-based controls, rather than replace them. Experience shows that when measures of P-T-B within a well-designed WEA programme are implemented, they result in reductions of releases of hazardous substances into waste water. The key is to design WEA to complement other control measures within an effective environmental management system.

2.2.1.2.2   Reduction of Water Usage and Waste Water Discharge

Because of its increasing importance in many areas of the European Union, it is appropriate to devote an extra paragraph to water conservation (i.e. reduction of water usage and waste water arising) and/or re-use as a water management tool. Water conservation, for example, often helps to reduce the negative impact of pollutant transfer from the gaseous medium to the aqueous. It is probably not an exaggeration to state that the extent of water re-use and recycling is limited by the creativity and willingness of the people involved rather than by technical barriers. This depends, however, on local circumstances. Items to consider are, e.g.:

- develop strategies to minimise (fresh) water consumption and waste water arising in the production process(es) [cww/tm/67d], such as:
  - process alteration, which might lead to a reduction of water required, e.g. substitution of air cooling for water cooling
  - direct waste water recycling, i.e. re-use of slightly contaminated waste water in other processes not influenced by these contaminants, which results in a reduction of fresh water and waste water without changing the contaminant load
  - pretreatment of waste water and subsequent re-use (same or other process), which results in the reduction of fresh water, waste water and load of contaminants;

- challenge waste gas abatement techniques (e.g. wet scrubbers, bioscrubbers, refrigerators with water cooling, wet cyclones, wet electrostatic precipitators) on their fresh water consumption and, if possible, avoid them, when the availability of fresh water is a limiting factor or when the receiving water is sensitive to disturbances.

The procedure for the reduction of water consumption and waste water generally follows the pathway illustrated in Figure 2.4 [cww/tm/67d].

As a first step, a balance of water and the main contaminants that might prevent its direct re-use is carried out. When the data collection for the waste water register has not delivered consistent data, a subsequent data reconciliation is necessary, combined with additional elaborated measurement.

Based on the stationary mass balances, various options to minimise water consumption can be developed and evaluated for operability. To minimise the amount of (waste) water, it might be useful to collect and mix streams from several different production processes and recycle the complete mixture, increasing the potential for precipitation and corrosion. Tools to administer these process developments are described in Section 2.2.1.3.

It must, however, not be overlooked that enrichment of pollutants that cannot be removed by internal abatement or purification techniques may confine water re-use in water cycles.
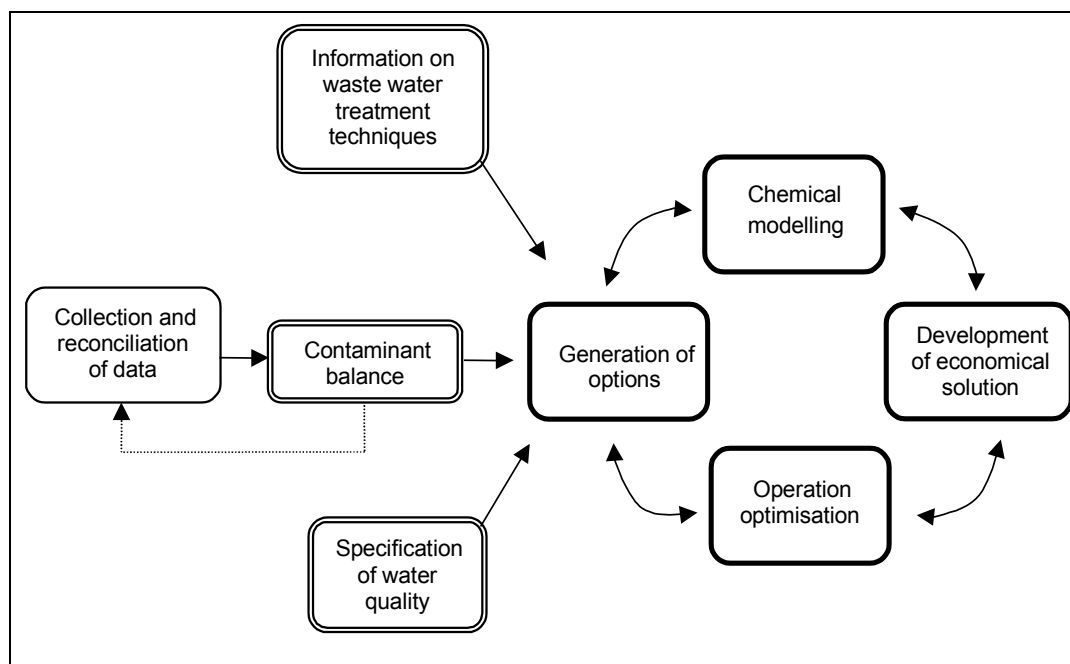
Figure 2.4: General Procedure to reduce Water Consumption and Waste Water Arising

2.2.1.2.3   Waste Gas Emission Quantification

The waste gas emissions from some sources may have different causes, and therefore the emission resulting from each cause may need to be evaluated separately to quantify the aggregate emissions through this source. Furthermore, source reduction will mean concentrating on the cause of emissions rather than on the source through which they are emitted.

Emission quantification by source

Emissions can be quantified by source in a way that is adopted in Council Directive 1999/13/EC (VOC-Directive) [cww/tm/88].

To prepare a waste gas inventory, emissions from all potential sources have to be quantified. This can be done either by estimation, calculation or measurement according to the type of emission and its relative importance to total waste gas emissions. Some emissions are best estimated by output source, others by cause of emissions. In particular, uncaptured emissions are very difficult to measure. They require quantification by contributing cause.

The following examples are offered by way of illustration:

- The emission from product (normally VOC) can be estimated, when the gaseous content of the product is known. The amount of solvent contained in the product, for example, is well defined, and quantities sold or recovered are also known.

- If gaseous substances are contained in waste, their content needs to be measured, or otherwise be defined to calculate the quantity that could be emitted. This will also depend on the method used for the disposal of the waste.

- Ducted emissions to the atmosphere can be quantified by adequately measuring the air flow rate and waste gas concentration (preferably at different stages of the process). This measurement can, however, be relatively expensive to make and can be complicated by access difficulties, presence of water vapour or particulate matter, or other circumstances, and may represent only a snapshot of a situation which is often variable with time. A calculation method is therefore usually preferred, where measurement is not feasible. This possibility depends on the cause of the emission. For example, if a ducted emission is produced by evaporation of a solvent in a drying operation (VOC emission), it is normally easier to calculate the quantity of solvent evaporated by measuring the solvent content in the product before drying, whereas pollutants in combustion exhaust gases (NO_x, SO_x, etc.) or hazardous pollutants require measurement in the stack.

- Quantities not abated in an abatement system can be calculated if the quantities sent to the abatement system are known and the abatement efficiency is known.

- Uncaptured emissions are by nature difficult and often expensive to measure and often need to be evaluated by considering the causes of the emissions and the related evaluation methods detailed below. Nevertheless, before abandoning the possibility of measuring, an evaluation of its feasibility should be done.

Emission quantification by cause

A quantification of the emissions based on their cause might often prove to be the only practical solution, particularly for uncaptured emissions, but often also for ducted emissions. Several methods exist to perform these calculations. All calculation methods provide estimates, which in some cases indicate only the order of magnitude.

Examples are:

- Process emissions quantification needs to be based on a detailed understanding of the process that is taking place. In many cases this provides a fairly accurate evaluation of the emitted quantity, which may sometimes need to be confirmed by measurements. In performing these calculations and measurements, care should be taken to account for the variability that may be inherent in the process. This may be a time variability – in batch processes the amount emitted typically varies as the batch processing progresses – or a grade variability – different grades of products emit different quantities. Calculations need to reflect these, and when measurements are performed, the operating conditions during each measurement have to be recorded carefully, and also measurements in sufficient number have to be made to account for the full range of variability. A yearly material balance needs to take the actual yearly production into account to reflect properly the grade slate effect.

- Storage tank emission calculations can be based on the methodology developed by the United States Environmental Protection Agency (USEPA) [cww/tm/89]. The calculations are cumbersome and require knowledge of some meteorological data that can be obtained from the local meteorological institute. Significant storage emissions can be generated from above-ground atmospheric tanks. However, breathing losses from underground tanks or tanks with a set pressure higher than atmospheric are significantly reduced. Working losses depend on the number of turnovers per year (i.e. how many times the volume of the tank was filled/emptied during the year) and are low for low turnover. If vapour balancing is applied during tank filling, the working losses are eliminated. Therefore in many facilities the storage emissions are low compared with the other emissions. It is advisable to evaluate the storage losses based on material balance before embarking on detailed calculations. If detailed calculations are required, it is strongly advised to use the TANKS computer tool [cww/tm/90] developed by the USEPA, which is a computerised version of the USEPA calculation method.

- Handling emissions can be calculated assuming a vapour content of the air being exhausted from the container being loaded corresponding to the vapour pressure of the product being loaded at the loading temperature, multiplied by a saturation factor. The saturation factor depends on the method of loading, and represents the degree of saturation achieved on average in the vapour space during the loading. Saturation factors for road tankers of BLCs are [cww/tm/72]:
  - submerged loading in a clean cargo tank: 0.5
  - submerged loading in a wet cargo tank (dedicated service): 0.6
  - splash loading: 1.45
    (a factor greater than 1 represents over-saturation caused by liquid droplets being expelled with the vapour).

- Equipment leak emission calculations rely on methods developed by the USEPA and vary from simple (based on counts of leak points and average emissions per point) to complex (based on correlations between a measured ppm concentration at the leak interface and a leak rate specific to the type of equipment considered). Additional description is provided in the USEPA-453 Protocol [cww/tm/152], which is also detailed within the IMPEL project "Diffuse VOC Emissions" [cww/tm/154]. These calculation methods provide rough estimates of actual emissions, and usually a more sophisticated calculation method will yield lower results. Calculations based on equipment counts are the only ones not requiring measurements with an organic vapour analyser at each potential leak point. If these calculations provide a satisfactory result for the purpose, no further analysis is required. If the equipment leak emissions become significant, a Monitoring and Maintenance programme [also called Leak Detection and Repair (LDAR)] should be implemented, entailing measurement of each potential leak point and opportunity for repair of leaks being discovered. This work requires skill in performing the measurements and recording them in a database and is therefore best carried out by specialised contractors.

- Non-routine emissions caused by start-up, shutdown and maintenance operations need to be taken into account. These depend heavily on the operating methodology. No widely accepted method exists to estimate these emissions. They can, however, become significant in batch operations with frequent opening/closing of vessels. In these cases the best practical approach is to set up a measurement campaign to quantify the emissions linked to each operating step.

- Accidental emissions should not occur. Since they happen, however, the related solvent loss should be reflected in a material balance. It is recommended that these incidents be tracked and a record kept of the estimated quantity emitted during each event.

2.2.1.3 Energy and Material Flow Analysis (EMFA)

EMFA comprises a whole family of tools to optimise the consumption of energy, raw material, water and the discharge of effluent by pursuing systematically the internal streams of energy and mass in production processes. As such it is either part or extension of a stream inventory, using the obtained data to draw the necessary conclusions. To support this task, computer software of a different degree of complexity is available. The normal procedure of EMFA is:

- starting with input-output analysis of the process
- iteratively repeating the procedure to identify improvement potential by quantitative comparison of input and output data with target values
- simulation of different scenarios (process design) with individual evaluation of their environmental impact
- identifying the 'best' solution according to set targets (cost effectiveness, waste prevention, resource saving etc.).

The goal for implementing an EMFA tool is to operate processes more efficiently and lower their impact on the environment (e.g. reduce waste discharge and/or water consumption), eventually saving costs.

An example of an EMFA approach is detailed in Appendix 7.2.

2.2.2 Operational Management Tools

Whereas the inventory management tools provide all the necessary information without which no decisions about effective waste prevention, minimisation and/or treatment are imaginable, the operational management tools provide the basis to put these decisions into action.

2.2.2.1 Monitoring

Monitoring forms a bridge between inventory and operational tools, but is also connected with strategic and safety tools. The bulk of the information provided by inventory tools, e.g. the stream register(s), is collected with the help of monitoring systems and programmes. Probably the most important issue is controlling the proper operation of production and treatment processes, to check if the set environmental targets are met and to identify and help to track accidents (incidents).

"You can't manage what you can't measure." Therefore, to measure the effectiveness of an EMS, real data are required on the precise effects of the activities of the industrial site on the environment as well as on individuals. It is thus necessary to conduct a planned, regular sampling and monitoring programme. The parameters to be monitored should include [cww/tm/132]:

- point sources, diffuse and fugitive emissions to the atmosphere, water or sewer
- wastes, particularly hazardous wastes
- contamination of land, water and air
- use of water, fuels, energy, oxygen, nitrogen and other gases (e.g. argon)
- discharge of thermal energy, noise, odour and dust
- effects on specific parts of the environment and ecosystems (see e.g. Section 2.2.1.2.1)
- on-site accidents and near-misses
- staff injuries
- transport accidents
- complaints from community residents.

Monitoring, however, is not restricted to analytical measuring. It also includes regular maintenance, visual and safety checks.

Parallel to this document, a BREF on Monitoring is being produced to which the reader is referred for further information. Monitoring in the context of waste water and waste gas is further dealt with in Chapter 3; standards for analytical parameters are listed in Annex 7.4.

2.2.2.2 Setting and Regular Review of Internal Targets or Programmes

An EMS needs to establish an environmental programme where global, long-term and internal, site-specific targets are set. The global and long-term targets are part of company policy and thus not included in this BREF, but it is stated that such a policy is a necessary item.

The parameters for which internal targets are set should be selected according to their relevance. In order to limit the number of these parameters, the purpose of the target setting should be kept

in mind, i.e. an optimum running of production and abatement operations should be ensured, thereby minimising the impact on the environment as a whole. It is usually not necessary to set target levels for each and every parameter involved, but to use surrogate parameters to describe the emissions. The measurable target levels need to be set in such a way that the permit level of the final outfall as well as the specific local conditions can be readily met.

There are several classes of targets, one class given as general standards, another as site-specific standards. Examples of general standards are:

- the requirements of Environmental Quality Objectives (EQO) or Environmental Quality Standards (EQS) as well as technology standards and 'Good Manufacturing Practice' (GMP)
- the general requirements for River Basin Quality ('Water Framework Directive' or national regulations on water quality)
- the general requirements for emissions to air, international or national programmes
- requirements of internal company standards issued for all their sites, independent of local permit demands.

Examples of site-specific standards are:

- requirements of permit conditions (e.g. ensuring continuous compliance with emission limit values)
- specific limitations on the ecotoxic content of any final outfall in accordance with the limits set for the receiving medium (surface water, air), e.g. in Germany the achievable values for final discharge into a water body are [10]:
  - $T_F = 2$ (fish test)
  - $T_D = 4$ (daphniae test)
  - $T_A = 8$ (algae test)
  - $T_L = 16$ (luminescent bacteria test)
  - $T_M = 1.5$ (mutagenity).

  As a long-term target for the future, German chemical industry (according to VCI declaration May 2000 [cww/tm/166]) aims to further reduce the toxic impact of their waste water discharge, taking into consideration:
  - acute toxicity to fish, daphniae and bacteriae
  - chronic toxicity to algae
  - mutagenicity.
  They finally seek to achieve that their effluents into receiving water bodies do not exceed dilution factors of $T_x = 2$ ($T_M = 1.5$); toxicities caused by salt concentrations are not included.

When targets are being set, a plan should also be drawn up for actions to be taken when a target level of one or more tributary streams, or of the final outfall, is exceeded for a certain amount of time. These actions have to be clearly defined and the responsibilities and competence for these actions have to be assigned.

Examples of internal targets are:

- continuous reduction of pollution loads
- compliance with permit requirements
- reduction of eco-toxic effects (see Section 2.2.1.2.1).

The role of monitoring in target setting is mentioned in Section 2.2.2.1.

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[10]   The toxicity units (T-values or sometimes G-values) are expressed as 'dilution factors', $T_X = 2$ means the waste water stream has to be diluted to half of its original concentration for the test organisms to survive. See also Section 2.2.1.2.1.

The dynamic process of target setting, given that the chemical industry and the conditions in which it operates are subject to continuous development and constant change, implies a regular review, regardless of whether new legal requirements have been introduced. Thus, a programme to meet these changes needs to be set up. The goal of this regular review is the continuous improvement of the environmental performance of a chemical industry site as a whole. To achieve this permanent goal, a reduction programme should be established that contains the following elements:

- a periodic evaluation of environmental management practices associated with operations and equipment, taking into account:
  - environmental impacts
  - changing legislation
  - public concerns
  - implementation of ongoing improvement;
- incentives for the implementation of cost-effective actions and recognition for significant contributions to emission reduction targets, such as:
  - cost allocation of waste water and waste gas treatment by introducing a pricing system, e.g. the introduction of an internal 'Polluter Pays Principle (PPP)', for discharge from the individual production units, which are charged internally with the costs of the treatment facilities according to their share of pollutant input; this is a good incentive to minimise emissions and thereby reducing the shared treatment costs of the production unit
  - internal awards (bonus payment) for operational improvement proposals by staff
  - internal competition for reducing process disturbances and accidents;
- inclusion of objectives for release prevention in design of new or modified facilities and processes, such as:
  - introduction of recycling of starting compounds or products, when modifications of the installation are planned
  - introduction of water conservation measures, under the same conditions as above;
- preventive maintenance and appropriate control technology to minimise emissions and losses
- implementation of engineering and operating controls and procedures, with operating criteria, to improve prevention, early detection and containment of spills/releases either by
  - monitoring surveillance or
  - organisational measures, using personnel power, such as regular control rounds, or installing containment systems with sufficient collecting volume;
- investigation and evaluation of spills/releases that have occurred, to identify corrective actions to prevent a recurrence
- communication with employees and members of the public regarding information on emissions, the progress in achieving reductions and future plans, which should include a structured dialogue on the concerns and ideas of both employees and members of the public.

This review may lead to decisions to modify or even adapt the environmental objectives, programme or policy.

2.2.2.3 Choice of Treatment Options

With the necessary information concerning emissions arisings on a chemical site and the environmental targets and demands defined, the next step is the selection of appropriate control options. Usually the goal is to find a cost-effective treatment method offering an optimum environmental performance. An appropriate choice normally requires treatability and/or pilot studies.

Available control options are generally evaluated and selected according to:

- the characteristics of the emitted stream, e.g.:
  - flow rate
  - concentration and properties of contaminants
  - presence of impurities
  - temperature
  - pressure
- the amount of the part that needs treatment
- the targets and goals to be achieved, pollutant recovery being the first choice
- legal requirements
- the control options that exist for a given case.

This evaluation and selection process – the necessary data obtained by stream inventory (see Section 2.2.1.2) – always results in additional site-specific conclusions to be taken into account, the key factors varying from site to site, e.g.:

- plant location
- size and layout of the site
- current environmental and economic performance of the installations in question, their age, design and anticipated life time
- potential and degree of process integration within an installation and between installations
- type and quality of receiving medium
- impact on the environment as a result of an actual or foreseen emission
- remaining life time and performance of existing pollution abatement equipment
- availability of resources
- safety
- limitations and constraints on an installation imposed by other legislation
- results of cross-media analysis (water consumption, waste production, energy consumption)
- capital and operating costs.

When final or central treatment facilities are involved, source reduction options should be considered. As a result of the considerations mentioned above, the appropriate treatment system will be selected by considering the options for:

- source reduction
- collection (drainage) system
- treatment methods.

Special issues for waste water and waste gas are dealt with in Sections 2.2.2.3.1 and 2.2.2.3.2 respectively.

2.2.2.3.1   Selection of Waste Water Control System

Figure 2.5 illustrates a decision path for finding the appropriate waste water treatment system for the individual waste water streams [cww/tm/132]. Dotted lines symbolise alternative options.

The following questions, which contain the main objectives of the Directive – prevention, minimisation and control – should be addressed for each type of waste water.

- Can the amount and contamination level be reduced or eliminated by process-integrated or other means?
- Does the waste water stream in total require treatment, or would a segregation system be useful?
- Is the waste water stream suitable for biological treatment, or should it be subjected to decentralised pretreatment?
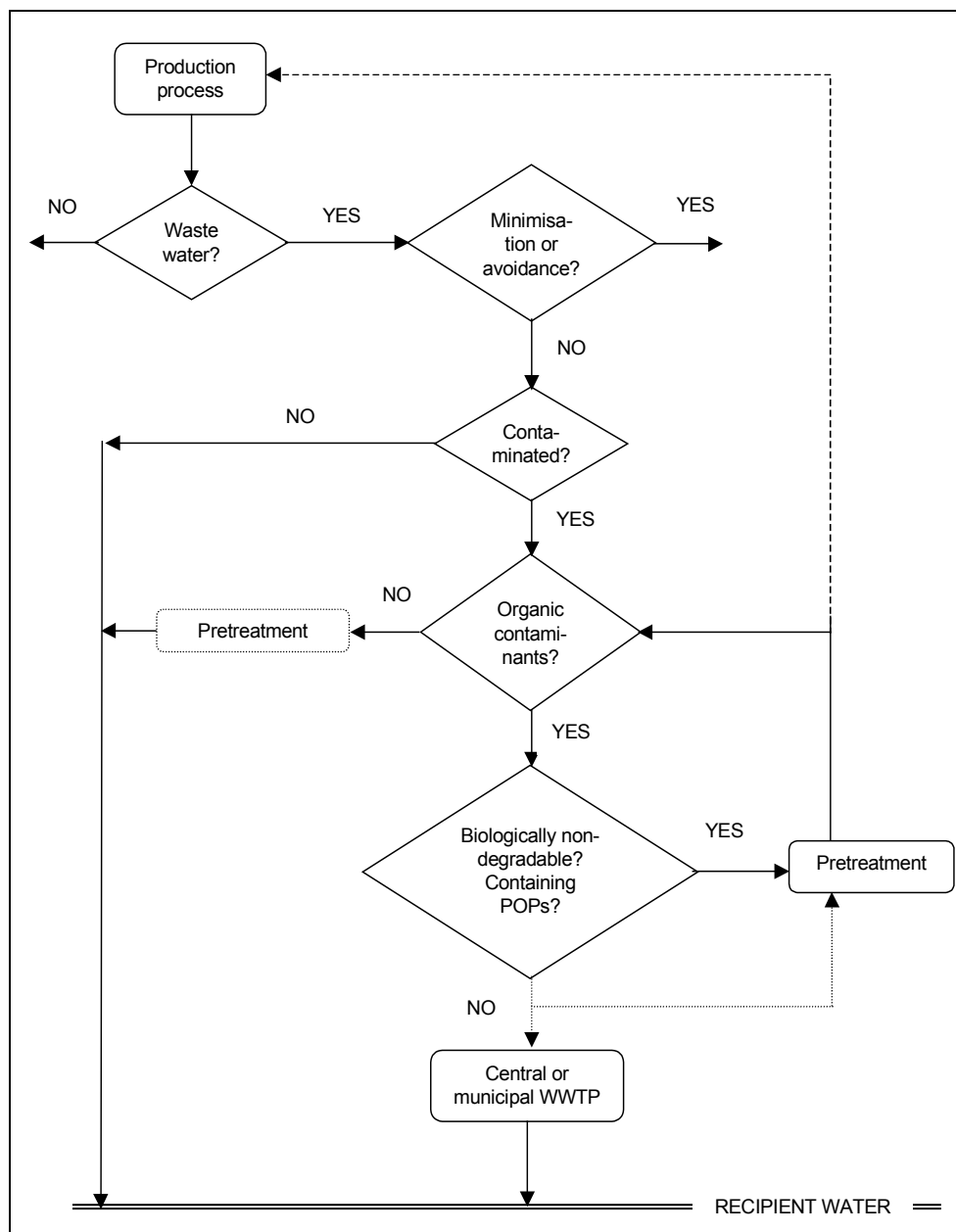
Figure 2.5: Decision Diagram for Appropriate Waste Water Control System

As an example criterion for prioritising a more thorough examination of tributary waste water streams, the presence of recalcitrant TOC load in the order of 20 – 50 kg/d has been used in parts of Germany. Other relevant parameters in this context are heavy metals, halogenated organic compounds and toxicity.

The selection procedure follows the steps mentioned in Section 2.2.2.3:

- **Source reduction**
  The options for waste water reduction at source should be considered first. In many instances, these will result from process considerations described in the related vertical BREF. Suggestions for frequently occurring causes of contamination are:

Process water usage depends on the manufacturing process. Its contaminant concentration depends mainly on the solubility of the process stream in water. The following suggestions should be taken into account:

- the segregation of process water from rainwater and other water effluent, to allow re-use or recycling, as well as to minimise the amount of water which requires treatment, the installation of a roof over certain process areas, loading and unloading bays etc. being an option to consider
- the use of process water in a recycle mode, whenever it is economically feasible, with a maximum number of recycles before discharge
- the avoidance of direct contact cooling systems whenever feasible
- a critical review of the need for water scrubbing systems or, when they are used, the investigation of the potential for water regeneration and re-use (see Section 2.2.1.2.2)
- the minimisation of water flow for water flushing and sealing systems, which are frequently needed for safety reasons but should not be allowed to flow without control or restriction
- the removal of free oil to a slop oil system before its discharge to the sewer
- an effective water / hydrocarbon separation as far as practicable in the process equipment before discharging the water to the sewer
- if feasible, the use of a process fluid instead of steam in Venturi jet devices, or of a liquid ring pump, preferably using a process fluid as seal liquid, or of a dry vacuum pump, to minimise the contamination generated by vacuum devices
- as far as possible the capture of the discharge from safety valves, thermal relief valves, bleeds from double block isolation or twin seal valves, because it is not recommendable to discharge them to areas where clean rainwater is collected
- laboratory effluent collection to a slop tank.

Unintended operational releases to the sewer can generally be avoided through enhanced operator attention. Additional instrumentation or slop collection will often be helpful to enable operators to perform their task efficiently. Also, slop collection facilities are recommended wherever hydrocarbon liquid releases frequently occur. To reduce unintended operational releases, the following suggestions should be taken into account:

- to plug or cap vents and drains whenever they are not in use
- to allow flush collection in a slop system rather than to send it to the sewer, preferably using closed loop sample systems or sampling valves that require no flushing (e.g. ram type sampling valves), the sample bottles sized in such a way that overfilling is avoided and the sampling frequency and sample kept to the minimum required
- to avoid the overfilling of vessels or tanks by installation of an adequate level of instrumentation or adequate procedures
- to minimise the use of hoses
- to consider facilities to collect hose drips
- to consider roofs over loading racks
- to install kerbs to ensure containment of spills
- to consider adequate instrumentation to protect against overfilling of road tankers
- to avoid product loss during water draw-off from tank bottoms
- to consider the installation of reliable interface detection instruments
- to consider the pigging of lines instead of flushing and draining, whenever applicable
- to vacuum-clean spills whenever possible rather than to hydrojet or steam them to the sewer
- to leave water hoses to run only when attended, which is good management / manufacturing practice.

Conservation of water by process-integrated and other measures, however, leads to more highly concentrated water streams that might be profitably recycled or exploited for higher production yields or be treated with higher efficiency. So, any means to reduce water consumption might directly lead to a reduction in the quantity of contaminants evacuated through the sewer.

<u>**Turnaround and other maintenance activities**</u> often result in significant water contamination. To minimise this requires careful planning well in advance, such as:

- to define a dedicated equipment cleaning site, equipped with adequate facilities to recover hydrocarbons and solid waste, making this the obligatory location for equipment cleaning as far as possible (e.g. exchanger bundle cleaning)
- to plan carefully the draining of equipment to avoid undesirable releases to the sewer
- to evaluate carefully the equipment cleaning needs and methods
- to define a disposal route for all cleaning effluent.

<u>**Releases resulting from equipment failure**</u> are by nature unpredictable. Preventive maintenance for equipment and implementation of a monitoring programme are ways to ensure that these are minimised, e.g.:

- to avoid as far as possible pump seal failure
- to consider the installation of seal-less pumps, vibration monitoring or leak alarms on seals
- to detect leaks to cooling water resulting from exchanger failure by periodically checking the hydrocarbon content, pH and electrical conductivity of the cooling water return
- to repair detected leaks as soon as possible
- to analyse frequently leaking systems to define the most suitable type of equipment, packing, gasket, etc.

<u>**Background contamination from foul sewer systems**</u> can be minimised by, e.g.:

- periodically checking sewer inspection chambers for the presence of, e.g., free hydrocarbons, to vacuum pump them, if needed, to the slop
- cleaning of dirty sewers that might cause a significant level of background contamination.

- **Selection of Drainage Systems** (see Section 2.2.2.4.1)

- **Installation of Buffer Capacity**
  The installation of buffer capacity is beneficial for particular waste water streams at production plants as well as for collected waste water streams before they enter the central WWTP, in case of an operating failure. Further details in Section 3.3.3.

- **Treatment Methods**
  Treatment options to consider are:

  - pretreatment for an individual waste water stream with downstream central biological treatment, e.g. a stream containing heavy metals or refractory COD, to reduce contaminants at source, which prevents undesired dilution and dispersion of contaminants that otherwise would escape undetected and untreated into a receiving water
  - final treatment for an individual waste water stream with direct discharge into the receiving water
  - treatment for distributed waste water, as pretreatment or final treatment
  - central treatment for a whole site, e.g. mechanical/biological treatment plant (central biological WWTP), precipitation/flocculation/sedimentation plant or a treatment plant for contaminated rainwater
  - no treatment for low-contaminated individual waste water streams or non-contaminated rainwater.

The various treatment techniques are described in Chapter 3.

2.2.2.3.2 Selection of Waste Gas Control System

The selection procedure follows the sequence mentioned in Section 2.2.2.3. When planning the modifications entailed in either source reduction or end-of-pipe treatment, it should always be kept in mind that all changes can have significant safety implications, particularly when dealing with flammable substances. Therefore it is absolutely essential to assess thoroughly the effect of any change on the safety of the installation.

- **Source Reduction**
  Controlling emissions at a cost-effective level requires, firstly, investigation of source reduction opportunities. Careful planning is needed to optimise the pollutant recovery and, consequently, the related capital and operating costs.

  Investigation can reveal further opportunities for source reduction of emissions. In most cases the related investment is lower than for an end-of-pipe treatment. A thorough investigation of the source reduction possibilities is therefore highly recommended. It should be based on the causes for emissions. Therefore a good knowledge of the relative importance of each cause will be essential for prioritisation purposes. Once all feasible source reduction possibilities have been exhausted, an end-of-pipe treatment may still be required.

- **Emission Collection** (see Section 2.2.2.4.2)

- **Treatment technology selection**
  When source reduction measures do not lead to the required emission reduction, an end-of-pipe treatment is required. All treatment devices can handle only ducted emissions. Therefore, if uncaptured emissions have to be abated by means other than source reduction, collection hoods and a ventilation system (including the necessary safety facilities) are required upstream of the end-of-pipe abatement system. Installation costs for these ventilation systems can be significant. Therefore these systems need to be designed with cost effectiveness in mind. The investment required for the end-of-pipe treatment itself will generally be a function of the total gas flow rate to be treated, therefore efforts to minimise this flow rate will pay off. Finally, selecting a suitable treatment technology will have a significant impact on the required capital and operating costs.

  The key design issues for waste gas treatment systems are the flow rate of the gas stream, its contaminant concentrations and, in addition to the maximum values, their degree of variability. The nature – or 'chemistry' – of the contaminants is of primary importance since all treatment systems are limited in this respect, e.g.:

  - only flammable vapours are suitable to be incinerated
  - contaminants containing halogen and/or sulphur may require flue gas treatment downstream of thermal and catalytic oxidation
  - the efficiency of condensation depends on the vapour pressure of the contaminants at condensation temperature, therefore substances with higher vapour pressure are less suited to condensation
  - only compounds of small molecular size can be effectively adsorbed and desorbed
  - biofiltration of non-biodegradable compounds will not be effective
  - membranes work better on specific compounds
  - the efficiency of wet scrubbing depends on the solubility and vapour pressure of the contaminants.

  The value of emitted product will determine the incentive to recover it from the off-gas, so the more valuable the product the more the use of techniques allowing recovery (e.g. adsorption, condensation, membranes) will be preferred to destruction (abatement) techniques (e.g. thermal and catalytic oxidation, biofiltration).

The presence of impurities in the off-gas affects the design of the system. Sometimes these impurities have to be removed in a pre-treatment step, e.g.:

- water vapour, which affects the adsorption efficiency, condensation systems, particularly refrigerated or cryogenic systems, or filter systems
- dust, which causes trouble for adsorption, absorption or catalytic oxidation where dust particulates plug the packing or adsorbent bed
- catalyst poisons, which destroy the efficiency of a catalytic incinerator or a catalytic filter
- acids, which affect the biofilter / bioscrubber activity.

The permitted exhaust concentration needs to be considered. Most technologies are limited in removal efficiency, and in particular condensation, absorption and biofiltration achieve far from 100 % removal efficiency. This is an advantage of thermal or catalytic oxidation systems, which reach very high destruction efficiencies of about 99 %, but on the other hand the additional consumption of energy and fuel and discharge of flue gas have to be considered. Adsorption systems are also very efficient, as long as care is taken to avoid saturating the adsorbent.

Safety issues are particularly important for thermal and catalytic oxidation systems. Most VOC / air mixtures are flammable at VOC concentrations above 40 g/m^3 at 20 ºC and atmospheric pressure. In order to avoid flashback, i.e. propagation of a flame in the inlet ducts to an incinerator, one has to ensure that the inlet concentration is always well below the LEL. The opposite option – VOC concentration well above the HEL – has to ensure that the VOC concentration does not under any circumstance fall below this higher limit. A detonation arrestor or a seal drum can be provided to prevent the risk of flashback for unexpectedly high concentrations. Besides this, the incinerator has to be installed at a location where there is no risk of presence of flammable vapours, and a detailed analysis is required to ensure safety of the installation. Also systems using other technologies have to be subject to a detailed safety review. Many systems (e.g. adsorption, membranes) will result in more concentrated streams, possibly producing concentrations within the flammable range. For adsorption systems, bed overheating risks have to be evaluated. Many systems include compressors or blowers which may have safety implications. Generally, a detailed safety review of each installation is required and it may have a significant impact on the selection of the system. Thus, safety issues are important for electrostatic precipitators (de-dusting of flammable gases should be avoided) and fabric filters (ignition possible because of hot gases, pyrophoric powders and sparks).

The investment required for the system is obviously also of primary importance. When evaluating the required investment, care should be taken to include the costs of all the required facilities. In particular, utility supply, vent collection ducting to the abatement unit and requirements in ancillary equipment (e.g. a seal drum for an incinerator, water treatment unit for a condenser) may have a significant cost impact.

Although the initial investment is important, the operating costs may be even more important. These include utility consumption, replacement of catalyst, adsorption media or membranes, costs of chemicals, operations and maintenance, by-product disposal, pre- and post-treatment, etc. When evaluating these, care should be taken to quantify the costs associated with each stage of the operations (normal operations, regeneration, idling). As an example, thermal oxidisers are normally fitted with refractory lining. This refractory is sensitive to humidity and therefore has to be kept warm at all times. The amount of fuel required to keep it warm during idling times is an important consideration for systems not operating 24 hours per day 7 days per week. Keeping a regenerative or a flameless system at temperature requires a fraction of the fuel needed for a simple thermal oxidiser.

Layout constraints may play an important role. Incineration systems have to be located outside of locations where flammable vapours could be present. The installation of a system within a hazardous area will require designing the electrical and instrumentation systems accordingly, which may affect the cost of the unit significantly. Access requirements to the unit should be considered as well.

Availability of utilities is yet another key aspect in the selection of the most appropriate abatement technology. Availability of a suitable fuel is required for an incineration system, and the fuel costs may have a big impact on the operating costs. Fixed bed adsorption systems normally use steam for desorption; however, if steam is not available in sufficient quantity, the design has to be adapted accordingly. Sufficient power supply is required for condensation systems and sufficient water for water scrubbing systems.

Treatment systems are dealt with in Chapter 3.

2.2.2.4   Choice of Collection System

The choice of an adequate collection system is influenced by the choice of the treatment systems and thus depends on the task and target of the waste water and waste gas treatment. The selection methodology is described in the following sections for waste water drainage and waste gas ducting.

2.2.2.4.1   Selection of Waste Water Collection and Segregation System

Taking into account the results of the waste water register, the choice of a suitable waste water collection system ensures the optimum discharge of waste water entailing the least possible impact on the environment. Depending on the downstream treatment requirements, a drainage system needs to be installed that meets the needs of:

- rainwater drains
- cooling water drains, according to the grade of pollution
- drains for waste water suitable for direct discharge without any treatment
- drains for sanitary waste water
- drains for process waste water according to its origin
- drains for decentralised or centralised (on-site or off-site) treatment facilities
- separate drains for organic waste water and inorganic waste water without relevant organic load, thus avoiding dilution of both parts, entailing loss of treatment efficiency.

Those prerequisites, as well as economic factors, require the implementation and maintenance of waste water separation/segregation systems. Waste water that does not need treatment – e.g. uncontaminated cooling water or uncontaminated rainwater – is segregated from waste water that has to undergo treatment, thus reducing the hydraulic load on the drainage and treatment system.

Waste water streams that fail to meet the quality requirement for central treatment are subject to special pretreatment operations. Thus, for each waste water stream, the decision process illustrated in Figure 2.5 should be followed and the appropriate sewer system designed accordingly.

The waste water can be collected either by underground or overground sewers or drainage. Existing plants are often equipped with underground systems because they can be operated as gravity sewers, saving power for pumping, and the pipelines are out of the way of process installations. Overground collectors have the advantage that leaks or breaches can easily be detected before much damage is done to the groundwater reservoir. If the groundwater level at an industrial site is near to zero, as happens with sites near embankments, estuaries or coastal areas, there is usually no choice other than ducting the sewers overground. Advanced technology uses overground sewers because maintenance, retrofitting and repairs are easier to

perform and thus their operation is economic. A disadvantage is the need for pressure ducts and the risk of formation of emulsions because of pumping. Climatic situations, however, might be a problem for overground sewers (e.g. areas with long periods of frost).

2.2.2.4.2 Choice of Waste Gas Collection Systems

Waste gas collection systems are often far less extensive than waste water collection systems. They are installed mainly:

- as vent collection systems, routing several vents to a common treatment system
- to capture diffuse and/or fugitive emissions by extraction hoods and duct them to a treatment unit
- as flaring systems, which are primarily installed to allow safe disposal of off-gas in emergency situations.

In order to minimise the air flow rate to the control unit, it is recommendable to encase the emission sources as much as possible by means of partitions separating the sources of emission from their surroundings. This, however, presents operability (access to equipment), safety (avoiding concentrations too close to the LEL) and hygiene concerns (where people access is required inside the enclosure). The enclosure needs to be designed in such a way that vapours are prevented from escaping by ensuring sufficient air velocity through the openings (0.5 m/s minimum recommended). The total flow rate should be sufficient to ensure dilution of vapours to a value well below the LEL. Where this concentration is likely to be exceeded, the installation of an LEL detector inside the enclosure is required, including appropriate control equipment.

In most cases, the emission treatment system will be installed on existing ducted emission points or vent collection systems. A critical review of these existing systems is warranted before determining the total flow rate of the treatment system. This review is required for two basic reasons:

- Actual flow rates delivered by blowers may be significantly different from the blower design flow rate, because of pressure drop upstream and downstream. Actual flow rates at less than 50 % of the blower design capacity are not infrequent. Therefore basing the treatment system flow rate on the sum of design blower flow rates delivering to the control unit may lead to a significantly oversized end-of-pipe treatment. Measurement of the actual flow rates is therefore recommended. Allowance has to be made in the final system design to account for a change in flow rates (increases or decreases) which may be caused by the installation of the treatment unit. In the case of a decrease in flow rate, the safety implications must be checked as well.

- The existing vents or fume extraction systems may not have been designed with flow rate minimisation in mind. Small adjustments to the design may lead to significant reductions in flow rate and consequently significant savings on the end-of-pipe treatment cost.

For VOC collecting systems the most important issues are personnel safety and hygiene. Devices that can be installed to prevent the ignition of flammable gas-oxygen mixtures or minimise its effect by preventing explosions are, e.g.:

- detonation arrestor
- seal drum
- water seals.

The concentration in VOC collection systems must be kept well below or above the explosive range, which means that the correct mixture of waste gases is crucial.

2.2.2.5 Implementation of the Selected Emission Control Options

Once emission control measures have been selected, their implementation must be planned in detail, regardless of whether they are of an organisational or hardware nature. When unexpected problems are identified during the detailed planning and/or review, the selection of the emission control options may need to be revised. It is fully understood that successful implementation of control techniques requires a good design stage. Otherwise the performance of the control option would show a low environmental standard and a poor cost-benefit ratio of the environmental investment.

The time required to implement emission control measures depends very much on the nature of the measures and the type of facility where they need to be implemented:

- organisational measures, e.g. revision of operating procedures or scheduling practices, can usually be implemented relatively quickly
- control measures, e.g. computer control optimisation routines, may take several months (or even more) to develop and test in the operating environment
- hardware measures, e.g. implementation of control devices or process modifications aimed at source reduction, may require from several months to several years, depending upon the size of the projects and the ability to implement them in a running plant environment. This duration includes the design of the facilities, permitting, detailed engineering, procurement of the equipment, installation and start-up. In many cases a full plant shutdown (turnaround) is required to make plant modifications, and in large chemical or petrochemical operations this may happen only once every few years.

2.2.2.6 Quality Control Methods

Quality control methods are tools which are used as a 'trouble shooter' when an existing treatment process runs out of control or cannot fulfil permit requirements. The releases from a treatment plant are a function of its influent characteristics and the efficiency of the treatment operation. To check whether the treatment process runs properly, the quality of the output is judged against a set of standards. If these standards are not met, there is an immediate need to re-establish performance within the standards by [cww/tm/129]:

- detecting the change
- identifying the cause of the change
- taking corrective action to restore the system to the status quo.

The problem solving and system improvement require the entire plant or site to be looked at, and corrective action requires the cooperation of several departments. In the following, these methods are illustrated for waste water treatment, the control method for waste gas treatment being adequate.

Exerting control [cww/tm/129]
Some variables can be controlled by an operator of a WWTP, such as clarifier blowdown, dissolved oxygen and chemical feed, which can be adjusted when circumstances dictate it. Others are out of his/her control, e.g. waste water flow rate and characteristics. These variables can severely influence the operation of the WWTP and ultimately have an impact on the quality of the discharged water.

The controllable aspects are all adjusted in reaction to a change in the system. Adjusting to operating conditions is a feedback activity that attempts to produce a constant output in light of erratic inputs. The variables that cannot be controlled are handled in a predictive or feed-forward fashion. On-line testing and monitoring will give the WWTP advance warning of step changes that occur to its input.

<u>**Control / improvement**</u> [cww/tm/129]
The common mode of operating a WWTP is that of process control. Only those operations that need to be done to meet standards and stay within control regarding effluent quality are performed, thus losing a part of system control. The steps to regain control when it has been lost are the well-known ones of detection, identification and corrective action (see above). The easy option of doing nothing is in most cases not acceptable.

In quality terms 'in control' means that the system is handling the variations the best it can, but the process may not be capable of statistically complying with the imposed effluent standards, because either there are new standards or the input has changed. A new set of standards requires improvement, which results from a remedial journey to reach a new zone of control, which lies within the new standards.

<u>**Quality improvement tools**</u> [cww/tm/129]
The goal of quality improvement is to reject the typical standards and reach a level of performance never achieved before, extending the scope of problem solving beyond the correction of obvious problems. While it is important to make the system work, it might be more important to review the entire system and identify areas of potential improvement. The way to do this is a three-step-process:

- identification of causes of potential problems
- acquisition of data and analysis
- statistical process control.

The first step in problem solving and quality improvement is to focus on a limited number of potential problems and attempt to identify their root causes. A **cause effect diagram** in the form of an ISHIKAWA Fishbone Diagram, as shown in Figure 2.6, provides an effective way to organise and display the various ideas about what those root causes might be.

Another tool is the **Pareto analysis**, which is a ranked comparison of factors related to a problem. It is a graphical means of identifying and focusing on the vital few factors or problems.

A **flow diagram** provides the steps required to produce a desired result and may be used to clarify the procedures used and give a common understanding of the overall process.

The second step of problem solving and quality improvement is acquisition of accurate and reliable data and their analysis by gathering the necessary information and preparing the data for better usage, e.g. as histograms and/or trend charts. These allow a visualisation of the degree of process variation and identification of special problems.

The third step on the way to improve the performance of a WWTP is the use of **statistical process control (SPC)**. SPC uses statistical methods to study, analyse and control the variation in a process. It is a vehicle through which one can extract meaningful information about a process so that corrective action, where necessary, can be implemented. SPC is used to quantify data variation and determine mathematically whether a process is stable or unstable, predictable or erratic. An SPC chart is a tool that can answer the following questions:

- Is the WWTP producing the same results it always has?
- Is it in a state of statistical control or are special causes of nonconformance evident?
- Is it operating as well as can be expected, given its physical constraints?
- Exactly when is corrective action required and when should the system be left alone?
- Should corrective action be taken by changing the process or changing procedures?
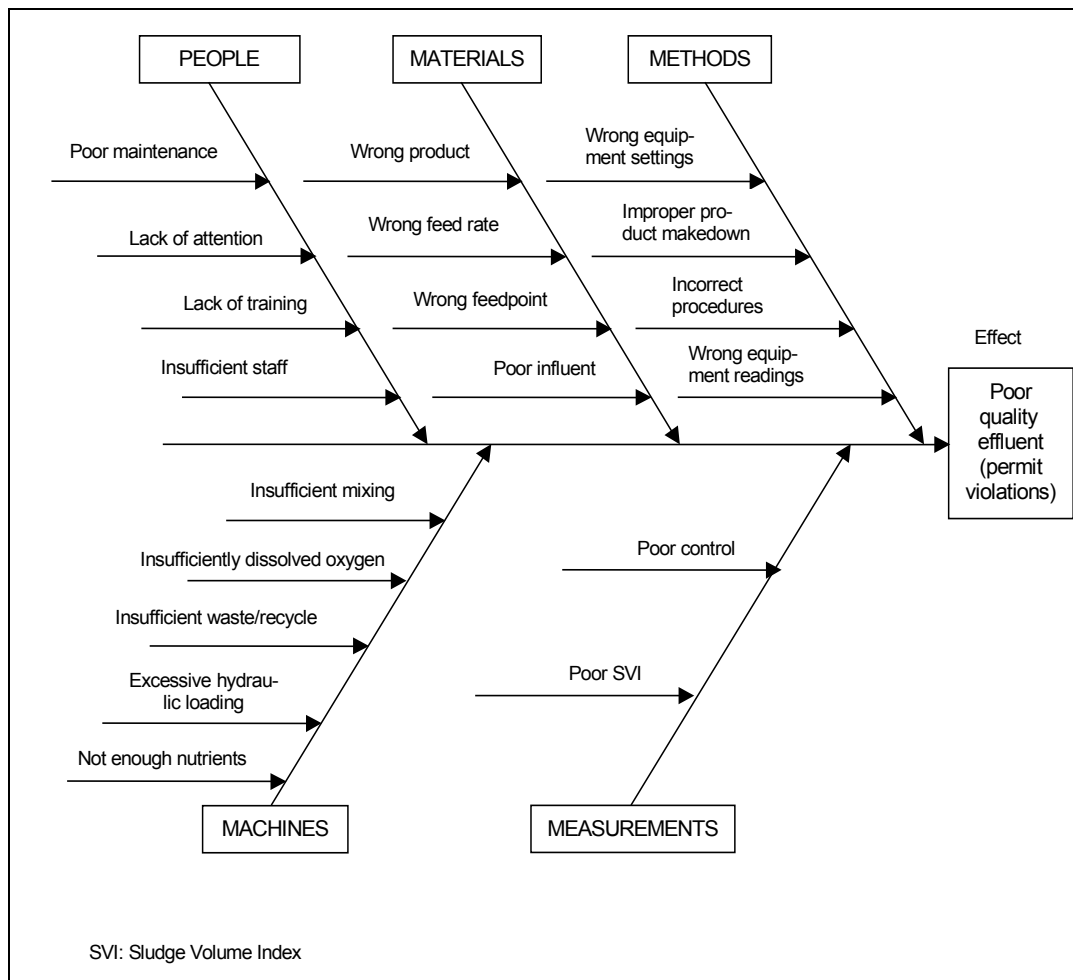
Figure 2.6: Cause Effect Diagram of Poor Quality Effluent

In constructing an SPC chart, upper and lower statistical limits are calculated from the data. These limits are set by the process and are based on earlier performance. They are not to be confused with the operating control limits, i.e. the limits used to operate the WWTP or meet the permit limits. The operating control limits need to be inside the statistical limits (upper and lower).

Immediate attention or action is required, when:

- data fall outside the statistical limits and thus are considered to be a special cause of variation, e.g. a sampling procedure, a liquor spill or an instrument requiring calibration
- the statistical limits are too wide and actual values will eventually fall outside of the control range or permit limits.

When the statistical limits defined by the process fall outside of the operating standards or requirements, the operator is probably reacting properly to changes he notices in the process. He is wrestling with a system that is expected to operate within a range, within which it is statistically not capable of operating consistently. The data indicate that there is too much variation to operate the WWTP consistently and that system changes need to be implemented to gain control.

2.2.3 Strategic Management Tools

Strategic management tools are described when they apply to the organisation and operation of release handling. Their application to process management might belong to the scope of the respective vertical BREFs or the BREF on economic and cross-media issues. Such tools that evaluate environmental and economic options, are, e.g.:

* risk assessment
* benchmarking
* life cycle assessment (LCA),

2.2.3.1 Risk Assessment

Risk assessment is a common methodology to calculate human and ecological risks as a result of activities of production processes. It may take into account continuous and discontinuous emissions, leakage losses, accidental emissions. It is a stepwise and iterative process, comprising at least the first of five steps [cww/tm/132]:

* hazard identification, i.e. identification of the capacity of a substance to cause adverse effects
* concentration-effect assessment, i.e. estimation of the relationship between the level of exposure to a substance and the incidence and severity of its effects
* exposure assessment, i.e. estimation of concentrations or doses to which environmental compartments (including human population) may be exposed
* risk characterisation, i.e. estimation of incidence and severity of the adverse effects likely to occur
* risk estimation, i.e. quantification of the estimated likelihood in a risk characterisation.

When the first step does not identify any hazard in the discharge stream, the application of an iterative process is obsolete.

The iterative process mentioned above characterises the risk, identifies who or what is at risk as well as the levels, sources and pathways of exposure. The next stage is – as a result of the risk assessment process – to reduce the risk and to mitigate the consequences of an adverse event [cww/tm/132]. Thus, risk assessment can give valuable recommendations on the requirements for treatment facilities as well as for the development of preventive and minimisation measures. Risk assessment might find that, e.g.:

* an emitted stream possesses toxic properties that do not allow its exposure to the environment at all, with the effect that complete abatement or recycling is required
* the installation of a process might not be possible, because the receiving medium is already pre-contaminated to such a degree that additional contamination would result in hazardous exposure
* a different kind of treatment might be advantageous when compared with a more common one
* a change in the production process might be required to meet environmental quality demands.

The decision process of appropriate measures falls outside the scope of risk assessment. Socio-economic and political considerations may influence these decisions. It is therefore important to separate the risk assessment based solely on technical data from this policital process [cww/tm/132], which normally includes risk-benefit considerations including cost allocation, and often entails subjective judgement. These thoughts will be taken into account in the BREF on economics and cross-media issues.

Computer programs exist for the application of risk assessment processes [cww/tm/84].

2.2.3.2 Benchmarking

Benchmarking is a process of comparison of the achievements of one plant or site with those of others. It is a tool for the operator to evaluate his/her way of performing, e.g. his/her way of waste water and waste gas management or treatment, by reference to similar activities elsewhere. Central elements are the calculation method of the ranking and the verification of the performances provided. Benchmarking can be an instrument to improve the environmental situation at a site.

2.2.3.3 Life Cycle Assessment (LCA)

LCA involves the comparison of the potential environmental effects of different ways of operating. The main objects of investigation are products and services, but it can also be transferred to facilities and disposal routes and thus bear on the subject of this document. The LCA consists of the phases [cww/tm/132]:

- goal definition and scoping
- inventory analysis, including material and energy flow as input and output over the entire life cycle
- impact assessment, entailing a determination of potential environmental impacts
- interpretation of the results, which are used to select the ecologically most favourable variants.

The LCA is still under development, with inventory analysis as the most and interpretation as the least advanced part. In spite of the partly subjective evaluation method, LCA is a very good decision tool, because complex relationships can be systematically reduced to comparably few data sets. LCA is performed under recognised rules, such as [cww/tm/132]:

- ISO 14040: Environmental management – life-cycle assessment – principles and guidelines
- ISO 14041: Environmental management – life-cycle assessment – life-cycle inventory analysis
- ISO 14042: Environmental management – life-cycle assessment – life-cycle impact assessment
- ISO 14043: Environmental management – life-cycle assessment – life-cycle improvement assessment.

LCA considers only environmental aspects, just one element for decision-making, whereas economic and social aspects are additive rather than integral, built up on the results of the LCA. With the help of LCA, the environmental relevance of the objects of investigation, e.g. production lines and treatment services, can be determined in a clear and reproducible way, which is the basis for ecological optimisation, i.e the selection of ecologically "better" alternatives. LCA can be used to determine the following items:

- the ecologically optimum disposal routes
- the ecological breakeven point for recycling and other environmental protection practices
- weak points in the life-cycle of the object of investigation
- priorities of necessary actions. [cww/tm/132].

Because of the methodology involved in LCA, there are limitations such as [cww/tm/132]:

- environmental burdens due to an object of investigation cannot be determined in absolute terms, but only relatively, because the true impact on the environment is not accessible
- no generally valid inferences can be made about the environmental compatibility of materials, auxiliaries and media, because neither their intended use nor their anticipated benefit is known
- general statements about disposal routes can only be derived when the reference values for the arisen waste are known (which is normally not the case).

LCA cannot dictate decisions, it can merely aid in making them. Thus it is insufficient to base an environmentally orientated decision on the result of the LCA alone, if the way in which the result is achieved has not been considered.

2.2.4 Safety and Emergency Tools

Since all chemical industry sites have the potential to cause significant environmental harm and to threaten water supplies and public health, measures have to be taken to avoid the risks as far as possible or to react to accidents in such a way as to minimise their effects. Though it is the task of engineers to construct equipment and run a plant so that no accidents can occur, it is common experience that this is not successful in all cases.

Spillages of chemicals and oil are obvious threats on chemical sites. However, materials non-hazardous to humans may also cause serious environmental problems, as can the run-off generated in the event of a fire. The environmental damage may be long term and, in the case of groundwater, may persist for decades or even longer. Rivers, sewers, culverts, drains, water distribution systems and other services all present routes for the conveyance of pollutants off-site and the effects of a discharge may be evident some distance away. In many cases, major pollution incidents can be prevented if appropriate pollution prevention measures are in place or immediately available. Contingency planning is the key to success and both preventive measures and incident response strategies as management tools need to be carefully addressed [cww/tm/147].

Accidental gas releases to air normally need to be prevented by appropriate safety equipment and proper operation of the installations, because in most cases gaseous releases cannot be caught. Exceptions are gases mixable with water such as acids or ammonia, which can be dowsed by a water curtain and thus become an item for waste water treatment.

Pollutants may escape from the site into the water environment by a number of pathways, such as [cww/tm/147]:

- the surface water drainage system of the site, either directly or via off-site surface water sewers
- direct run-off into nearby watercourses or onto ground, with potential risk to groundwater
- via the foul drainage system, with pollutants either passing unaltered through a sewage treatment works or affecting the performance of the works, resulting in further environmental damage
- through atmospheric deposition, such as vapour plumes.

2.2.4.1 Managing Fire-fighting Water and Major Spillages

The main focus of fire-fighting water and spillage management is on containment strategies and equipment to handle these spillages. Other management tools, however, such as operational and strategic tools, should also be considered and supported by contingency or pollution incident response plans (see Section 2.2.4.2) to reduce the impact of any unplanned event that does occur [cww/tm/147].

The first step, however, is to consider the fire-fighting strategies and possible methods to reduce the amount of fire-fighting water run-off generated, e.g. by the use of sprays rather than jets, controlled burn and the possible recycling of fire-fighting water, where safe and practicable [cww/tm/147].

Containment Systems
There will be one or maybe more levels of containment on chemical sites. In deciding the appropriate level of containment, a risk assessment (see Section 2.2.3.1) is helpful. The operator should consider the hazardous materials on site, the risks posed by accidents, fire, flooding and vandalism, likely failure mode of the primary containment (i.e. the tank or vessel in which the

material is stored), the sensitivity of the receiving environment and the importance of preventing any resultant discharge to it.

In many cases, primary and local containment (bunding) will prevent an incident from causing pollution. However, where local containment is not provided, or risk assessment indicates that additional security is required, e.g. to contain fire-fighting water run-off, which may amount to thousands of cubic metres, then remote containment systems may be employed. These may be used in isolation, or in combination with local containment, for anything from a small area, covering part of a site, to a number of large individual installations. They may be required to protect both surface and foul water drainage systems [cww/tm/147].

The capacity needed for remote containment systems has to take into account:

- the potential harm of the contaminated fire-fighting water (evaluation methods based on R-phrases can be used as well as systems like the German VCI-concept on fire-fighting water retention capacity, where hazard classes are defined)
- the primary capacity (i.e. the capacity of the vessel in which the material is stored or handled)
- the potential amount of rainfall during the emergency event
- fire-fighting and cooling water
- foam (as fire-fighting medium)
- dynamic effects, such as initial surge of liquid or wind-blown waves.

Remote containment systems can consist of:

- containment lagoons (or earth-banked containment basins), if the site topography and the ground and soil conditions are suitable, the lagoons being substantially impermeable
- tanks, built for the purpose, their actual size, design standards and protective finishes influenced by the risk rating of the site, the retention time, the quantity and the nature of the materials stored
- shut-off valves and penstocks, operated manually or triggered by means of automatic sensors, to isolate part or the whole of a site
- oil separators.

Although permanent containment facilities should be provided at many sites, there may be circumstances where a spillage cannot be dealt with by such facilities, e.g. if it occurs outside a bunded area. In other cases, particularly at smaller sites, fire-fighting water containment facilities may be impracticable because of cost and space considerations. In such cases, temporary containment systems or pollution control materials should be considered [cww/tm/147].

Examples of emergency containment measures include [cww/tm/147]:

- sacrificial areas, designed to allow infiltration and to prevent run-off, equipped with an impermeable lining system to prevent dispersal into other strata or groundwater
- bunding of vehicle parking and other hard standings
- pits and trenches, equipped with a liner, particularly in areas of high groundwater vulnerability
- portable tanks, overdrums and tankers.

Emergency Materials and Equipment
A variety of products are available to deal with spillages or to contain spills in emergency containment areas. Any materials or equipment used must be well maintained and strategically placed at accessible locations which are clearly marked with notices explaining their use. The pollution incident response plan (see Section 2.2.4.2) should identify pollution prevention equipment and materials and their location. Such materials and equipment are [cww/tm/147]:

- sand and earth to soak up spillages of oil and chemicals and to use in sand bags
- proprietary absorbents
- sealing devices and substances for damaged containers
- drain seals
- booms.

Measures should be in place to dispose of, as soon as possible, any spillage, contaminated material or fire-fighting water. Where re-use is possible, the spilled material should be returned to storage on site. If off-site disposal is required, it can be done by [cww/tm/147]:

- an ordinary waste carrier
- discharge to a foul sewer with the approval of the sewerage operator
- treatment of hydrocarbon-contaminated water with site oil separators.

2.2.4.2 Pollution Incident Response Planning

A pollution incident response plan, as mentioned several times in Section 2.2.4.1, is mainly a strategy to spread all information needed in a most efficient way to all those who may be concerned. The general way to implement such a plan is [cww/tm/148]:

- providing details of the site and of those for whom the plan is relevant
- listing key contact numbers, such as emergency services, relevant environmental regulators, local water supply and sewerage operators, HSE executive etc., key-holder and contact staff, specialist advisers
- having ready a site drainage plan, containing a clear diagram of the site, showing layout and access details, off-site discharge points for surface water and trade effluent, etc.
- providing a site oil, chemical and product inventory of all substances stored on site, giving the maximum quantity likely to be stored, with data sheets attached
- detailing emergency procedures, defining the scope of activities covered, staff responsibilities and the procedures for dealing with events such as spillages and leaking containers
- giving rules on staff training and exercises to be carried out periodically.

All staff and contractors working on the site should be made aware of the plan and should know their role if an incident occurs.

An exemplary form of such a pollution incident response plan is given in Annex 7.5.

3 APPLIED TREATMENT TECHNOLOGY

This chapter gives more detail on the considerations introduced in Sections 1.3 and 2.2.2.3 and describes the treatment techniques for waste water and waste gas according to their environmental performance and impact as well as to their economic viability. However, variants of well-known technologies with only slight variations to the general process are not mentioned separately.

The physical and chemical background of the treatment techniques can easily be found in available textbooks and is therefore not repeated in this BREF. The operations and processes dealt with in this chapter are end-of-pipe techniques that are commonly used in the chemical industry, so common treatment techniques for releases from power stations and waste processing are included, since large chemical sites are often equipped with their own energy production (power, steam) and waste incineration. For more details, however, the relevant BREFs on large combustion plants and waste incineration need to be consulted. Process-integrated measures are described when they are generally in use and not related to special production processes.

The systematic overview in this chapter follows the pollutant path and presents the techniques in relation to their application on a chemical site. Further details can be found in Sections 3.3.4 and 3.5.

3.1 Information Presented in this Chapter

The description of treatment techniques follows a fixed order to provide the necessary information to assist a permit writer in implementing BAT for an installation in the chemical sector. The information is also intended to help an operator to fulfil the BAT requirements and write a good permit application. This structure is chosen to make sure that for all treatment operations and processes the same kind of information is collected and presented and a comparison between different treatment options is feasible.

The description of treatment operations and processes is subdivided into the paragraphs:

- description
- application
- advantages/disadvantages
- achievable emission levels / performance rates
- cross-media effects
- monitoring
- economics.

The first paragraph, headed **description,** outlines the fundamentals of a treatment technique without going into detail. Theoretical physical and chemical background is left out deliberately. This information can be found in a variety of good textbooks. The use of chemical and mathematical formulae and equations is avoided wherever possible without loss of information. This paragraph also gives an overview of what equipment is involved in this technique and how the technique is operated. Whenever graphical information is available, either as a sketch or a flow diagram, it is used to replace verbal explanations, provided there is no loss of necessary information.

The second paragraph, headed **application**, describes how and where the technique in question could be commonly applied, also taking into account its use in related sectors, when it can be expected to be useful in the chemical sector as well. It also includes the related pollutants to be treated. Part of this paragraph is a listing of possible application limits and restrictions.

The third paragraph, headed **advantages/disadvantages**, tries to outline some benefits and problems associated with each technique, bearing in mind that some fundamental laws of mass and energy conservation prevent us controlling or abating anything without leaving any traces in the environment.

The fourth paragraph headed **achievable emission levels / performance rates**, shows the performance of the technique. It lists the achievable emission levels and/or removal performance. The values listed are those that can be expected under regularly good working conditions. They do not, however, imply that these values are achievable under all circumstances and with all applications. The explanation of the term "achievable emission levels" is given in Section 4.1. Performance rates are quoted relative to the feed load, with the result that low feeds give low performance (percentage) rates, whereas high feeds give high performance rates, though the residual concentration may still be high.

The fifth paragraph, headed **cross-media effects**, shows the impact on the environment arising from the action of this technique, e.g. generation of sludge, waste heat, gaseous releases, noise, odour etc. as well as the input of consumables, such as water, energy and auxiliary substances.

The sixth paragraph, headed **monitoring**, describes the examination of the input, the output and the regular working of the technical devices in compliance with best monitoring practice.

The seventh paragraph deals with **economics**. It tries to give information on costs of the said technique, as far as this information has been made available. To clarify what is meant by costs in this horizontal document, Section 3.2 gives some explanations without claiming to present special economic issues, for which reference to the BREF on economics and cross-media effects is recommended.

3.2 Information on Costs in this Horizontal Document

Costs of erecting a new emission control technology, retrofitting existing technologies or implementing process-integrated measures, are largely dependent on site-specific and production-specific issues. Thus, the absolute costs of actually building or installing a treatment technology have no real information value for a horizontal approach, because they are not comparable with anything. The costs to implement the appropriate and necessary infrastructure are not included either. Another important factor in the selection of a suitable treatment technique is the payback period for a process-integrated measure. Since the costs involved will always be plant- and/or process-specific, this horizontal document cannot consider that adequately. It does, however, point out the supplier equipment costs relative to a production capacity, waste water / waste gas stream or pollutant amount (i.e. costs per tonne of product, m^3 of waste water or 1000 Nm^3 of waste gas or kg of a pollutant). Items to consider when evaluating cost data that are not generally included in this document because of their site- and process-specific characteristics are explained in the following paragraphs [cww/tm/48].

3.2.1 Total Installed Costs vs Supplier Equipment Costs

When trying to determine the cost of emission control techniques, it is often thought easiest to select a technique that appears to suit the requirements at hand, and solicit a cost quotation from a supplier. While fast and convenient, this approach can lead to vastly inaccurate estimates of the actual cost of the emission control technique. This occurs on an absolute basis, like cost per tonne of emission reduced, and on a relative basis when comparing technology options. Different techniques can often have very different distributions of individual cost elements between the various types of costs that make up their total installed cost. Typically 20-30 % of the total erected cost is for major equipment purchase, but can also be as low as 10 %.

Operating costs must also be critically considered when making the absolute and/or relative cost comparisons of various control techniques. These can be overlooked when taking a hardware view of control technology, as is often done when considering the implementation of techniques. It is important to take account of the fact that operating costs can vary greatly between technologies, depending on utilities usage, auxiliary chemicals consumption, labour requirements, waste generation potential and the cost of its disposal, etc.

Supplier costs will typically include only the cost of the specific equipment supplied. Often this is a relatively small fraction of the overall cost of a project. Additionally, the engineering costs associated with project design and supervision are often ignored, but can easily equal the cost of the supplier equipment. Expenditure often not thought of when estimating the cost of a project includes items such as the need to:

- relocate existing facilities
- stop production during retrofitting
- enlarge and/or move existing sewer lines
- perform soil investigations
- develop new as-built drawings, process and instrumentation diagrams
- modify existing piping and facilities such as blowers, pumps, etc.

An example is given in Table 3.1 [cww/tm/48] for a tail gas clean-up unit at a refinery with total erected costs, prices from 1997 given in euros. The direct equipment costs – or supplier costs – are EUR 7.9 million, compared with the total costs of EUR 29.4 million, i.e. just 27 % of the overall erected costs.

Description	EUR million
Equipment costs (vendor costs)	
Materials	7.3
Catalysts and chemicals	0.6
Subtotal	**7.9**
Indirect costs	
Detailed engineering	8.0
Field supervision	1.6
Owner	2.4
Subtotal	12.0
Direct costs – non equipment	
Subcontracts	8.6
Temporary construction and consumables	0.4
Subtotal	9.0
Total capital	28.9
Expense	
Licensing fee	0.5
Subtotal	0.5
Final total	**29.4**

Table 3.1: Example of Costs of an Actual Project

3.2.2 Greenfield Costs vs Retrofitting Costs

Greenfield installations and existing operations and units require essentially the same technology to improve environmental performance (e.g. control of specified pollutants and meeting specified emission limit values). The differences between these two types of installations are essentially driven by the fact that on a greenfield site it is possible to ensure that all the essential requirements are explicitly considered when the facility is designed. In the case of a retrofit (or revamp), the original design choices may result in otherwise available or even preferred control techniques being of limited applicability or possibly even unfeasible.

Specific assessment of the suitability of a technique for retrofitting is required, but many of the techniques mentioned in the following sections of this chapter have already been successfully

retrofitted to chemical installations and deliver an environmental performance equivalent to that which could be expected from new plants. Revamp projects on existing installations or sites encounter a variety of technical and managerial issues, the most common of which are outlined below. These issues are not excuses to avoid the adoption of environmental improvement techniques, but are some of the factors pertinent to a revamp:

- a more complex and time-consuming project definition phase
- test runs or pilot studies to assess the impact of a change on the whole process
- consideration at the design stage of the knock-on effects on all existing facilities
- surveys of the existing facilities at the detailed engineering stage to define the exact location of all interfaces. Space availability may introduce constraints (e.g. equipment placed in an elevated structure, pipe routing, need to relocate some existing facilities, construction of temporary facilities)
- special precautions so that works can be carried out safely, and without damage, even while the plant continues to operate
- taking advantage of a planned shutdown (turnaround) to carry out any construction work that cannot be done during normal operations. These multi-year events may dictate revamp timing
- a longer, or earlier, shutdown than planned (with commercial and financial implications)
- the decommissioning and dismantling of old, redundant equipment
- staff training in the operation of new equipment
- revised plant documentation (e.g. operating instructions, permit revision, manuals for maintenance, inspection and safety).

In addition to the prime purpose of improved environmental performance, the retrofitting of chemical installations can confer other significant benefits. Some techniques (e.g. pretreatment techniques with recovery potential, process-integrated measures) bring major economic returns in the form, for example, of increased efficiency and higher yields or of cost reductions associated with savings of energy and water (or reduced charges for discharges, where such a regime applies), that can offset the investment and operating costs of the retrofit. Retrofitting can also bring competitive advantage by showing product buyers and stakeholders (e.g. shareholders, local communities, regulators and environmental groups) that the company has adopted cutting edge technology.

Considerations of whether a technology constitutes an appropriate technique for a retrofit application deal primarily with the ability of the existing installation to meet the process, physical and structural requirements of the control facility. This distinction in available technology being applicable to new and existing facilities is a crucial one to include in any determinations of techniques. Where information is available, this chapter gives information about the potential retrofittability of a technique.

3.2.3 Capital Costs vs Operating Costs

Different control techniques (equipment-based controls and procedural techniques) can be very different in terms of the distribution of costs between capital and operating expenses. Some expensive equipment has low running costs, while other very low-cost equipment involves severe increases in operating costs such as labour, utilities or consumable chemicals. It is generally easier to quantify the cost of hardware than the full implications of the likely expenses incurred by a technique. Also equipment items will become more costly over time due to inflation, etc.

Labour costs are an important element in operating costs and can have different consequences on a decision in favour of or against a technique, depending on the different wage rates in the Member States. So, if labour costs are referred to in this document, labour hours are given – when available – as well (or instead).

3.2.4 Initial Emission Control Costs vs Incremental Control Costs

An important consideration of the cost of a technique relates to the changing cost effectiveness of a given technology depending on the point of control from which one starts the cost effectiveness calculation. Usually the costs and effectiveness – given as a percentage emission reduction, or tonnes of emissions reduced – of installing or implementing a technique are presented against an uncontrolled baseline operation. In such a case one calculates the cost effectiveness easily by dividing the costs by the emission reduction achieved.

There are many situations where certain levels of control already exist within specific industry sites. In these cases the costs to achieve a given emission reduction target are significantly increased over the initial cost effectiveness values for an uncontrolled baseline operation. This needs to be accounted for in determining the cost effectiveness of a technology or technique.

So, for incremental control costs, the cost effectiveness K_{eff} [kg reduction/currency unit] can be calculated as:

$$K_{eff} = (B - A)/C$$

B: emission reduction for technique considered [kg]
A: emission reduction for technique already installed [kg]
C: costs for technique considered

3.3 Waste Water Treatment Techniques

3.3.1 Process-Integrated Measures

Some important – and normally easily retrofittable – production-integrated measures relevant to waste water are described below. Some illustrative examples are mentioned in Section 3.3.1.3. Their introduction, e.g. as water saving measures, however, has to be carefully assessed. Though their influence is normally environmentally beneficial, they might under specific circumstances lead to negative impacts in other environmental compartments that might over-shadow the benefits of water conservation or pollutant decrease.

3.3.1.1 Counter-current Extraction as an Example of Water-saving Processes

Conventional product washing processes are multiple extractions working batchwise by treating the product phase with water in order to remove salts or other soluble minor components. The amount of water used is generally several times the amount of product to be washed. At each individual extraction step there are unavoidable losses of product caused by its solubility, emulsification and the formation of solid layers at the phase boundary, etc.

By optimising the extraction process, and/or introducing advanced extraction processes, such as counter-current extraction, a considerable reduction of waste water (and waste) can be achieved. A simultaneous increase of pollutant concentration might allow an easier and/or more effective treatment, or, under special circumstances, recycling of material. The degree and method of optimisation depends on the production capacity and on having frequent production runs. Counter-current extraction is economic specifically for large-scale plants. There it can be tailored to a particular production process. For plants dealing with small outputs, pilot-scale productions or seldom-used campaign productions, other processes are more suitable.

3.3.1.2 Multiple Use and Recirculation Operations

A distinction has to be made here between:

- waste water originating directly from production (e.g. reaction water, distillates, washing water, filtrates)
- waste water originating from equipment cleaning (e.g. during maintenance, rinsing of blockages or product caking, cleaning of multi-purpose equipment because of campaign or product change).

Specific treatment steps to remove interfering constituents can improve the efficiency of a recirculation operation. Thus, for example, neutralisation, stripping or filtration of process water streams can enable water to be re-used, e.g. as raw water or utility water supply. The re-use of process water (make-up water, mother liquors) is possible, when constituents such as by-products or salts will not adversely affect the quality of downstream productions. In fact, in multiple stage product washing, washing water streams can frequently be used as make-up water, or as input water into a preceding washing step.

The re-use of water from washing, rinsing and equipment cleaning, has, in addition to the reduction of waste water load, the advantage of product recovery and increase of product yield, provided the water is recirculated into the production process itself. This requires facilities for collection, buffering or storage of waste water, which might be a limiting factor.

3.3.1.3 Indirect Cooling with Vapour Phases

The injection of water into a gaseous phase is used to cool or condense vapours. The direct contact of water with vapour phases, however, generates large amounts of waste water polluted by the vaporous contaminants. Introduction of surface heat exchangers instead of injection condensers / coolers avoids the generation of polluted cooling water streams, the pollutants remaining in the condensate. So, indirect cooling / condensing leads to water saving. To give some idea of the potential savings, it takes approximately 27 m^3 of water to cool one tonne of steam down to 35 ºC (the temperature generally accepted as an upper limit for discharge). With indirect cooling this amount is run in a cooling cycle [cww/tm/82] replacing only water lost by evaporation.

Water saving effects are decreased when entrained particles, sublimating material, crystals or caked matter coat the heat exchange surfaces, or plug the spaces between the exchange surfaces, so they need regular maintenance.

There are, however, processes where a conversion to indirect cooling is not appropriate [cww/tm/82]:

- It can be necessary for crystallisation to stir a liquid organic phase vigorously together with warm or hot water, and then to bring down the temperature rapidly below solidification temperature by adding ice or cold water ('temperature shock'). The goal of this procedure is to get a filterable suspension without lumps or clots.

- Another example is the diazotization of amines. In this process, temperature is kept at a constantly low level by the addition of ice, to prevent thermal decomposition of the diazonium compound as well as its deposition on equipment, which otherwise would mean a considerable risk of explosion.

- One further example is the quenching of hot gas streams, where cold water is injected into the gas stream to decrease its temperature so effectively and rapidly that reactions of components in the gas stream are prevented (e.g. recombination reactions in flue gas from combustion processes resulting in generation of PCDDs and PCDFs) and simultaneously to abate one of its pollutants (e.g. HCl).

3.3.1.4 Waste Water-free Processes for Vacuum Generation

Owing to their almost undisturbed operation, their low maintenance requirement and their low costs, water jet and vapour jet vacuum pumps are used universally.

Waste water-free vacuum generation can be achieved by using mechanical pumping systems in a closed circuit procedure, discharging only a small amount of water as blowdown, or by means of dry-running pumps. This discharge amounts to less than 5 % of that of the once-through system [cww/tm/82]. In some cases, waste water-free vacuum generation can be achieved by use of the product as barrier liquid in a mechanical vacuum pump, or by use of a gas stream out of the production process.

Whether waste water-free vacuum generation is possible has to be determined in each particular case. In selecting the proper process, account needs to be taken of the potential problems, particularly with respect to corrosion, tendency to caking, explosion risk, plant safety and operational reliability. Appropriate limitations have to be considered, especially in the case of mechanical vacuum pumps with a closed cycle, such as liquid ring pumps, rotary sliding-vane pumps or diaphragm vacuum pumps. Here, for example, vapours can decrease the lubricity of the oil.

Provided that gas condensation in the pump is prevented by, e.g., high gas outlet temperature, dry-running pumps are an attractive option when solvents are to be recovered, or when a high vacuum is necessary. These pumps cannot be employed if the gas stream contains large amounts of condensable, dust-forming or coating material.

3.3.1.5 Waste Water-free Processes for Exhaust Air Cleaning

About one third of the exhaust air cleaning systems in the chemical industry work with a water-based or alkaline (caustic) scrubbing process. This particularly captures inorganic compounds such as hydrogen chloride, sulphur dioxide and water-soluble organic substances.

Waste water-free technologies for exhaust air cleaning are used, in particular, when hazardous substances or non-degradable organic substances would otherwise enter a biological waste water treatment plant, where they might cause disturbances or be discharged untreated into the receiving water.

Examples of waste water-free techniques for exhaust air cleaning are:

- collection and subsequent thermal or catalytic oxidation of calorific waste gas streams, preferably with energy recovery
- application of appropriate dry de-dusting equipment (e.g. demisters, cyclones, electrostatic precipitators, fabric filters) to separate particulates and aerosols
- use of dry / semi-dry gas treatments (e.g. activated carbon adsorption, lime/sodium bicarbonate injection) for waste gas streams loaded with organic or inorganic gaseous contaminants
- use of regenerative organic solvents (or oils) instead of water as scrubbing liquid for specific gaseous contaminants.

3.3.1.6 Substance Recovery or Retention from Mother Liquors or by Optimised Processes

Substance recovery of waste water constituents with reasonable expenditure is normally only feasible for concentrated waste water streams. So it is usually limited to mother liquors. Depending on the method of synthesis, mother liquors are generally aqueous solutions kept after product separation, or washing water. Recovery might comprise, e.g.:

- removal of utilisable individual compounds, such as starting materials, products, solvents or catalysts
- material conversion with subsequent substance recovery, e.g. thermal or catalytic oxidation with recovery of chlorine (from organic chlorides) as hydrochloric acid.

Substance recovery is viable for higher waste water concentrations (e.g. 10 g/l or more). If easily removable components are involved, e.g. volatile, solid, precipitable or extractable compounds, recovery processes might be viable even at lower concentrations.

Substance retention by way of optimised processes encompasses the modification of process steps as well as additional measures, such as improvement of mother liquor work-up.

Substance retention – aside from pollutant prevention such as modification of formulation or improvement of production yield – can also be achieved by pollutant removal, e.g. adsorption or extraction, or by conversion, e.g. oxidation or incineration.

3.3.1.7 Use of Low-contaminated Raw Materials and Auxiliaries

Contaminated raw materials and/or auxiliaries can import pollutants into the production chain and thus into the waste water system. Examples are:

- metals from crude vegetable fats
- chloro-organic compounds (AOX/EOX) and other impurities from technical-grade hydrochloric acid
- mercury as contamination in sodium hydroxide from chlor-alkali electrolysis using the amalgam process
- contaminants of, in particular, intermediates and externally acquired precursors.

The operator's ability to influence this situation is limited by:

- insufficient information from suppliers
- increase of contaminant importation because of recycled materials
- transferring emission problems to other locations by work-up of the raw material.

Purification of raw material can be implemented by manufacturers who have technical facilities to reduce and dispose correctly of the removed contaminants, such as resin exchange for hydrochloric acid or filtration/adsorption for crude sodium hydroxide.

3.3.2 Flow Balancing

In general, waste water treatment plants operate most effectively at reasonably constant conditions of hydraulic load (or flow rate) and contaminant load. In practice, however, both flow rate and contaminant load can fluctuate markedly due to factors such as:

- process conditions
- use of water for washing
- ballast water treatment
- maintenance times
- rainfall.

To buffer the production against short-term (e.g. daily) and long-term (e.g. weekly) variations, equalisation facilities should be considered, either decentralised at the various production sites or centrally in or near the WWTP. Sometimes they can also be installed downstream of a WWTP. The appropriate capacity of the buffer containment is a function of the anticipated

fluctuations [cww/tm/132]. The buffer containment may be installed either in-line or as a side-stream to which the flow can be diverted at peak periods or in case of production disturbances, and run down at a controlled rate when the flow has moderated. For process waters which can emit to the environment, tanks are used for this purpose, whereas for surface water drainage, open lagoons or retention ponds are used (see Section 3.3.4.4.1) [cww/tm/48].

The result of buffering and equalising is, e.g.:

- equalisation of loads, such as:
  - organic load
  - salt concentrations
  - nitrogen load, e.g. as a prerequisite, together with TOC load, for optimum denitrification
- adjustment of the required C : N : P ratio
- neutralisation of acidic and alkaline waste water streams
- equalisation of waste water flow rate
- fulfilment of legal requirements by cutting peaks of the waste water discharge.

Flow balancing or buffering might also be used as a control facility for unusual influx events to the WWTP, and so the capacity of the buffering containment might be determined not only by the fluctuations, as mentioned above, but also by the extent of the hazard potential. Details are illustrated in Section 3.3.3.

3.3.3 Storage or Retention Capacity for Failure Events

Operational failures, equipment leakage, unintentional contamination of cooling water or other disturbances in production or storage units can lead either to an increased discharge of pollutants into the receiving water via the WWTP, or to its malfunction. The risk of such events can create the need for centralised or decentralised receiving (or buffer) facilities. For the operation of a barrier or buffer system, timely detection of the failure event is crucial. This detection can be ensured by both analytical and organisational means [cww/tm/132].

There are several buffer devices used for this purpose. Their capacity has to be sufficient to store all waste water, probably including rainwater, incurred during a production failure. They can be combined with flow balancing tanks.

One device (see Figure 3.1), the self-contained buffer, contains two buffer tanks that receive the waste water stream alternately. While one tank is filled the other is checked and then released to the waste water discharge or downstream WWTP or disposed of as waste, depending on the results of the check. The receiving capacity of each containment needs to be sufficient to take the entire amount of waste water arising during the period of analysis and depletion of one tank. For complex and large chemical sites with large amounts of waste water, this is often an option for selected waste water streams, because otherwise the requirement for tank volume is immense. The larger the tank the longer the depletion time and vice versa, which might result in a circle with no exit.

Another device is the connected buffer, either discontinuously (see Figure 3.2) or continuously flooded (see Figure 3.3). The discontinuously operated buffer is disconnected when not in use, i.e. when there is no failure reported by the control and alarm system. During normal operation the waste water circumvents the buffer system, and only when the control system detects an unusual event is the buffer tank filled. The required tank capacity is the amount of waste water arising during the time of malfunction. This device is used with single production installations, a collection of selected waste water streams and with the total amount of waste water. The required volume is normally much less than with the self-contained buffer mentioned above.
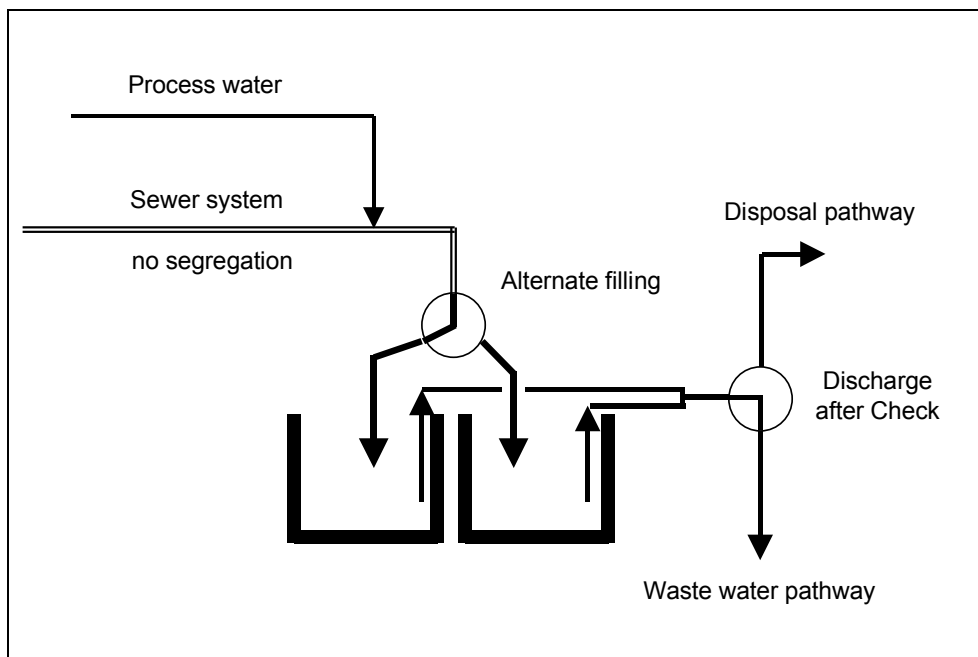
Figure 3.1: Self-Contained Buffer with Alternative Filling
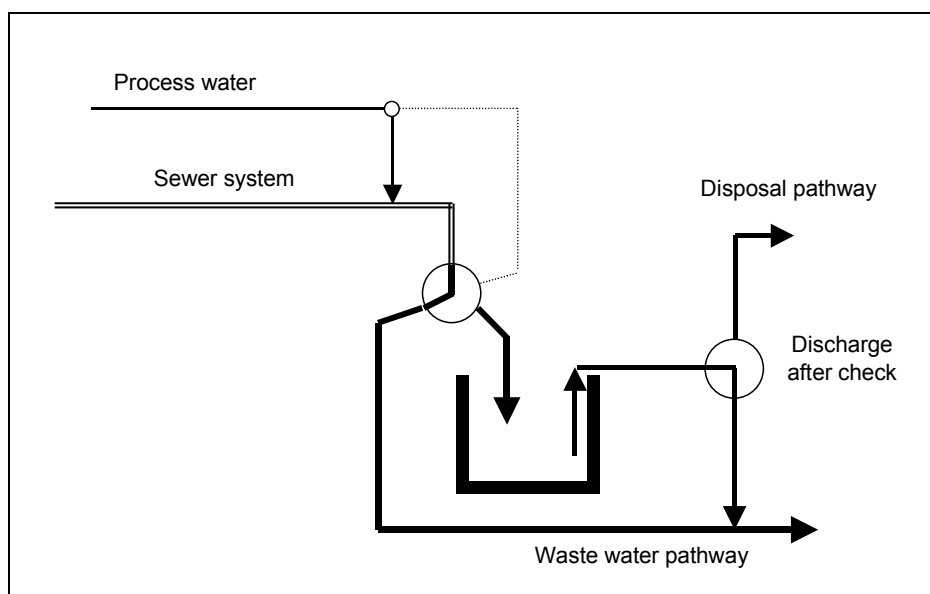
Figure 3.2: Connected Buffer, Discontinuously Flooded

The continuously flooded connected buffer can also be used as an equalisation or flow balancing tank. A control and alarm system has to ensure that the outlet to the WWTP is immediately closed in the case of an unusual event. The capacity of the tank must be sufficient to receive all the incoming waste water until the failure is remedied, so this system might be recommendable only for tributary streams. Before the operation can continue with the input of routine waste water, the tank has to be depleted.
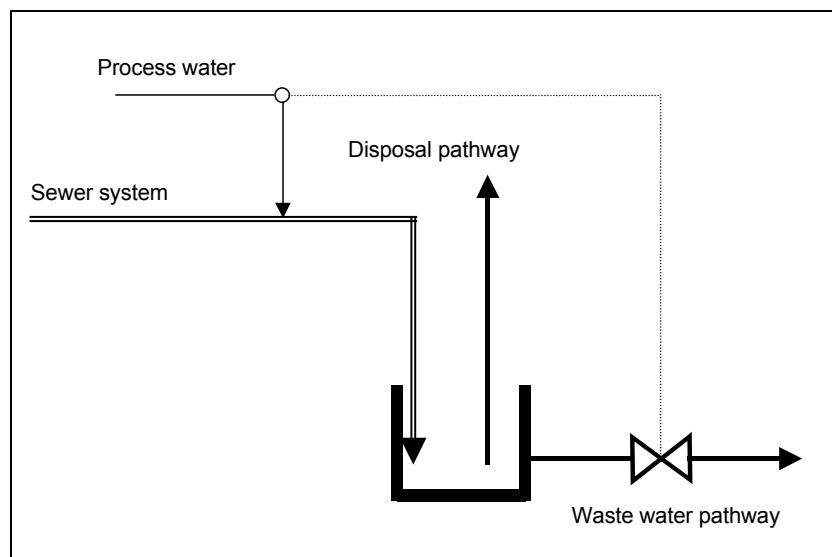
Figure 3.3: Connected Buffer, Continuously Flooded

A further system (see Figure 3.4) is suited to receive and buffer leakage losses, when leakages are collected in a separate sewer. Such a sewer is used as a drainage system for potentially polluted outdoor areas with, e.g. production installations or tank fields. The capacity of the tank matches the largest possible leakage loss and the amount of rainwater to be expected. This buffer system is applicable to installations with separated sewers for process water and drainage of risk areas. Events that might influence the process water stream cannot be controlled. Its advantage is the ability to collect leakage losses in a concentrated state to enable recycling.
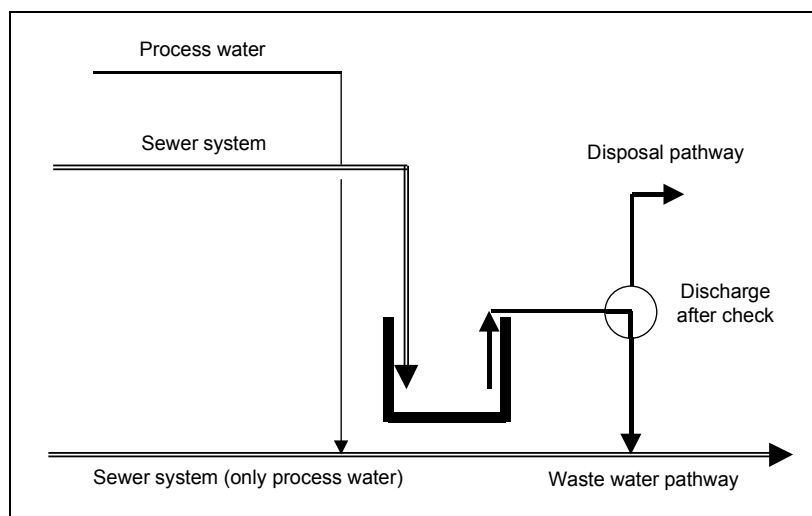
Figure 3.4: Leakage Buffer System

3.3.4 End-of-Pipe Techniques

To introduce a logical order in the description of treatment techniques, the relationship between pollutant and respective typical treatment technology is taken as reference, as pointed out in Section 1.3.2.1 and illustrated in Figure 3.5.

The first treatment step for waste water and rainwater – and often also the final step – is the separation of suspended solids and immiscible liquids (with regard to water) from the main water stream. Separation or clarification techniques are:

- Gravity Separation [Grit Separation (see Section 3.3.4.1.1), Sedimentation (see Section 3.3.4.1.2), Oil-Water Separation (see Section 3.3.4.1.6)]
- Air Flotation (see Section 3.3.4.1.3)
- Filtration [Filtration (see Section 3.3.4.1.4), Membrane Filtration (see Section 3.3.4.1.5)].

They are mainly used in combination with other operations, either as a first or a final clarification step. As a first step they, for example, protect other treatment facilities against damage, clogging or fouling by solids. As a final step they remove solids formed during a preceding treatment operation or process, or remove oil before further biological treatment. They often follow treatment techniques applied to soluble pollutants, when these are transferred into solids. Examples are given later in this chapter.
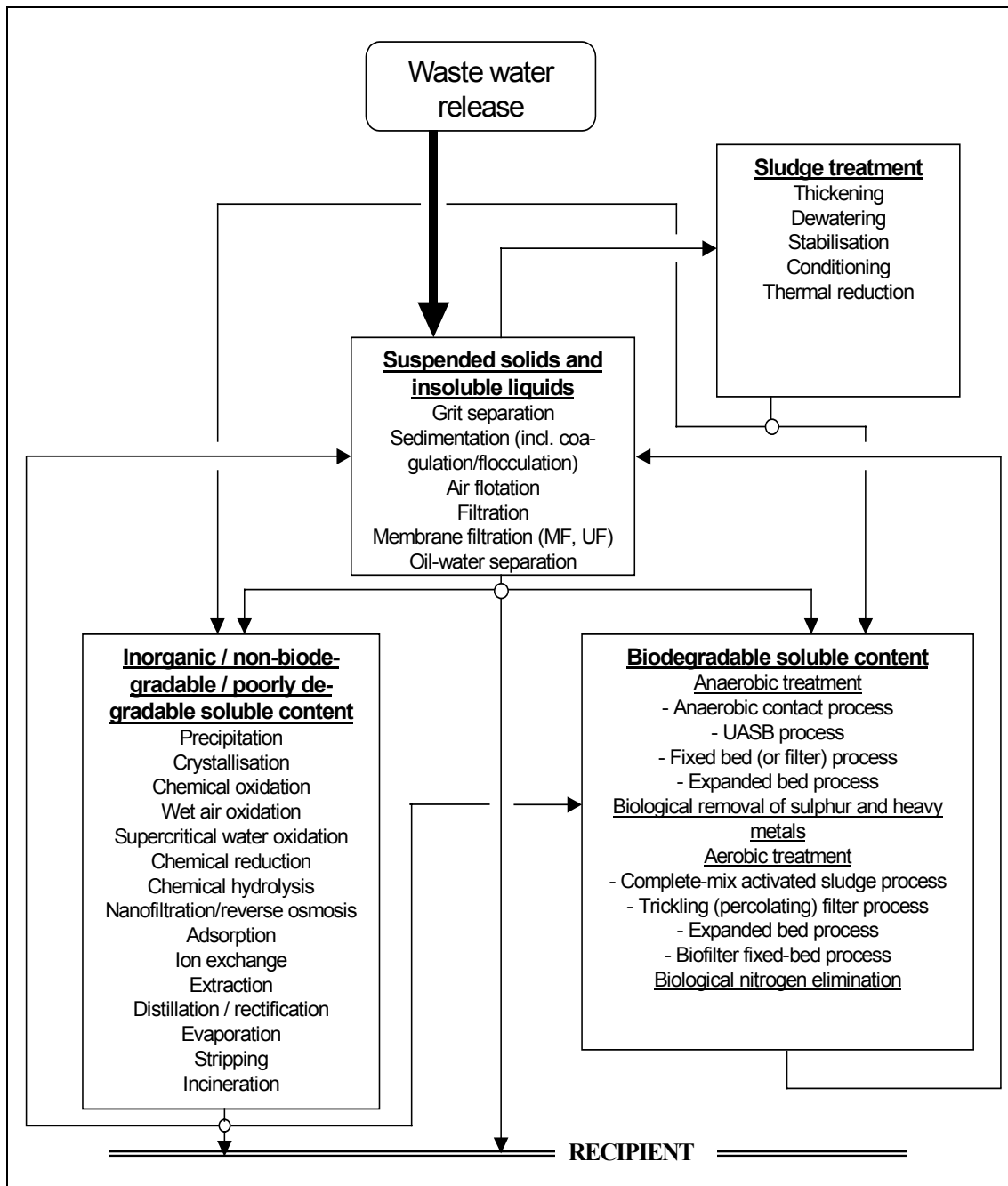
Figure 3.5: Range of Waste Water Treatment Techniques in Relation to Type of Contaminants

Solid-free waste water can either be segregated into a biodegradable and a non-biodegradable part, or the contaminants responsible for the non-biodegradability may be separated before further treatment. The treatment techniques for the non-biodegradable waste water part are based on physical and/or chemical operations, such as:

- Precipitation / sedimentation / filtration (see Section 3.3.4.2.1)
- Crystallisation (see Section 3.3.4.2.2)
- chemical reactions [Chemical oxidation (see Section 3.3.4.2.3), Wet air oxidation (see Section 3.3.4.2.4, Supercritical water oxidation (see Section 3.3.4.2.5), Chemical reduction (see Section 3.3.4.2.6) and Chemical hydrolysis (see Section 3.3.4.2.7)]
- Membrane 'filtration' (Nanofiltration and Reverse osmosis) (see Section 3.3.4.2.8)
- Adsorption (see Section 3.3.4.2.9)
- Ion exchange (see Section 3.3.4.2.10)
- Extraction (see Section 3.3.4.2.11)
- Distillation / rectification (see Section 0)
- Evaporation (see Section 3.3.4.2.13)
- Stripping (see Section 3.3.4.2.14)
- Incineration (see Section 3.3.4.2.15).

After adequate treatment, the waste water stream can either be discharged into a receiving water body, into a subsequent central biological WWTP or a municipal WWTP.

Biodegradable waste water – or the remaining waste water part after elimination of the cause of the non-biodegradability – normally undergoes treatment techniques, either centralised or decentralised, that are based on biological processes, such as:

- anaerobic digestion [Anaerobic contact process (ACP), UASB process, Fixed-bed process, Expanded-bed process (see Section 3.3.4.3.1) and Biological removal of sulphur compounds and heavy metals (see Section 3.3.4.3.2)]
- aerobic digestion, [Complete-mix activated sludge process, Membrane bioreactor process, Trickling filter process, Expanded-bed Process, Biofilter fixed-bed process (see Section 3.3.4.3.3)]
- Nitrification / denitrification (see Section 3.3.4.3.4)
- Central biological waste water treatment (see Section 3.3.4.3.5).

The degraded waste water leaves the biological treatment plant and is piped to a clarification stage.

Many waste water treatment techniques require – or optionally use – treatment aids, which in most cases are chemicals, or the treatment media / equipment need regeneration, which can cause the release of chemicals. These aids or process steps might generate, generally depending on local conditions, a pollution that needs to be taken into account when considering the use of a treatment technique. Thus, an assessment of treatment aids and chemicals released from regeneration facilities and their fate during the whole process might be necessary in specific situations.

Almost all waste water treatment techniques have one thing in common: the production of solids during the process, which enables the pollutant to be separated from the aqueous medium, such as excess activated sludge or filtered or settled residue from filtration or sedimentation operations. If sludge is not recycled, it needs to be disposed of – i.e. external treatment and disposal – or treated on the site. Sludge treatment techniques are e.g.:

- Thickening (see Section 3.4.1)
- Dewatering (see Section 3.4.1)
- Stabilisation (see Section 3.4.2)
- Conditioning (see Section 3.4.2)
- Thermal sludge reduction (see Section 3.4.3).

3.3.4.1 Insoluble Contaminants / Mechanical Separation

Insoluble content in the chemical industry waste water may consist of inert substances such as dust from rainwater drainage or sand (as ballast in raw materials such as lime). But it may also consist of hazardous materials such as heavy metals and their compounds, originating from precipitation processes of preceding treatment operations or production processes using catalysts. Even dioxins can be adsorbed to solid contents (e.g. catalyst of vinyl chloride production via oxychlorination). On the other hand, insoluble contaminants need not necessarily be solid particulates. Liquids immiscible with water, such as oil, substances of oily consistency, grease and colloids belong to this category as well. Waste water containing insoluble contaminants usually has to get rid of them by separation processes as described below.

3.3.4.1.1   Grit Separation of Solids

<u>Description</u>

Grit separation is the removal of sand from rainwater. Grit chambers are used for this purpose because the sand might otherwise be deposited in inconvenient places, disturbing the treatment process and leading to rapid abrasion in the pumps [cww/tm/132].

Grit chambers are part of the WWTP and usually situated immediately downstream from the screen installed as protection from coarse and fibrous material. They are designed to handle the required horizontal flow rate (about 0.3 m/s), i.e. only sand is separated whereas the lighter solids are carried on with the waste water stream.

There are three different types of grit chambers [cww/tm/132]:

- channel-shaped horizontal-flow chamber, which maintains the required flow rate in combination with a venturi flume, suitable for highly fluctuating waste water streams (Figure 3.6) [cww/tm/132]
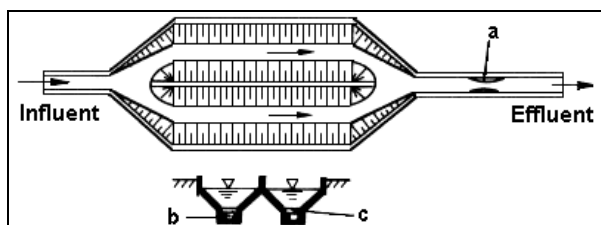
Figure 3.6: Channel-Shaped Horizontal-Flow Grit Chamber

- circular chamber, where the water is introduced tangentially, causing the content to circulate and the sand to be washed to the centre to be removed by air-jet lift; this chamber type being less suitable for highly fluctuating flow rates, (Figure 3.7) [cww/tm/132]
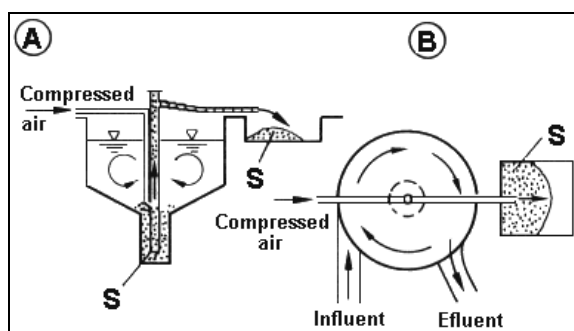
Figure 3.7: Circular Grit Chamber

- aerated chamber, where the circulation of the content is caused by air injection in a way that achieves the required flow rate at the bottom of the chamber; this type causing no problems with fluctuating flow rates (Figure 3.8) [cww/tm/132].
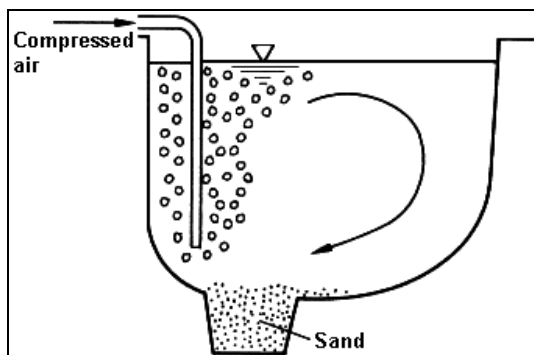
Figure 3.8: Aerated Grit Chamber

Storage facilities for the separated sand are necessary until its discharge.

Application

Grit chambers are used when the WWTP also has to deal with rainwater, which normally entrains a considerable amount of sand [cww/tm/132].

Application limits and restrictions:

	Limits / restrictions
Flow rate	flow rate of about 0.3 m/s required to make sure that only sand is separated
Flow rate fluctuation	restrictions to flow rates, dependent on chamber type

Advantages and Disadvantages

Not relevant – essential equipment.

Achievable Emission Levels / Performance Rates

Grit chambers are not installed for environmental protection reasons but as protection for downstream equipment.

Cross-media Effects

The separated sand has to be discharged or otherwise used, depending on the contamination.

Consumable is the electric energy for the waste water pumps and the air-jet.

The grit chamber, being part of the WWTP, contributes to the emissions of noise and odour for the main plant, depending on the kind of waste water being treated. Enclosing the equipment might be necessary.

Monitoring

The necessary waste water flow rate of 0.3 m/s needs to be controlled.

3.3.4.1.2 Sedimentation of Solids

<u>Description</u>

Sedimentation – or clarification – means the separation of suspended particles and floating material by gravitational settling. The settled solids are removed as sludge from the bottom, whereas floated material is skimmed from the water surface. When the particles cannot be separated by simple gravitational means, e.g. when they are too small, their density is too close to that of water or they form colloids, special chemicals are added to cause the solids to settle, e.g.:

- aluminium sulphate (alum)
- ferric sulphate
- ferric chloride
- lime
- poly aluminium chloride
- poly aluminium sulphate
- cationic organic polymers.

These chemicals cause the destabilisation of colloidal and small suspended particles (e.g. clay, silica, iron, heavy metals, dyes, organic solids, oil in waste water) and emulsions entrapping solids (coagulation) and/or the agglomeration of these particles to flocs large enough to settle (flocculation). In the case of flocculation, anionic and non-ionic polymers are also used.

The influence of coagulation is shown as an example in Table 3.2 [cww/tm/27]. The removal levels in this table, however, should not be confused with achievable performance rates of a treatment technique.

Substance	Removal [%]
Inorganic mercury	70
Cadmium and compounds	98
DDT [1,1,1-trichloro-2,2-bis-(p-chloro-phenyl)ethane]	75-80
HCB (hexachlorobenzene)	59
Aldrin	100
Dieldrin	50
Endrin	43
PCBs (polychlorinated biphenyls)	30–40
Tributyltin compounds	>90
Trichloroethene	36
Perchloroethene	30

Table 3.2: Removal of Waste Water Contaminants under Influence of Coagulation

The sedimentators (or settlers) commonly operated are:

- sedimentation or flat tanks, either rectangular or circular, both equipped with an appropriate scraper and of such a size as to provide a necessary residence time of about 1½ to 2½ hours (see Figure 3.9 as example of a circular tank [cww/tm/4])
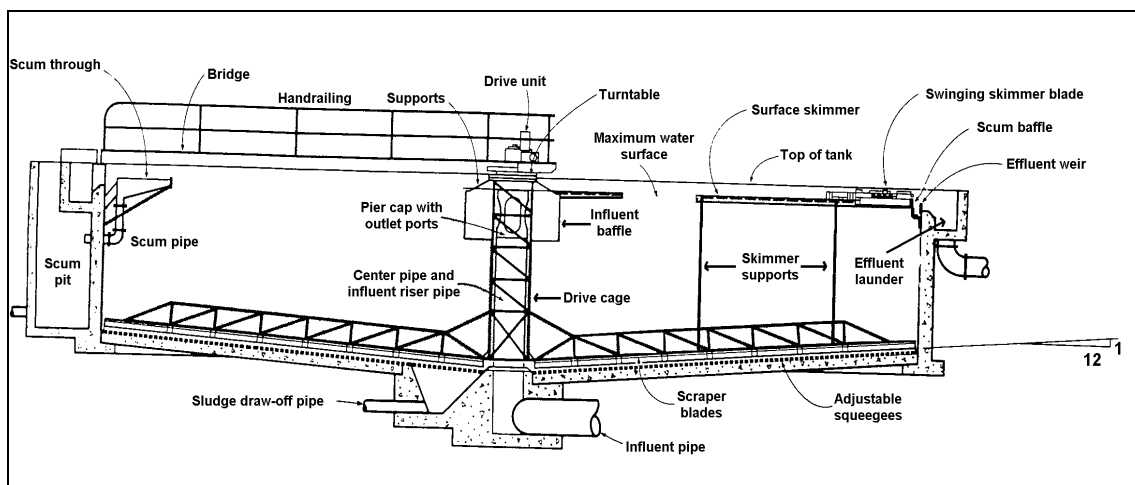
Figure 3.9: Sedimentation or Settler Tank

- hopper-bottom tank, with vertical flow, usually not equipped with mechanical sludge removal system (see Figure 3.10 [cww/tm/132])
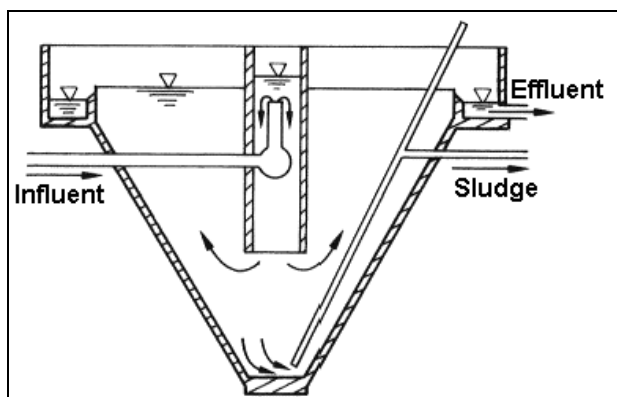
Figure 3.10: Hopper Bottom Tank

- lamina or tube settlers, where plates are used to enlarge the sedimentation surface (see Figure 3.11 [cww/tm/91]).

The equipment for coagulation and/or flocculation is installed as part of the tank. The need for rapid mixing with coagulation is fulfilled by:

- simultaneous dosing of coagulants via multiple injection points
- preference for plug flow systems, where applicable
- flash mixer or mixing where the coagulant is added at or before the flash mixer, static mixers or orifices.

With flocculation, a mixing chamber is added. Picket fence or low-speed mixers are used, causing hydraulic mixing within the fluid as it flows through the tank. Partial recycling of the floc back into the flocculator can result in a better floc structure and optimum exploitation of flocculant.

To ensure optimum settling operation, an upstream oil separation or emulsion decomposition stage, etc., is normally installed to remove interfering substances.

The equipment of the sedimentation facilities needs to be such that there is no waste water transference into the ground, at least when the tank might contain substances hazardous to groundwater. Storage facilities for the coagulant / flocculant chemicals and the sedimented sludge need to be equipped to suit the characteristics of the sludge.
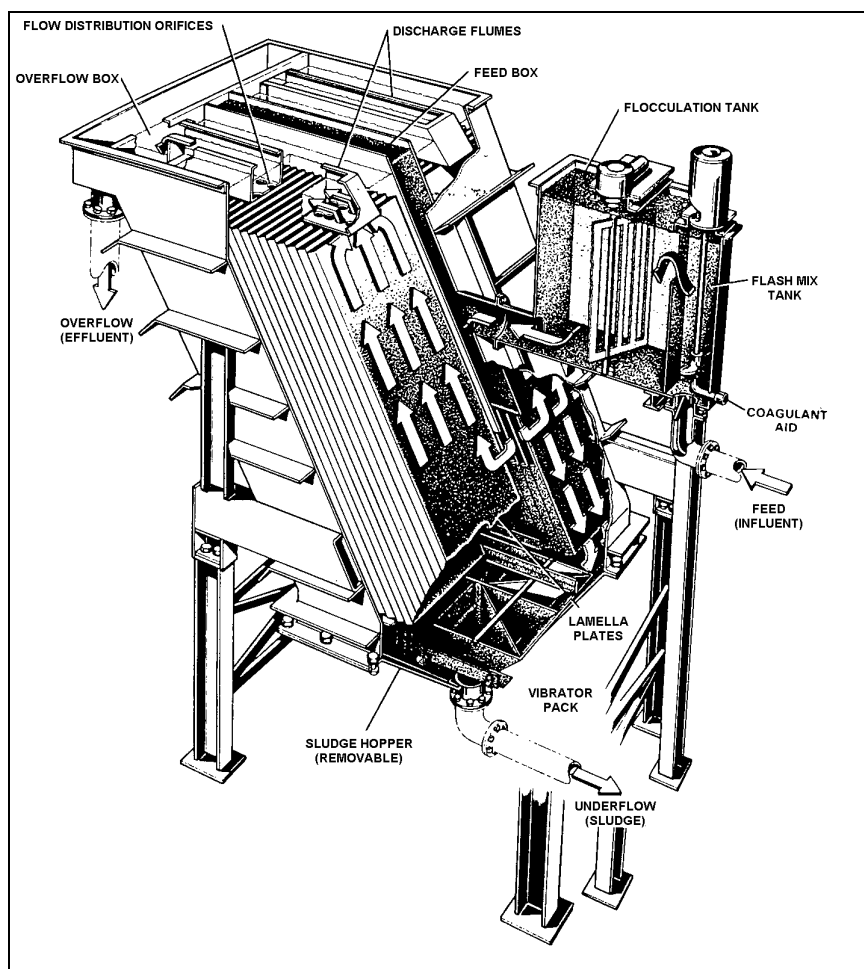
Figure 3.11: Lamina or Tube Settler

<u>Application</u>

Sedimentation is a separation technique widely used for many purposes and usually not used alone. The main examples are:

- clarifying collected rainwater from solid content such as sand or dust in a sedimentation tank
- clarifying process waste water from inert contents such as sand or comparable particles
- clarifying process waste water from reaction material such as emulsified metal compounds, polymers and their monomers, supported by addition of appropriate chemicals
- separation of heavy metals or other dissolved components after preceding precipitation (see Section 3.3.4.2.1), often with chemical support, followed at the end by filtration processes (see Sections 3.3.4.1.4 and 3.3.4.1.5)
- removal of activated sludge in a primary or secondary clarifier of a biological WWTP (see Section 3.3.4.3.5), often supported chemically.

Application limits and restrictions:

	Limits / restrictions
Particle size	particles must be large enough to be settleable, otherwise coagulation and/or flocculation chemicals need to be applied
Presence of volatile substances	volatile substances need to be avoided because of the long residence time in the tank (as well as the mixing action when coagulation and/or flocculation are used) and thus the potential release of VOC
Solid concentration	no limits, provided the aqueous phase is still separable
pH (in the case of coagulation / flocculation)	controlled pH range is essential during operation, otherwise poor clarification performance
Emulsions	stable emulsions cannot be separated and broken by coagulation / flocculation; preceding emulsion breaking is required

Advantages and Disadvantages

Advantages	Disadvantages
• Simplicity of the installation, and thus not tending to failure. • Removal efficiency can be increased by addition of coagulation and/or flocculation chemicals.	• Unsuitable for fine material and stable emulsions, even with coagulants and flocculants. • Floc can embed other contaminants that might cause problems in disposing of the sludge.

Achievable Emission Levels / Performance Rates

When sedimentation is used upstream of subsequent treatment steps, its purpose is to protect downstream facilities, so its removal efficiency needs to be high enough to achieve that. When it is used as a final treatment, its performance depends on the properties of the particles to be removed.

Reported achievable emission levels are:

Parameter	Performance rate [%]	Emission level [mg/l]	Remarks
TSS	60–90		
		<10 [1]	after final clarifier of central WWTP
Settleable solids	90–95		
Heavy metals			in particulate form, see Section 3.3.4.2.1

[1] [cww/tm/67c]

TSS can also include particulate organics, i.e. sedimentation will reduce TOC / COD as well, as long it is present as insoluble solid material. Its removal efficiency, however, depends on the proportion of solid TOC in total TOC.

Cross-media Effects

Sedimented sludge and skimmed scum, if not suitable to recycle or use otherwise, need to be disposed of as waste. Depending on the waste water origin, this waste might contain hazardous compounds to be treated accordingly. These compounds can be carbonates, fluorides, sulphides or hydroxides (or oxides) of heavy metals, oily scum, etc. and under certain circumstances even dioxins.

Sources of noise are the pumps that can be enclosed and the sludge / scum removal system.

When the waste water contains odorous substances, it might be necessary to cover the sedimentation tank – or at least the coagulation or flocculation unit – and to duct the arising

waste gas, if necessary, to a treatment system. The necessary equipment – ducts and vents – probably needs to be provided with an appropriate safety system, e.g. a pressurised nitrogen gas flow system, to avoid explosion risk.

Consumables can be:

Consumable	Amount
Chemicals (coagulant / flocculant) [a]	53–93 [kg/t oil, solid] [1]
	0.5–100 [g/m^3 waste water] [2]
Electric energy [kW] [b]	0.5–1.5
Nitrogen for inert atmosphere	
[a] organic polymer [b] for tank diameter of 25–35 m [1] [cww/tm/96] [2] [cww/tm/128]	

Monitoring

The effluent needs to be regularly monitored for solid content, i.e. suspended solids, settleable solids or turbidity. When chemicals (e.g. coagulants, flocculants) are used to improve the settling process, the pH needs to be controlled as the main operational parameter.

Economics

	Capital costs [million]	Operating costs
Sedimentation tank	EUR 1.2 [a]	
	BEF 4.8 [b][1]	
Laminar or tube settler [1]	BEF 4 [c]	BEF 20–100 per m^3
[a] per 1000 m^3 tank volume [b] capacity of 100 m^3/h [c] capacity of 25 m^3/h [1] [cmm/tm/128]		

3.3.4.1.3   Air Flotation

Description

Flotation is a process where solid or liquid particles or particulates are separated from the waste water phase by attaching to air bubbles. The buoyant particles accumulate at the water surface and are collected with skimmers [cww/tm/4].

Flocculant additives, such as aluminium and ferric salts, activated silica and various organic polymers, are commonly used to support the flotation process. Their function, besides coagulation and flocculation, is to create a surface or a structure able to absorb or entrap the air bubbles.

There are three methods of flotation, distinguished by the way air is added:

- vacuum flotation, where air is dissolved at atmospheric pressure, followed by a pressure drop to allow the formation of bubbles
- induced air flotation (IAF), where fine bubbles are drawn into the waste water via an induction device such as a venturi or orifice plate
- dissolved air flotation (DAF), where pressurised air (0.4–0.8 MPa, or 1.0–1.2 MPa for aluminium compounds) is dissolved into the waste water – or a part of the total waste water – and subsequently released to form small bubbles.

A typical DAF device is presented in Figure 3.12 [cww/tm/4].

Depending on the waste water content, it might be necessary to cover the flotation basin and duct the exhaust air to a gas abatement device. Facilities are necessary to store the flocculant/coagulant chemicals and the skimmed material.
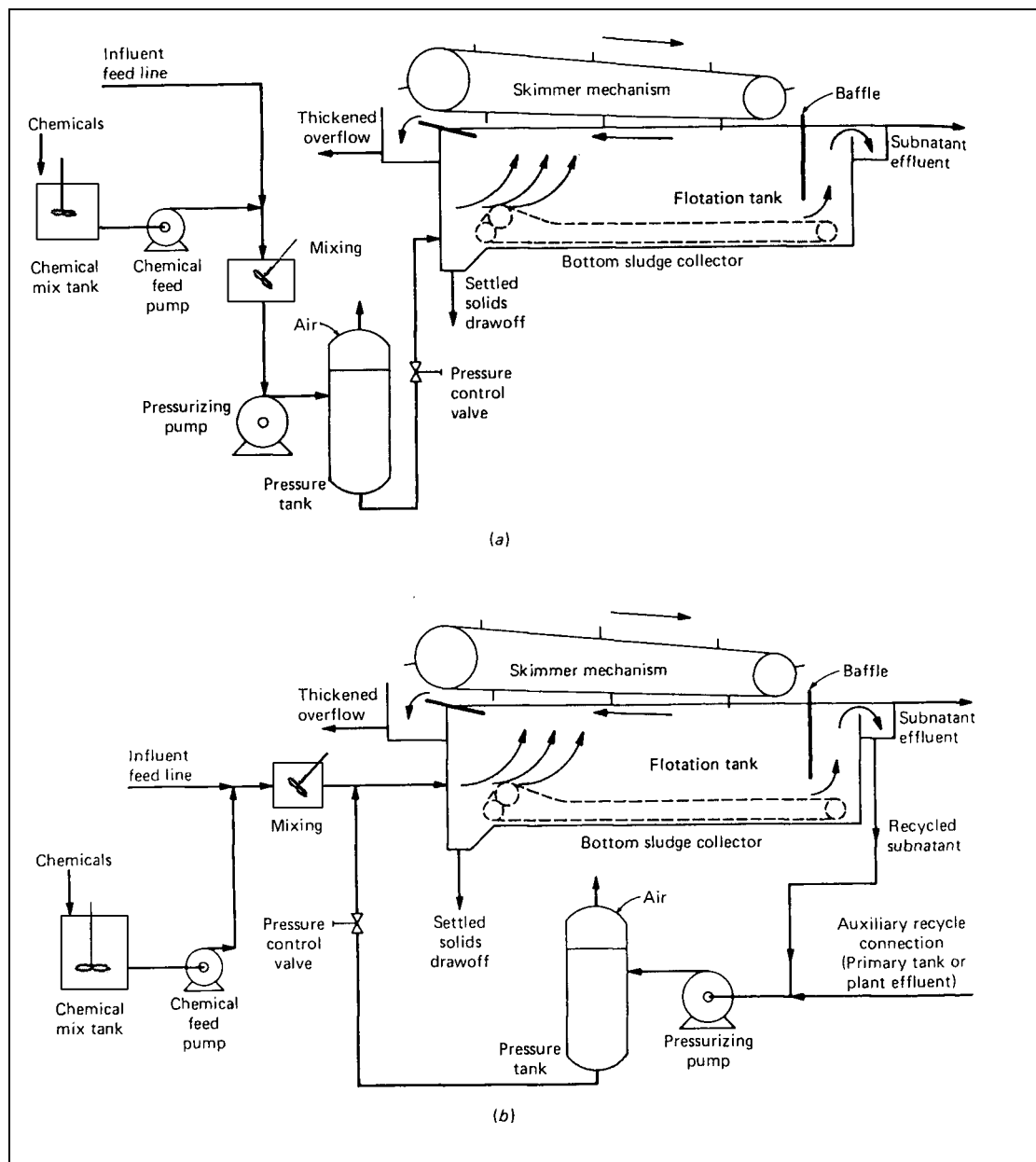
Figure 3.12: DAF System:
a) with Recycle, b) without Recycle

Application

Flotation is applied when sedimentation is not appropriate, e.g. when:

- the particulates have poor settling characteristics (in the case of a poor sludge volumetric index (SVI), however, there is no advantage over sedimentation)
- the density difference between the suspended particles and the waste water is too low
- there is a space constraint at the actual site
- oil and grease are to be removed.

Examples are:

- in refineries and petrochemical sites as a subsequent treatment downstream of oil separation and prior to a biological WWTP
- removal of dyes and pigments from respective production waste water
- recovering product or raw material, e.g. toluene from toluene/water emulsions [cww/tm/132], silver halides from production of photographic chemicals, butylthion or polysilan from waste water streams
- separation of heavy metals from waste water
- separation of activated sludge from biological waste water treatment, either after final clarification [cww/tm/67b] or replacing it
- thickening of activated sludge from a biological WWTP.

Application limits and restrictions:

	Limits / restrictions
Presence of substances	foaming detergents need to be excluded
Oil	though very efficient to remove free oil from waste water, gross free oil cannot be handled

Advantages and Disadvantages

Advantages	Disadvantages
• Less volume and thus lower capital costs required than with sedimentation. • Removal efficiency unaffected by changes of flow rate and thus superior to sedimentation, see Figure 3.13 [cww/tm/132] • Material recovery possible. • High separation efficiency, higher dry-matter content than with sedimentation.	• Clogging of valves is possible. • High potential for odour release, so a cover normally required. • Higher operational costs than sedimentation.
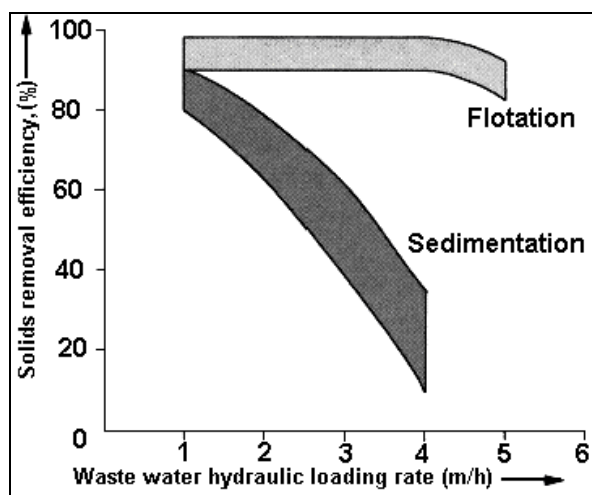
Figure 3.13: Comparison of Separation Efficiency of DAF versus Sedimentation [11]

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[11]   Insolubles content 90 – 450 mg/l, pressurised water addition for flotation 20 %

Achievable Emission Levels / Performance Rates

Parameter	Performance [%]	Emission level [mg/l]	Remarks
TSS	90–98		see Figure 3.13
	85–96 [1]	10–20 [1]	activated sludge after final clarifier, input 20–250 mg/l
Oil		10–20 ppm [2]	refinery, IAF and DAF treatment
		2–10 [3]	chemical production, after several APIs
Metal sulphides	95 [2]		refinery, IAF and DAF treatment
[1] [cww/tm/67b] [2] [cww/tm/131] [3] [cww/tm/93]			

COD/TOC are removed to the extent that they are present as solids or a suspension of droplets.

Cross-media Effects

The separated material, if not recyclable, is disposed of as waste. The amount depends on the material to be removed and the amount of coagulant and flocculant chemicals. Those can be quite different, according to the respective application of air flotation.

Consumables are:

Consumable	DAF-treatment of activated sludge [1]	Air flotation for refinery waste water [2]
Compressed air [a]	0.53–0.55	
Flocculant dose mg/l [b] kg/t [c]	0.6–1.2 2.4–4.7	3.7 53-93
Energy [kWh/1000 m^3]	20.6	
[a] expressed as compressed air relative to pressurised water [m^3/m^3] [b] flocculant concentration in waste water [c] amount of flocculant relative to mass of suspended solid in waste water [1] [cww/tm/67b] [2] [cww/tm/96]		

Sources of noise are the pumps, mixer and compressor, which have to be equipped with adequate noise containment measures.

The release of odorous or other volatile substances – if these are to be expected – can be prevented by covering the vessel or operating in a closed tank and ducting the exhaust air to a gas abatement system.

Monitoring

To ensure reliable operation, the turbidity of the effluent has to be monitored for disturbances. Any foam arising has to be detected in good time. Effluent detection of COD/TOC and TSS is obligatory.

Economics

The costs of a flotation unit vary widely, depending on the purpose:

	Flow rate [m^3/h]	Capital costs [million]	Annual operating costs [thousand]
DAF / activated sludge [1]	1200	DEM 5.0	DEM 800
DAF / refinery [2]	300–800	EUR 1.6–1.8	EUR 20–130
IAF / refinery [2]	400–820	EUR 0.5–2.1	EUR 55–130
DAF / as decentralised final treatment [3]	50		DEM 4500
DAF [4]	100 m^3/h 100 m^3/day	BEF 40 BEF 4	
[1] [cww/tm/67b] incl. capital costs, engineering design, civil engineering works, site preparation, etc. [2] [cww/tm/48] [3] [cww/tm/132] total operating costs, incl. chemicals for neutralisation, precipitation and flocculation, dewatering of flotate, incineration of sludge [4] [cww/tm/128]			

Indicative capital and operating costs for a DAF plant are given as relative to the flow rate. Though these values are not very near the actual figures, they estimate the degree of cost increase with increasing plant size [cww/tm/92]:

Flow rate [m^3/h]	Capital costs [GBP, million]	Annual operating costs [GBP, thousand]
10	0.1	10
100	0.1	20–30
1000	0.5	50–80
10000	1.0	500-800

The cost of flotation, which is the most widespread approach to solid-liquid separation in decentralised waste water treatment, is lower than that of evaporation or incineration (by a factor of approximately 10). But the benefits of evaporation and incineration are greater, since they result in complete disposal of highly contaminated effluent, whereas the precipitation and flotation processes achieve only partial treatment of a moderately contaminated split stream. Since the value of this partial treatment is also a subject of some dispute, it remains an open question whether it is wise to spend DEM 10 per cubic metre of waste water (or DEM 4.5 million per year for a 50 m^3/h tributary waste water stream) as operating costs for the pretreatment of a stream that comprises only a small fraction of the total amount of waste water from a large chemical plant [cww/tm/132].

Compared with sedimentation, flotation offers considerable advantages in many cases, not only in water treatment and recovery of valuable materials but also in the separation and thickening of sludge. As a rule, it leads to a higher dry-matter content of the resulting concentrate. Because of higher hydraulic load rates and shorter residence times, smaller apparatus volumes are required as well. This in turn generally implies lower capital costs, albeit at the expense of higher operating costs. A comparison may yield a space requirement for sedimentation 50 times greater than that for flotation. On the other hand, energy costs for flocculation / flotation can be about 50 times greater than for flocculation / sedimentation. Better opportunities exist with flotation than with sedimentation for control and adaptation to fluctuating operating conditions, although taking advantage of these opportunities requires the availability of more highly trained personnel [cww/tm/132].

3.3.4.1.4   Filtration

<u>**Description**</u>

Filtration describes the separation of solids from waste water effluents passing through a porous medium. Filters typically require a cleaning operation – backwashing – with reverse flow of fresh water and the accumulated material returned to the sedimentation tank (Section 3.3.4.1.2).

Commonly used types of filter systems are, e.g.:

- the granular-medium filter, or sand filter, which is widely used as a waste water treatment device (the medium of sand filters need not be literally sand), mainly used with low solid content
- the gravity drum filter, used for sewage treatment and removal of activated sludge flocs, its efficiency dependent on the screen fabric
- rotary vacuum filter, well-suited to precoat filtration, which is used for oily sludge dewatering and slop de-emulsification
- membrane filter (see Section 3.3.4.1.5)
- the belt filter press, which is largely used for sludge dewatering, but also for liquid/solid separation operations
- filter presses, which are usually used for sludge dewatering, but also for liquid/solid operations, suitable for high solid content.

Sand filters consist of a granular-medium filter bed with either downward or upward flow. The filter bed can be mono- or multi-medium. The operation can be semi-continuous – filtration and backwashing occur sequentially – or continuous – filtration and backwashing operate simultaneously. The main difference between the two operation modes is:

- semi-continuously operated sand filters are run up to turbidity breakthrough, when the solid content in the effluent starts to increase, or to limiting headloss
- continuously operated sand filters have no turbidity breakthrough or terminal headloss.

Sand filters work either by the force of gravity or an applied pressure force. Examples are given in Figure 3.14 [cww/tm/4] for the conventional downflow multi-medium, gravity-flow filter and in Figure 3.15 [cww/tm/4] for the pressure filter.

Drum filters consist of a cylinder on which the filtration surface is wrapped. They are either operated as a gravitational drum filter that can be charged on the inside or the outside, or as a rotatory vacuum filter with the inside or outside of the drum enclosed and connected to a vacuum pump. The filter cake is removed from the drum by different means. An example is given in Figure 3.16 [cww/tm/132].

Belt filter press and filter press as typical sludge dewatering facilities are described in Section 3.4.1.

Filter media can be characterised in terms of criteria, such as [cww/tm/132]:

- cut size, i.e. the particle size that can just pass through the filter medium
- permeability, high permeability characterised by low pressure drop
- chemical stability with respect to the filtrate
- blocking tendency, particularly for fabrics in cake filtration
- mechanical strength in relation to loads imposed in back-blowing or the movement of filter cloths
- smooth surface to promote cake removal.
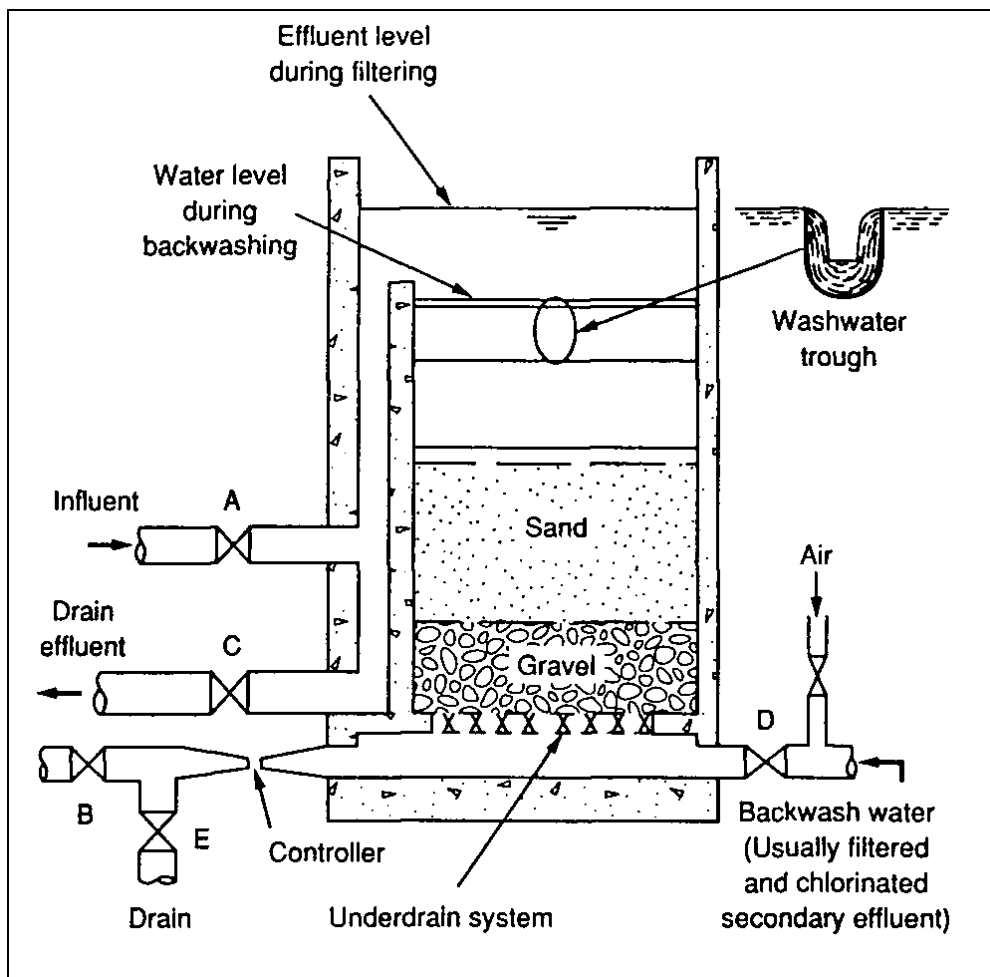
Figure 3.14: Conventional Downflow Multi-Medium Sandfilter
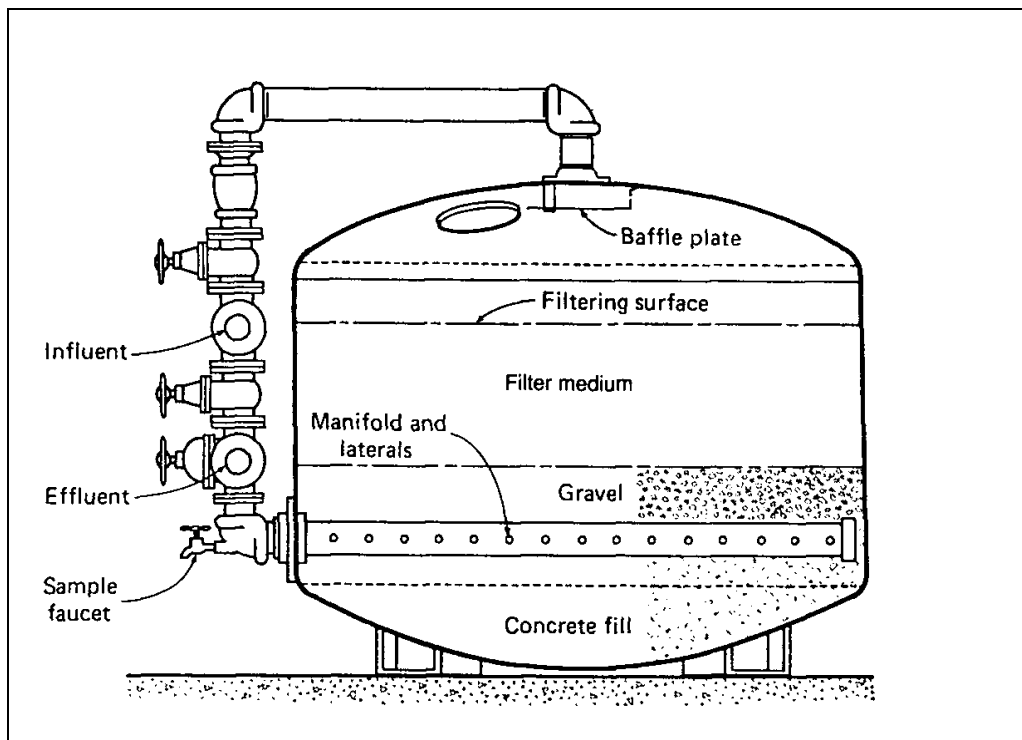
Figure 3.15: Pressure Filter
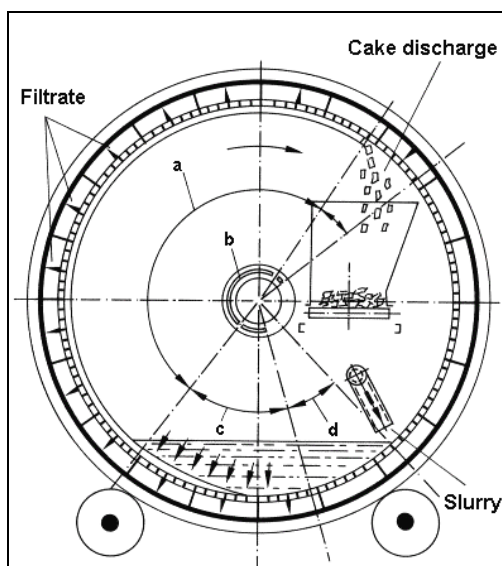
Figure 3.16: Rotary Vacuum Filter
a Dewatering zone, b Rotary valve, c Settling zone, d Suction zone

Suspensions made up of relatively fine, soft or compressible solids often fill or block the filter medium, unless this blocking is prevented by filter aids, i.e. inert, readily filterable granular material. These filter aids form a layer permeable to the filtrate and at the same time carry out the functions of a loose filter cake. The retained particles are deposited on the filter aid. Examples of filter aids are [cww/tm/132]:

- diatomaceous earths
- perlites
- Fuller's earths
- powdered glass
- coal preparations
- cellulose fibres
- wood pulp
- paper stock
- bagasse
- talc
- plastics.

Filter aids are used in pre-coating, i.e. a layer of filter aid is deposited on the filter medium before filtration starts. During filtration it is added continuously to the slurry to maintain the necessary ratio for proper and efficient filtration.

Application

In waste water treatment, filtration is frequently used as the final separation stage after sedimentation processes (see Section 3.3.4.1.2) or flotation (see Section 3.3.4.1.3), if low emissions of particulates are wanted, e.g.:

- separation of floc, heavy metal hydroxides etc. after sedimentation, to cope with discharge requirements
- removal of activated sludge after the central WWTP, in addition to sedimentation, to improve the quality of biologically treated waste water effluent
- dewatering of sludge, flotate etc.
- recovery of free oil, with rotary drum filters and the help of polymer addition.

Application limits and restrictions:

	Limits / restrictions
Colloids, emulsions	cannot be separated without additional chemical treatment
Finely dispersed or slimy solids	can block the filter medium, if filter aids not used

Advantages and Disadvantages

Advantages	Disadvantages
• High separation efficiency. • Pollutants other than suspended solids can be removed under certain circumstances, such as oil. • Operation under a wide range of conditions.	• Clogging and fouling processes are possible with semi-continuous sandfilters. • Breakthrough can cause additional pollution of the effluent.

Achievable Emission Levels / Performance Rates

Parameter	Performance [%]	Emission level [mg/l]	Remarks
TSS		<10 mg/l	activated sludge floc
	50–99.99 [1]		sand filter, dependent on filter aids
Free oil		<5 mg/l	
Heavy metals			after precipitation, see Section 3.3.4.2.1

[1] [cww/tm/128]

Cross-media Effects

When a granular filter, e.g. a sand filter, is used, the backwashed material is normally recirculated to the process from where it originated, e.g. to the sedimentation tank or the activated sludge basin of the biological WWTP. The residue from other kinds of filters (drum filter, belt filter etc) can either be recycled or needs to be discharged of as waste or undergo further treatment.

Sand filtration, as an example of deep-bed filtration, entails less frequent backwashing than cake filtration (e.g. belt or drum filtration) and thus a lower requirement for backwash water. For this reason, cake filtration is applied only in exceptional cases in waste water treatment (examples above in this chapter) [cww/tm/132].

Consumables are:

Consumable	Sand filter	Drum filter
Water for backwashing		–
Water for vacuum generation	–	
Filter aids		
Energy [kWh/1000 m^3]		
Pressure drop		

The operating equipment can be a relevant noise source which can be controlled by enclosing the main sources.

If odorous substances may be released, closed devices might be necessary. Pressure filters and filter presses are placed in closed vessels and the exhaust air is ducted to a gas abatement system.

Monitoring

To ensure reliable operation, the turbidity of the filter effluent has to be monitored to recognize disturbances, or a breakthrough with the semi-continuous sandfilter. The pressure drop has to be registered to indicate clogging and barring.

Economics

	Flow rate [m³/h]	Capital costs [million]	Operating costs
Sand filter [1]	100	BEF 4	BEF 2/m³
[1] [cmm/tm/128]			

3.3.4.1.5   Microfiltration and Ultrafiltration

Description

Microfiltration (MF) and Ultrafiltration (UF) are membrane processes that segregate a liquid that permeates through a membrane into permeate, which passes the membrane, and concentrate, which is retained. The driving force of the process is the pressure difference across the membrane. Both are special and elaborate filtration techniques, already mentioned in the preceding chapter.

Membranes used for MF and UF are 'pore type' membranes which operate like sieves. The solvent and particles of molecular size can pass the pores, whereas suspended particles, colloidal particles, bacteria, viruses, and even larger macromolecules are held back.

Typical characteristics are shown in Table 3.3.

Parameter	Microfiltration	Ultrafiltration
Pore diameter [µm] [1]	0.1-1	0.001–0.1
Operating pressure [MPa] [2]	0.02–0.5	0.2–1
Cut-off size [nm]	>100, includes bacteria	10-100, includes macromolecules, viruses, colloidal particles 1000–100000 g/mol for solutions
Permeate flow [l m^{-2} h^{-1}]	50–1000	<100
Cross flow speed [m/s] [2]	2-6	1-6
Membrane type [3]	symmetrical polymeric or ceramic, 10–150 µm thick	polymeric, or ceramic asymmetric
Membrane configuration [3]	spiral-wound hollow-fibre tubular	spiral-wound hollow-fibre tubular
[1] [cww/tm/27] [2] [cww/tm/132] [3] [cww/tm/93]		

Table 3.3: Characteristics of Microfiltration (MF) and Ultrafiltration (UF)

Membranes for MF and UF are available in several materials and configurations. The optimum modification for a particular application will depend on the nature of the waste water, since the different materials have varying resistances to dissolved substances. Membrane materials for MF are, e.g.:

- glass fibre
- polycarbonate
- PVDF (poly vinylidenfluoride)
- cellulose acetate
- polyamide.

Suitable materials for UF are normally organic polymers, e.g.:

- cellulose acetate
- polyamide
- polyimide
- polycarbonate
- polyvinylchloride
- polysulphone
- polyethersulphone
- polyacetal
- copolymers of acrylonitrile and vinyl chloride
- polyelectrolyte complexes
- cross-linked polyvinyl alcohol or polyacrylates.

PVDF membranes have the advantage that they can be cleaned with strong acids, caustic soda and bleaches.

The membrane filter process is usually run cross-flow, i.e. the permeate flow is directed perpendicular to the feed flow. The impurities remain in the feed which, reducing in volume, leaves the membrane system as a concentrated waste stream.

Storage facilities for the concentrate should be available.

Application

Membrane filtration (MF and UF) is applied when a solid-free waste water for downstream facilities, e.g. reverse osmosis or the complete removal of hazardous contaminants such as heavy metals, is desired. The choice between MF and UF depends on the particle size.

Common MF applications include [cww/tm/93; cww/tm/67a]:

- degreasing processes
- metal particle recovery
- metal plating waste water treatment
- sludge separation after activated sludge process in a central biological WWTP, replacing a secondary clarifier (activated membrane process), though UF can also be used.

Common UF applications include:

- removal of non-toxic degradable pollutants such as proteins and other macromolecular compounds and toxic non-degradable components, e.g. dyes and paints, with molecular weights greater than 1000
- segregation of oil/water emulsions
- separation of heavy metals after complexation or precipitation
- separation of components not readily degradable in sewage treatment effluents, which are subsequently recycled to the biological stage
- pretreatment step prior to reverse osmosis or ion exchange.

Application limits and restrictions:

	Limits / restrictions
Membrane material	vulnerable to chemical attacks, depending on waste water content

Advantages and Disadvantages

Advantages	Disadvantages
• High separation efficiency. • Modular systems, i.e. flexible in usage.	• Clogging, plugging and fouling processes are possible. • Compaction in the presence of softening agents. • High operating pressure, therefore high pumping energy. • No mechanical stability.

Achievable Emission Levels / Performance Rates

Parameter	Performance [%]	Emission level [mg/l]	Remarks
TSS	about 100	close to 0	
COD			
Heavy metals			see Section 3.3.4.2.1

Cross-media Effects

Membrane treatment produces a residue (concentrate) of approximately 10 % of the original feed volume, in which the target substances are present at levels approximately 10 times their concentration in the original feed. An assessment should be made of whether this residue can be disposed of.

With organic suspended substances the concentration increase might improve the conditions for subsequent oxidative destruction processes. With inorganic suspended substances, the concentration stage could be used as part of a recovery process. In both cases, the permeate water from a membrane process can potentially be re-used or recycled in the industrial process, thus reducing water input and discharge.

Consumables are:

Consumables	MF	UF
Membrane material		-
Chemicals (antiscaling, antifouling, backwashing etc.)	-	
Energy [kWh/m^3]	2-20 [1]	1-10 [1]
Pressure drop	see Table 3.3	see Table 3.3
[1] It seems rather surprising that MF, the process with the lowest pressure drop, consumes more energy than the processes with high pressure drops. The reason is the occurrence of concentration polarisation and fouling. In MF, and to a lesser extent in UF, this phenomenon is very severe and it results in a drastic flux decline [cww/tm/161].		

The energy consumption is directly related to the cross-flow rate and pressure requirements. It is generally associated with maintaining a minimum velocity of about 2 m/s across the membrane surface.

A source of noise is the pumping equipment, which can be enclosed.

Monitoring

To ensure reliable operation, the pressure difference across the membrane has to be monitored continuously.

Economics

	Flow rate [m³/h]	Capital costs	Operating costs	Replacement costs
MF		GBP 400–1500 [1] per m² membrane [a]		GBP 80–350 [1] per m² membrane [a]
		BEF 40000 [2] per m² membrane	BEF 2-200 [2] per m³ waste water	
UF		GBP 400–1500 [1] per m² membrane [a]		GBP 80–350 [1] per m² membrane [a]
		BEF 60000-200000 [2] per m² membrane [b]		
[a] for hollow fibre, spiral and ceramic membranes [b] lower figure organic membranes, higher figure inorganic membranes [1] [cww/tm/93] [2] [cww/tm/128]				

The capital costs, including automated cleaning facilities, can be broken down approximately as follows [cww/tm/93]:

pumps	30 %
replaceable membrane components	20 %
membrane modules (housings)	10 %
pipework, valves, framework	20 %
control system	15 %
other	5 %

The operating cost [cww/tm/93] is derived from:

- energy cost of maintaining the hydrostatic pressure and flow rate of the systems
- expected membrane life
- cleaning regime required
- site-specific factors, e.g. labour requirement.

They can be broken down approximately as follows [cww/tm/93]:

replaceable membrane components	35–50 %
cleaning	12–35 %
energy	15–20 %
labour	15–18 %

3.3.4.1.6   Oil-Water Separation

Description

The separation of oil and water and subsequent oil removal can be divided into:

- gravity separation of free oil, using separation equipment
- emulsion breaking, using emulsion breaking chemicals, such as:
    - polyvalent metal salts such as alum, aluminium trichloride, ferrous chloride, ferrous sulphate
    - mineral acids such as sulphuric acid, hydrochloric acid, nitric acid
    - adsorbents such as pulverised clay, lime
    - organic polymers such as polyamines, polyacrylates,

and subsequent separation of de-emulsified oil by coagulation / flocculation and air flotation (see Section 3.3.4.1.3).

The commonly used oil-water separators are:

- the **American Petroleum Institute Separator (API)** as the simplest type, consisting of an open rectangular basin and a flight scraper, the latter moving the sludge to a collection pit and the oil to the skimming device, able to intercept large slugs of oil (see Figure 3.17 [cww/tm/91])

- the **Parallel Plate Interceptor (PPI)**, equipped with plates parallel to the current which enlarge the active surface area immensely and an oil skimming device, not suitable to intercept large slugs (see Figure 3.18 [cww/tm/91])

- the **Corrugated Plate Interceptor (CPI)**, equipped with corrugated plate packs placed counter current and an oil skimming device, not suitable to intercept large slugs, but possessing a good separation efficiency (see Figure 3.19 [cww/tm/91]).
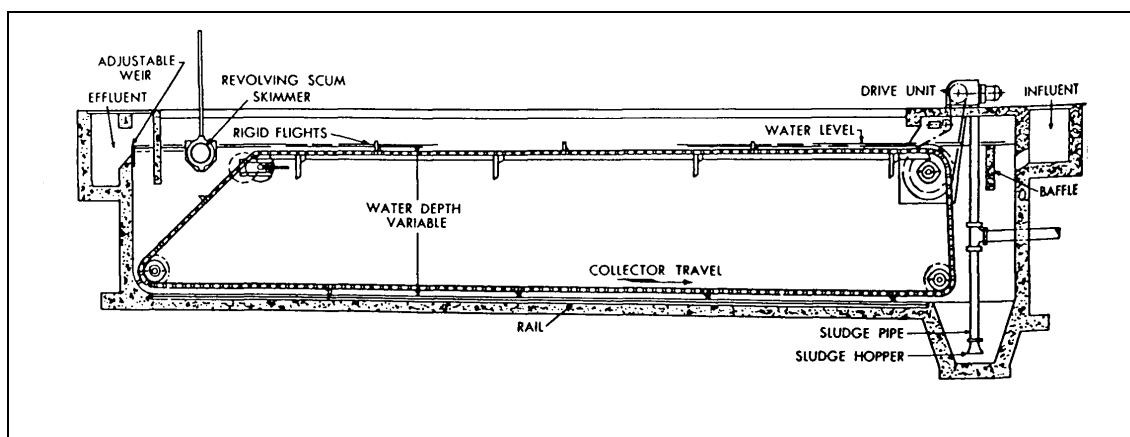
Figure 3.17: American Petroleum Institute Separator (API Separator)

To collect the oil phase and remove it either to recovery or further treatment, several kinds of skimming equipment are used, e.g.:

- fixed pipe skimmers
- rotating trough skimmers
- rotating disc or drum skimmers.

Storage facilities for the skimmed oil and the sludge are necessary if the oil cannot be recycled immediately.
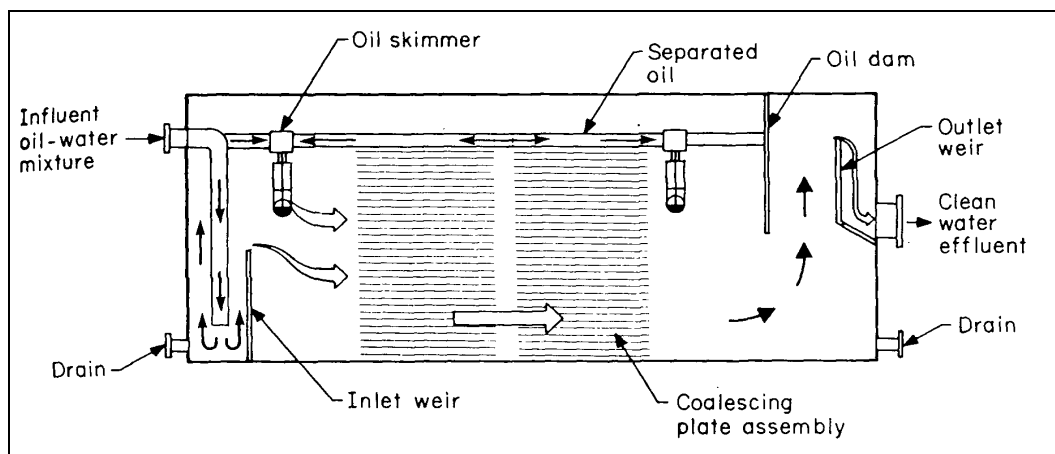
Figure 3.18: Parallel Plate Interceptor (PPI)
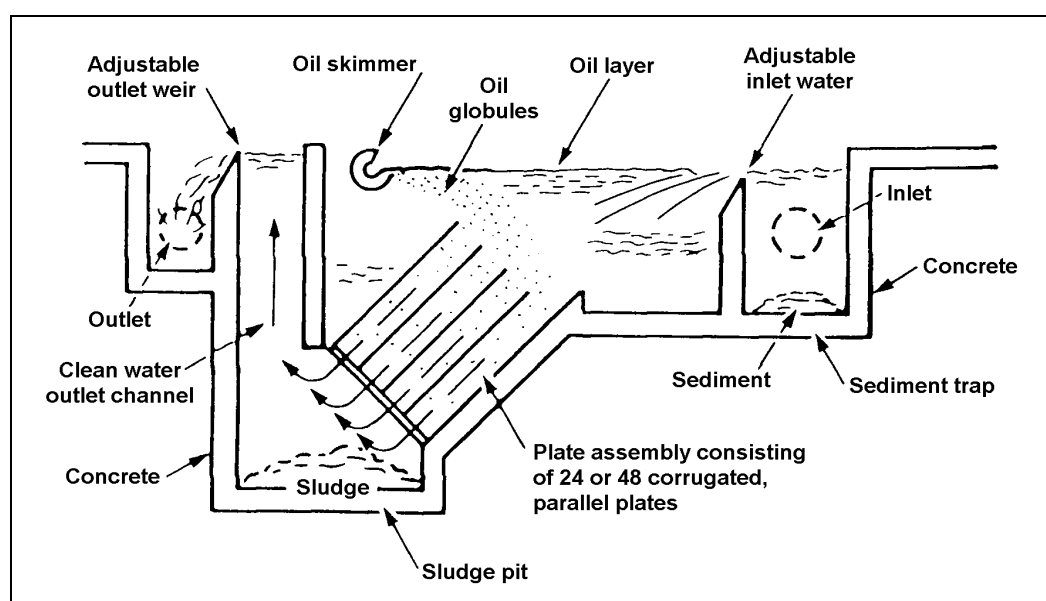
Figure 3.19: Corrugated Plate Interceptor (CPI)

Application

Oil-water separation is applied to remove oil, grease and other non-soluble liquids lighter than the aqueous phase from waste water, mainly in refineries and petrochemical sites. It is normally not a stand-alone process, but followed by flotation (IAF or DAF), supported by coagulation / flocculation (see Section 3.3.4.1.3). The API is also used as a control device to protect downstream equipment against large oil slugs, originating e.g. from an operational failure, whereas PPI and CPI show a higher efficiency in the removal of smaller oil droplets.

Advantages and Disadvantages

Advantages	Disadvantages
• Oil can be recovered and recycled to the process units. • Efficiency increase in the order API – PPI – CPI concerning removal of small oil droplets and the ratio of active surface area / ground area.	• Only API can intercept large slugs of free oil and solids (as in an emergency case). • In the case of PPI and CPI, plates are susceptible to fouling, so increased maintenance requirement. • Cannot separate soluble substances.

Achievable Emission Levels / Performance Rates

Parameter	Performance [%]	Emission level [mg/l]	Remarks
Oil	90–95		
		6-90 mg/l [1]	API, refinery
		40–70 mg/l [2]	API, chemical industry
Solid	90–95		
[1] [private information] [2] [cww/tm/93]			

Cross-media Effects

The skimmed oil is generally sent back to the process units, where it is re-used after minor cleaning operations. Otherwise it is chemical waste and has to be adequately disposed of, together with the separated solids.

Oil-water separators, when not covered, are the main contributors to VOC releases in waste water treatment systems of which they are part and are thus the main source of odour and health risks. Surface covering achieves a VOC release reduction of about 95 % [cww/tm/48]. On the other hand, covering can cause skimming problems and the operation of the equipment cannot easily be checked. The local situation will determine which option is taken. If the separator is covered, the waste gas needs to be ducted to an abatement system that includes an adequate safety system, such as pressurised nitrogen, to avoid explosion risk.

Sources of noise are the pumps, which are usually enclosed, and the skimming device. Where appropriate, control measures need to be taken.

Consumables are:

Consumables	API	PPI	CPI
Nitrogen from pressurised system as safety device [a]	0.05 m/h		
Energy [kWh/m^3]			
[a] nitrogen gas flow relative to surface area [m^3/(m^2 h)]			

Monitoring

The outlet has to be regularly monitored visually to ensure proper operation, e.g by oil build-up checks. Skimmer device and oil dam have to undergo regular maintenance.

Economics

	Flow rate [m^3/h]	Capital costs [million]	Operating costs	Remarks
API	1200	EUR 2.0 [1]		
PPI				
CPI	100	BEF 2–10 [2]	BEF 2–4 / m^3 [2] a	
[a] labour costs 3 h/day [1] [cww/tm/48] [2] [cww/tm/128]				

3.3.4.2 Soluble Non-biodegradable or Inhibitory Contaminants / Physico-Chemical Treatment

Soluble non-biodegradable or inhibitory waste water contaminants can be subdivided into three classes of compounds:

- inorganic compounds such as salts or heavy metal compounds
- organic compounds as source for refractory TOC
- inhibitory organic or inorganic compounds that disturb the biological process in a biological WWTP.

Inorganic compounds are not affected by biological treatment and can, like refractory TOC, tend to disturb the biological process in a biological WWTP. Both usually need special pretreatment upstream of a central WWTP. Pretreatment operations are:

- chemical transformations to form solid products that are separated in a follow-up process as described in Section 3.3.4.1 (see Section 3.3.4.2.1 and 3.3.4.2.2)
- chemical degradation processes to form biodegradable contaminants (see Sections 3.3.4.2.3 to 3.3.4.2.7)
- physical elimination processes (see Sections 3.3.4.2.9 to 3.3.4.2.14)
- incineration processes to form gaseous and solid residues that can be separated from the waste water stream (see Section 3.3.4.2.15).

On new chemical sites in Germany it is common practice to use these pretreatment operations (or process-integrated measures instead) with tributary streams carrying a relevant non-biodegradable load (e.g. TOC elimination rates below 80 % and recalcitrant TOC load of about 20 kg/d, 300 kg/yr and 1 kg/tonne of product, independent of the local situation). With existing ones, those measures are taken that can achieve an optimum performance, considering the ratio between environmental benefits and costs; for details see Section 2.2.1.2.

3.3.4.2.1   Precipitation

<u>Description</u>

Precipitation is a chemical way to form particulates that can be separated by an additional process, such as sedimentation (Section 3.3.4.1.2), air flotation (Section 3.3.4.1.3), filtration (Section 3.3.4.1.4) and if necessary followed by MF or UF (Section 3.3.4.1.5). Fine separation by membrane techniques might be necessary to protect downstream facilities or to prevent the discharge of hazardous particulates. It might also be a useful technique to remove colloidal precipitates (e.g. heavy metal sulphides).

A precipitation facility usually consists of one or two stirred mixing tanks, where the agent and possibly other chemicals are added, a sedimentation tank and storage tanks for the chemical agents. If needed – as mentioned above – further treatment equipment is added. The sedimentation tank might be replaced downstream by other sludge collecting systems.

Typical precipitation chemicals are:

- lime (with lime milk the preparation devices are part of the treatment unit) (for heavy metals)
- dolomite (for heavy metals)
- sodium hydroxide (for heavy metals)
- soda (sodium carbonate) (for heavy metals)
- calcium salts (other than lime) (for sulphates or fluorides)
- sodium sulphide (for mercury)
- polyorganosulphides (for mercury).

These are often accompanied with flocculants to assist further separation, such as:

- ferrous and ferric salts
- aluminium sulphate
- polymers
- polyorganosulphides.

Application

Precipitation can be applied at different stages of the waste water stream, e.g.:

- directly at source to remove heavy metals most effectively to avoid dilution by unloaded streams
- as central treatment technique for the removal of phosphates, sulphates and fluorides, provided inadequate dilution is not expected
- to remove phosphate after the biological stage in a central WWTP, where the sludge is collected in the final clarifier.

The performance of further liquid/solid separation normally depends on factors such as pH, mixing quality, temperature or residence time at the precipitation step, the actual conditions to be found in a case by case study.

Application limits and restrictions:

	Limits / restrictions
pH adjustment	optimum pH range for heavy metals, phosphate, fluoride: pH 9–12, when sulphides are used, hydrogen sulphide is generated under acidic conditions
Complex-forming substances	can prevent precipitation of heavy metals, such as copper, nickel

Advantages and Disadvantages

Advantages	Disadvantages
With lime as agent	With lime as agent
• Prevention of increasing salt content in the waste water. • Increase of the buffering capacity of the central biological WWTP. • Improvement in sludge sedimentation. • Sludge thickening. • Improvement of mechanical dewaterability of sludge. • Reduction of dewatering cycle time. • Low cost.	• Operating problems associated with the handling, storage and feeding of lime [cww/tm/4]. • Increase of sludge amount due to excess of calcium hydroxide • Maintenance problems [cww/tm/4].
For sodium sulphide	For sodium sulphide
• Decrease of amount of sludge (about 30 % in volume compared to lime treatment). • Decrease of amount of chemicals used (about 40 %, compared to lime treatment). • Produces lower metal levels in treated effluent. • No pre- or post-treatment needed. • Highly efficient at removing suspended and dissolved metals from a waste water stream.	• Generation of hydrogen sulphide when the batch becomes acidic by failure. • Odour problems associated with sodium sulphide.

Achievable Emission Levels / Performance Rates

Parameter	Emission level [mg/l]	Agent	Remarks
Mercury			
Cadmium			
Copper			
Nickel			
Lead			
Chromium(III)			
Chromium(VI)			
Zinc			
Tin			
Aluminium			
Iron(III)			
Iron(II)			
Sulphate			
Phosphate			
Fluoride			

Achievable emission levels for heavy metals vary greatly, depending on the particular situation, such as:

- removal of a single heavy metal species from inorganic waste water matrix
- removal of a heavy metal mix from inorganic waste water matrix
- removal of heavy metals from organic waste water matrix with tendency for formation of metal complexes, e.g. dye agents.

At the time of writing, the necessary information to fill the table above has not been made available.

Cross-media Effects

The precipitants usually have to be disposed of as sludge. Often this sludge is chemical waste, at least if heavy metals are involved. This waste may contain carbonates, fluorides, hydroxides (or oxides), phosphates, sulphates, sulphides of heavy metals.

Sources of noise are pumps and sludge removal facilities. Appropriate measures for noise control have to be taken.

If the release of volatile and odorous substances can be expected, precipitation should be operated in closed tanks or covered basins with ducts to gas abatement facilities.

Consumables are:

Consumable	Amount
Precipitation agent (lime, dolomite, ferrous and ferric salts, ferrous sulphate / sodium sulphide, alumi-nium sulphate, polymers, polyor-ganosulphides)	dependent on con-taminant load
Energy [kWh/m^3]	

Monitoring

During the precipitation process the pH value and the dosage of agents, flocculants and/or coagulants have to be carefully adjusted.

Economics

Type of costs	Costs	Flow rate [m³/h]	Remarks
Capital costs			
Operating costs			

3.3.4.2.2   Crystallisation

Description

Crystallisation is closely related to precipitation. In contrast to precipitation, the precipitate is not formed by chemical reaction in the waste water, but is produced on seed material such as sand or minerals, working in a fluidised-bed process – a pellet reactor system. The pellets grow and move towards the reactor bottom. The driving force of the process is the reagent dosage and pH-adjustment. No waste sludge arises. The principle of a crystallisation device is illustrated in Figure 3.20 [cww/tm/97].
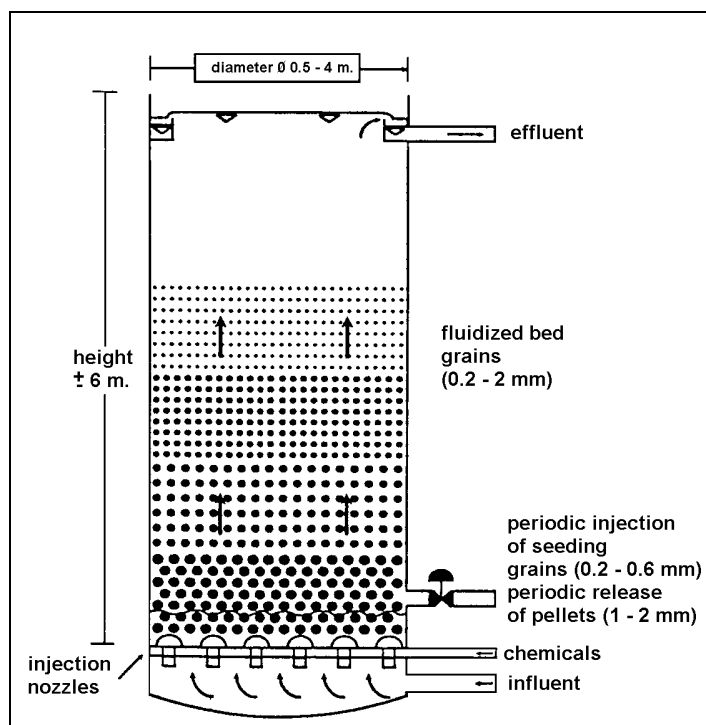
Figure 3.20: Principle of Crystallisation Process

The crystallisation device consists mainly of:

- the cylindrical reactor with bottom influent and top effluent
- seed material, i.e. pellets of filter sand or minerals, kept in a fluidised-bed condition
- the circulation system with recirculation pump.

The velocity of the influent waste water (40–120 m/h) keeps the pellets in a fluidised state [cww/tm/97]. The process conditions at the bottom of the reactor are chosen in such a way that a relatively high supersaturation of the desired salts occurs. The fluidised bed provides a very large crystallisation surface (5000–10000 m^2/m^3) so that, in a fast and controlled reaction, almost all the anion or metal content crystallises on the pellets. Periodically, a part of the pellets is discharged and replaced by new seed material. Typically this takes place once a day.

The principle of the circulation system is to mix the influent waste water with the circulation stream of lower anion or metal concentration. Because of the circulation system the reactor can work more flexibly, e.g.:

- fluctuations in the influent flow and composition are easily eliminated
- all kinds of waste water with concentrations in the range of 10–100000 ppm can be treated by simply adapting the circulation ratio (more highly concentrated waste water requires a larger circulation ratio)
- fluidisation of pellets is also maintained if no waste water is fed.

If very strict demands have to be met, the effluent can be polished by conventional or continuous sand filtration or membrane filtration. This filtration stage can be situated either inside the circulation loop or at the effluent flow. The effluent is used for back-washing of conventional sand filters. The carry-over removed by the filter is re-dissolved by mixing with the acid feed or acidified and returned to the reactor. An example of a crystallisation process in a chemical production is given in Figure 3.21 [cww/tm/97].
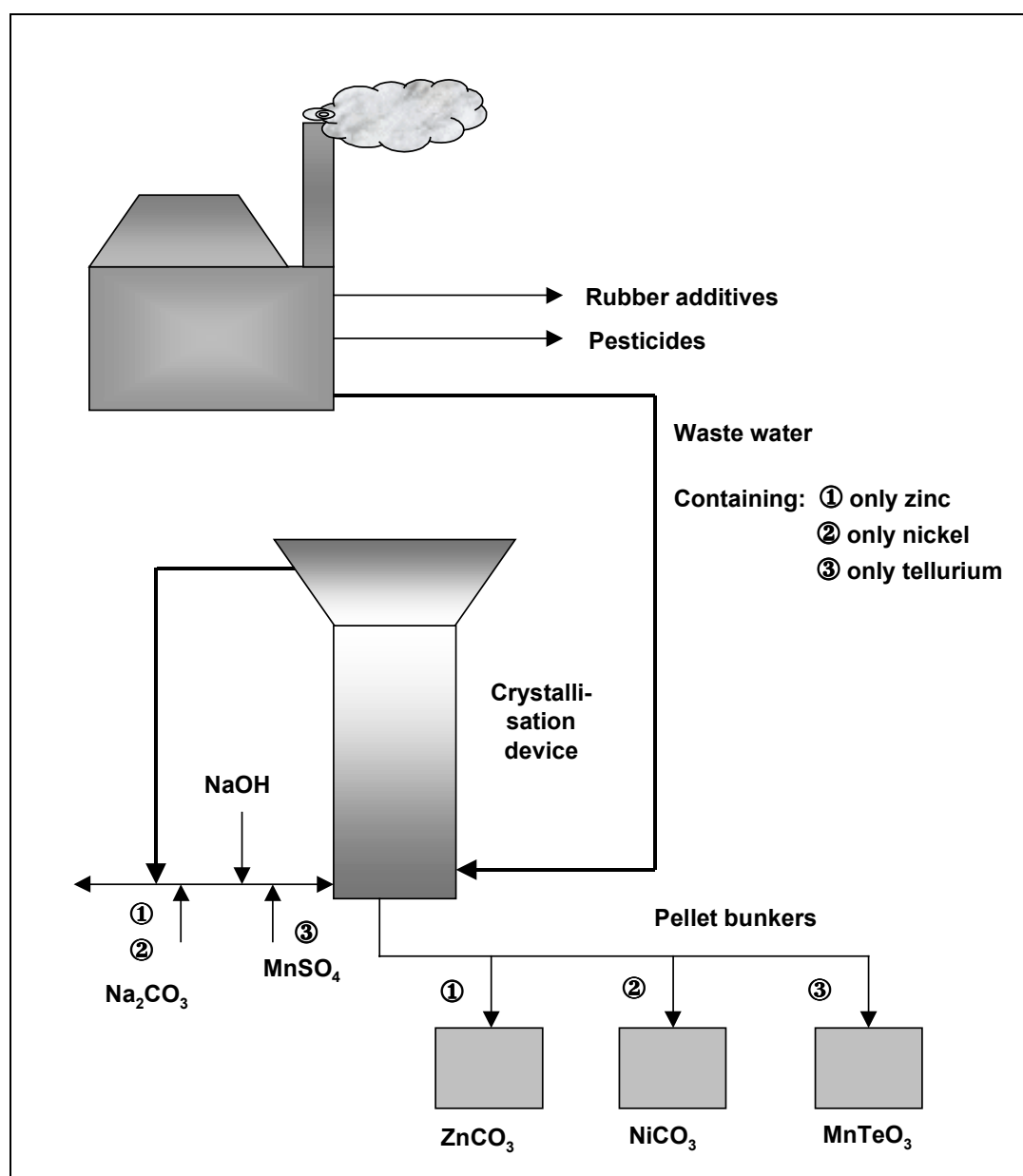
Figure 3.21: Multi Purpose Application of Crystallisation in a Chemical Production

Application

In most cases, crystallisation is applied to remove heavy metals from waste water streams and to recover them subsequently for further usage, but fluoride, phosphate and sulphate can also be treated. Examples of usage in the chemical industry are [cww/tm/97]:

- recovery of zinc, nickel and/or tellurium in the production of rubber additives, with feed concentrations between 50 and 250 ppm
- recovery of nickel and aluminium in the production of elastomers, the crystallisation device working prior to a central biological WWTP, with feed concentrations between 50 and 400 ppm for nickel and aluminium respectively.

In principle, almost all heavy metals, metalloids and anions can be removed from all kinds of waste water by crystallisation. The formation of salt pellets is feasible when the solubility of the generated salt is low and the metal or anion crystallises quickly into a stable crystal lattice. Whereas metals are normally abstracted as carbonates, hydroxy carbonates, hydroxides, sulphides, phosphates, sulphates, fluorides etc, anions are generally removed as calcium salts [cww/tm/97].

Application limits and restrictions:

	Limits / restrictions
Flow rate	0.1–10000 m^3/h
Pollutant content	10 mg/l–100 g/l
Removal capacity	up to 100 kg metal/anion per hour per unit

Advantages and Disadvantages

Advantages	Disadvantages
- Compact and flexible units, thus enabling modular set-up and tailor-made materials selection. - No sludge production. - Water-free pellets with high purity which enables recycling or further usage of the metal content in other sectors. - Raw material recovery / recycling. - Nearly waste-free process.	- Only applicable to ionic constituents forming insoluble or hardly soluble salts. - Reagents restricted to non-hazardous substances. - Total salt content of waste water is not decreased.

Achievable Emission Values / Performance Rates

The main purpose of crystallisation is the abatement or recovery of heavy metals. Achievable effluent emissions are:

Parameter	Emission level [mg/l]	Agent	Remarks
Zinc	1 [1]	soda, caustic soda	feed 50-250 mg/l, pH 10
Nickel	1 [1]	soda, caustic soda	feed 50-250 mg/l or 1000 mg/l, pH 10
Tellurium	1 [1]	manganese sulphate, caustic soda	pH 9, after filtration
Aluminium	20 [1]	sulphate, caustic soda	feed 50-400 mg/l
[1] [cww/tm/97]			

Cross-media Effects

To achieve good removal results, the reagents necessary to form the precipitates are normally added in an over-dosage. This means that the removal of one substance has as a consequence the addition of another compound not present in the original waste water stream.

Normally no waste or sludge arises, since the precipitated salts are attached to the pellets. They are almost free of impurities and their moisture content is only up to 5–10 % after atmospheric drying [cww/tm/97]. Thus the pellets can be used to recover the abated pollutant substances.

Sources of noise are the pumps, which may need to be housed for noise abatement.

Consumables are:

Consumable	Amount
Crystallisation chemicals	
Energy [kWh/m^3]	

Monitoring

Important parameters to control are:

- water flow, to keep the fluidised bed working
- the concentration / load of the metal or anion in question in the influent
- the reagent dosage, to maintain the optimum conditions for crystallisation
- pH, for the same reason
- the concentration of the metal or anion in the effluent.

Economics

The economic situation is [cww/tm/97]:

Type of costs	Costs [a] [USD/kg]	Remarks
Capital costs		
Operating costs:		
Depreciation	3–25	depending on capacity
Chemicals	0.50–2.50	depending on concentration
Energy	0.25	
Staff		1 hour per day
Maintenance		3-5 % of investment
Benefits:		
Re-use	0–14.50	depending on anion or metal
Reduction of chemical waste	2–8	depending on concentration in sludge
Reduction of operating cost for precipitation	0.50–3	in the case of pretreatment
Saving on investment for precipitation plant	3–12	in the case of final treatment
Reduction of discharge fee	30-40	in the case of final treatment
[a] per kg recovered anion or metal		

3.3.4.2.3 Chemical Oxidation

Description

Chemical oxidation is the conversion of pollutants by chemical oxidation agents other than oxygen/air or bacteria to similar but less harmful or hazardous compounds and/or to short-chained and easily biodegradable organic components. Chemical oxidation agents are, e.g.:

- chlorine
- sodium or calcium hypochlorite
- chlorine dioxide
- ozone (with or without UV irradiation)
- hydrogen peroxide / UV irradiation
- hydrogen peroxide / ferrous salts (Fenton's agent).

Frequent operations in connection with chemical oxidation are:

- oxidation with ozone
- oxidation with hydrogen peroxide
- oxidation with ozone / UV irradiation
- oxidation with hydrogen peroxide / UV irradiation
- oxidation with ozone, hydrogen peroxide and UV irradiation
- oxidation with chlorine, hypochlorite.

The design of an oxidation reactor depends on its special purpose:

- Oxidation processes are normally operated at pressures of up to 0.5 MPa [cww/tm/82]. Depending on whether UV irradiation is acting as an accelerator, the equipment of the reactor has to provide for the radiation source, e.g. a low-pressure mercury lamp. In such a case the reactor usually consists of quartz tubes, transparent to UV rays, confining the waste water, and the UV lamps outside, or the UV lamps inside the quartz tubes that are enclosed by the waste water.

- If ozone is involved in the process, an ozone generator is part of the equipment, because ozone as an unstable compound cannot be transported and has to be generated in situ. After treatment, surplus ozone has to be eliminated. Safety requirements to handle ozone are strict.

- With hydrogen peroxide as oxidation agent, a GAC adsorber (see Section 3.3.4.2.9) is necessary to eliminate surplus agent.

- Application of chlorine entails special equipment, such as titanium manufactured vessels. Additional installations should be provided that can eliminate surplus chlorine or hypochlorite by, e.g., sulphite.

Storage facilities have to be provided for the oxidation agents, bearing in mind the hazardous potential of these substances.

<u>Application</u>

Chemical oxidation is normally applied when the waste water contains contaminants that are not readily biodegradable, or not biodegradable at all (e.g. inorganic components), might disturb the biological or physico-chemical process in a downstream WWTP or have properties too harmful to allow them to be released into a common sewer system. Examples of such contaminants are:

- oil and grease
- phenols
- polycyclic aromatic hydrocarbons (PAHs)
- organic halides
- dyes (with Fenton's agent)
- pesticides
- cyanides
- sulphides
- sulphites
- heavy metal complexes.

Some of these contaminants are biodegradable to a certain extent and can alternatively be treated with specially adapted micro-organisms. In these cases, whether chemical oxidation is preferred to biological oxidation depends on the local situation. When small quantities of waste water are involved or when there is no biotreatment available at a site, chemical oxidation might be a recommendable treatment option instead of installing a central biological WWTP.

Oxidation reactions with active oxygen (ozone, hydrogen peroxide), often accompanied by UV irradiation, are used, e.g., to treat leachates from landfills or remove refractory COD, odorous components or colour pigments.

Oxidation with chlorine or sodium chlorite can be used under special conditions to remove organic contaminants, even organic halides. An example is the SOLOX®-Process to eliminate (at elevated pressure and temperature) COD/TOC and AOX from waste water originating from epichlorohydrin production. But the use of chlorine, hypochlorite and chlorite (or the respective halogen compounds) has to be carefully examined in each case, because of the risk of generating organic halides from organic content in the waste water stream.

Application limits and restrictions:

	Limits / restrictions
UV irradiation	• high turbidity results in poor transmission of UV • ammonia content needs to be low, competes with the organics consuming radicals [cww/tm/27] • substances that tend to fouling will decrease the efficiency • incomplete oxidation or formation of intermediate contaminants can hamper the effectiveness of the process

Advantages and Disadvantages

Advantages	Disadvantages
• Waste water with refractory COD concentrations over a range of some g/l down to less than 1 µg/l can be treated [cww/tm/77]. • Inorganic substances can be treated. • Large fluctuations can be managed. • Small residence time and thus small tank volume required (H_2O_2 oxidation proceeds at atmospheric pressure and room temperature within 60–90 minutes [cww/tm/132]) • Process can be combined with any other to achieve optimum results (GAC adsorption, stripping, activated sludge biology).	• High energy consumption: ozone generation, UV generation, pressure and heating for chlorine oxidation. • High feed quality demands. • Generation of organic halides possible, when halogen compounds are used as oxidation agent.

Achievable Emission Levels / Performance Rates

For hydrogen peroxide as oxidation agent the COD elimination of various organic substances as a function of hydrogen peroxide utilisation is illustrated in Table 3.4.

Substance	Dosage H_2O_2 / COD [%] [a]	COD elimination [%] [b]	H_2O_2 utilisation [%]
Morpholine	100	20	20
2-Aminoethanol	100	37	37
Diethyleneglycol	100	45	45
Polyethyleneglycol	100	35	35
Hexamethylenetetramine	100	32	32
2,4-Difluoro-5-chloro-6-methylpyrimidine	100	30	30
Phenyltrifluoroethylcarbamide	80	75	94
Ammonium trifluorothyldithiocarbamate	80	79	99
[a] percentage of stoichiometric amount [b] percentage of initial value			

Table 3.4: COD Elimination of Various Substances as a Function of H_2O_2 Utilisation [cww/tm/132]

Further achievable performance rates are:

Parameter	Performance rate [%]	Oxidation agent	Remarks
TOC	>90 [1]	chlorine / hypo-chlorite	feed about 1 g/l TOC
AOX	80 [1]	chlorine / hypo-chlorite	feed about 40 mg/l AOX
Oil			
Phenols			
PAH			
Cyanide			
Sulphide			
Sulphite			
[1] [cww/tm/82], SOLOX process			

When waste water with refractory organic contents is treated, the main task is to break these components into more easily degradable / less harmful compounds. Bearing that in mind, the most practical source of performance evidence might not be just the removal efficiency of the oxidation process itself, but rather the overall reduction of these contaminants, achieved in co-operation with preceding and subsequent treatment processes.

Cross-media Effects

Whereas oxidation with ozone and/or hydrogen peroxide does not normally create a problem transfer from the water to the air and/or the disposal section, the use of chlorine or hypochlorite has to be validated critically for each application. As already mentioned, chlorine and hypochlorite might – in contrast to the example of the SOLOX-process – generate chlorinated organic compounds that are poorly degradable and/or toxic. This can also be detected when waste water loaded with organic compounds is mixed with other streams that contain surplus hypochlorite from preceding oxidation steps. Waste water treated by chlorine oxidation has to be relieved of surplus chlorine or hypochlorite before it is discharged into the general sewer system.

Consumables are:

Consumable	Amount
Oxidation agent	
Agent to destroy surplus oxidant	
Energy [kWh/m^3]	
for ozone production [kWh/kg O_3]	9-12 (1-3 wt-% ozone from oxygen; double value with dry air)

Monitoring

During the oxidation process a thorough monitoring of operation parameters is crucial, e.g.:

- pH
- redox potential
- ozone concentration (ozone concentrations of 15-20 % in air are very unstable and tend to decompose [cww/tm/27])
- oxygen concentration (for safety reasons)
- content of surplus oxidant in the effluent
- AOX content in the effluent, if chlorine base agents are used.

Economics

Chemical oxidation does not operate cost-effectively when high contaminant concentrations are expected, because large amounts of agent are then required. Advanced oxidation processes such as:

- UV / hydrogen peroxide
- UV / ozone
- UV / hydrogen peroxide / ozone

entail high capital and operating costs and require more extensive waste water pretreatment than irradiation-free processes.

Type of costs	Costs	Remarks
Capital costs		
Operating costs		

3.3.4.2.4 Wet Air Oxidation

Description

Wet air oxidation is the reaction with oxygen in the aqueous phase under high pressure and temperature. The reaction often takes place in the presence of catalysts. Reaction products are, dependent on the waste water content:

- carbon monoxide from organic content
- carbon dioxide from organic content
- water from organic content
- nitrogen from hydrazine, or from ammonia / ammonium and N-containing organics, if a catalyst is used
- nitrate from nitrite and N-containing organics
- ammonium, in the absence of a catalyst
- (hydrogen) chloride from organic chlorides
- sulphate from sulphides, sulphites and thiocyanates
- phosphate from phosphorous-containing compounds.

For a better assessment of the potential range of applications for wet oxidation, it has proven advantageous to develop two process variants with differing reaction conditions:

- low-pressure wet oxidation
- high-pressure wet oxidation.

The corresponding distinctions in temperature and pressure are also associated with major differences in process engineering factors, material considerations and plant safety requirements [cww/tm/132].

Typical properties of the two variants are:

	Low-pressure	High-pressure
Temperature range [°C]	30–200	150–340
Pressure range [MPa]	0.5–2	>2
Residence time [h]	0.5–3	0.5-3

Equipment and design for the low-pressure wet air oxidation process are [cww/tm/51]:

- the reactor vessel according to the applied pressure and temperature, e.g.
  - a well mixed, vertical bubble column without mechanical mixing
  - a horizontal reactor with agitated compartments in series
  - a deep shaft reactor (see Figure 3.44)
  - a packed bed reactor with catalyst
- the high-pressure pump for waste water or sludge transportation
- the compressor for air/oxygen supply
- the gas/liquid separator
- pressure-reducing valves
- the heat exchanger system with pre-heating facilities for the waste water input.

Material requirement for the hot parts of the plant is very high. Suitable equipment for temperatures <160 °C needs to be enamelled or lined with PTFE, metal parts to be operated at temperatures up to 200 °C must be manufactured from titanium or its alloys with palladium. The requirements for the high-pressure variant are special titanium alloys for heated areas and a chloride-resistant stainless steel for cold parts [cww/tm/132].

An example of the low-pressure wet oxidation process is shown in Figure 3.22.
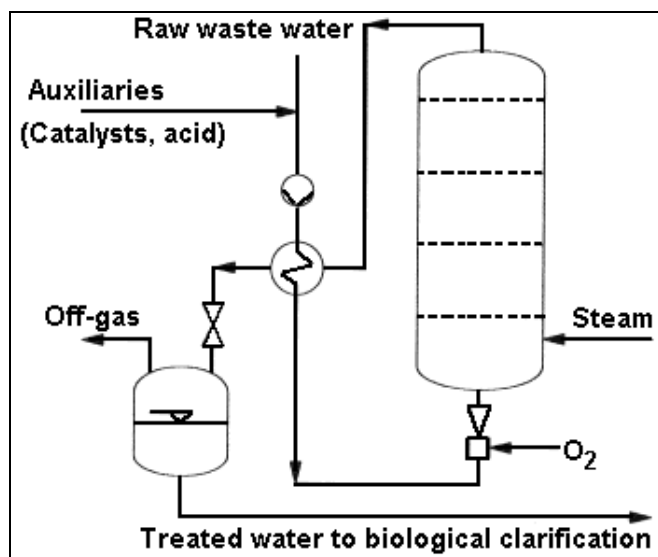
Figure 3.22: Flow Diagram of a Loprox Facility
operated at 120 – 200 °C and 0.3 – 2.0 MPa with a Retention Time < 3 h [cww/tm/132]

<u>**Application**</u>

Wet air oxidation is applied to waste water containing contaminants that are either not readily biodegradable or might disturb the biological process in a downstream biological WWTP, or that have properties too harmful to allow them to be released into an ordinary sewer system. It is also used for sludge treatment (see Section 3.4). The substances preferably considered for this technique are, e.g.:

- nitrite that is converted to nitrate in a one-step process at 30–50 ºC
- sulphite from dye manufacturing which is converted to sulphate in a two-step, homogeneously catalysed process at 120-140 ºC and 0.6 MPa [cww/tm/132]
- phenol and naphthene derivatives that are converted at 120–150 ºC
- chlorinated aromatics that are converted in a catalysed process at 120–190 ºC,

using the low-pressure variant, and

- organic nitro compounds that are converted to nitrogen
- organic amino compounds or aromatics containing nitrogen hetero atoms that are converted to ammonia
- organic sulphur compounds that are converted to sulphate
- organic phosphorous compounds that are converted to phosphate
- chlorinated organic compounds that are converted to hydrochloric acid,

using the high-pressure-variant.

Examples for production processes where wet air oxidation is applied are, e.g. [cww/tm/160]:

- production of dyes and intermediates
- oxidation of aromatic sulphonates
- production of derivatives of phenol or naphthol
- production of aromatic hydrocarbons.

Wet air oxidation might also replace a central biological WWTP, if the amount of waste water is too small to warrant such a plant or if there is no biotreatment available.

Application limits and restrictions:

	Limits / restrictions
Contaminant concentration	- no advantage for low COD concentrations; recommendable for COD concentrations between 5000 and 50000 mg/l [cww/tm/160], concentrations between 6000 and 8000 mg/l being autothermal [cww/tm/132] - concentrations over 100000 mg/l demanding dilution [cww/tm/27] - with the high-pressure variant, COD concentrations above 50000 mg/l are required to equal the total energy demand of the process [cww/tm/132] - fluoride concentrations <10 mg/l (low-pressure variant) [cww/tm/160], higher concentrations to be pretreated, e.g. by precipitation with calcium salt and subsequent filtration; <5 mg/l (high-pressure variant) [cww/tm/160] - fluoride concentrations consistent with the solubility product of calcium fluoride are sufficient to initiate corrosions at pH <5 (high-pressure variant) [cww/tm/132] - salt loads have to be minimised as far as possible, at least with the high-pressure variant, because of corrosion [cww/tm/82], e.g. [cww/tm/160]: salt <150 g/l chloride <50 g/l phosphate <400 mg/l NH_4-N <2.5 mg/l Ca, Fe, Al, Cu <100 mg/l
Waste water fluctuations	waste water needs to be collected and equalised upstream of the oxidation facilities

Advantage and Disadvantage

Advantages	Disadvantages
- Waste water with relatively high refractory COD concentrations can be treated. - Inorganic contaminants can either be eliminated or transferred to less hazardous substances. - Can be combined with other treatments.	Dioxins can be generated [cww/tm/82].

Achievable Emission Levels / Performance Rates

When the elimination of refractory organic contents and/or inhibitors to subsequent biological treatment is the main goal, this is normally done in a two-step approach:

- break the refractory components into short chain or easily degradable compounds
- then send this waste water to a downstream (central) biological WWTP.

Thus performance evidence is not assessed by looking just at the efficiency of the oxidation process, but also by taking into account the efficiency of the subsequent biological process.

For the low-pressure variant, the following data are reported:

Parameter	Performance	Remarks
COD	60–90 % [1]	example: 85 % reduction by wet oxidation (190 °C, 2 MPa), followed by 90 % reduction after biological clarification step, in total 98 % COD reduction [3]
	50 % [2]	90 % after biological treatment
AOX	60–>90 [1,3]	reaction temperature of 190 °C
BOD/COD	increase from 0.1 to 0.5 [3]	reaction temperature of 190 °C
Sodium sulphide	<1 mg/l [4]	initial concentration 30 g/l, 160 °C, 0.9 MPa
[1] [cww/tm/82] [2] [cww/tm/160] [3] [cww/tm/132] [4] [cww/tm/149]		

For the high-pressure variant, the following data are reported:

Parameter	Performance rate [%]	Remarks
COD	99 [1]	initial concentration 30 g/l, 250 °C, 7 MPa
TOC	95 [2]	280 °C, 12 MPa
AOX	80 [2]	280 °C, 12 MPa
Aromatic amines	76–83 [3]	initial TOC 14.6 g/l, pH 1.1-10, 280-300 °C
Nitrogen heterocycles	77–92 [3]	initial TOC 1.1-14.3 g/l, pH 1.1-10, 280-300 °C
Azo compounds	97–99 [3]	initial TOC 13.1 g/l, pH 1.5-10, 280-300 °C
Nitrosulphonic acids	76–84 [3]	initial TOC 14.0 g/l, pH 1.5-10, 280-300 °C
Oxygen heterocycles	80–87 [3]	initial TOC 52 g/l, pH 11.5, 280-300 °C
Cl-containing sulphonic acids	90–93 [3]	initial TOC 3.5 g/l, pH 1.6, 280-300 °C
Aminosulphonic acids	80–88 [3]	initial TOC 20-24 g/l, pH 1.4-2.2, 280-300 °C
Aminopolysulphonic acids	64–65 [3]	initial TOC 47.6 g/l, pH 0.5, 280-300 °C
Nitro compounds	93–94 [3]	initial TOC 6 g/l, pH 9.3, 280-300 °C
Oxy compounds	75–81 [3]	initial TOC 9.2 g/l, pH 2.2, 280-300 °C
Mixed waste water	77–81 [3]	initial TOC 11.4 g/l, pH 1.9, 280-300 °C
[1] [cww/tm/149] [2] [cww/tm/160] [3] [cww/tm/132]		

As an example of the application of high-pressure wet air oxidation to low TOC concentrations, the removal of pesticides is reported as [cww/tm/27]:

Contaminant	Influent concentration [µg/l]	Effluent concentration [µg/l]	Remarks
Aldrin	500	<50	
DDT	21000	<300	
Endosulfan	18400	291	
Endrin	3600	<100	
2,4-Dichlorophenol	180	<3.1	

Cross-media Effects

Under adverse conditions, generation or regeneration of dioxins can occur, so residues might need further treatment. The effluents from this process – aqueous and off-gas (carbon monoxide, lower hydrocarbons) – have to undergo downstream treatment, e.g. biological treatment, adsorption or stripping of waste water, and gas scrubbing, biofiltration or thermal/catalytic oxidation of waste gas.

Consumables are:

Consumable	Amount
Air, oxygen	
Energy [kWh/m^3]	

The energy consumption depends on the TOC load. When the TOC content exceeds the autothermal range, the generated heat can be used by means of installed heat exchangers.

Monitoring

During the whole process a thorough monitoring of operation parameters such as pressure, temperature and oxygen content is vital to ensure faultless working.

Economics

Type of costs	Costs	Remarks
Capital costs		
Operating costs	DEM 5/m^3 [1]	at 100 °C
	DEM 20–40/m^3 [1]	at 200 °C
	EUR 1.5/kg TOC [2]	
[1] [cww/tm/132] [2] [cww/tm/160]		

3.3.4.2.5   Supercritical Water Oxidation (SCWO)

Description

SCWO is a special application of the high-pressure variant of wet air oxidation (see Chapter 3.3.4.2.4). The oxidation reaction takes place in the supercritical region of water, i.e. temperatures over 374 °C and pressures above 22.1 MPa. The process is illustrated in Figure 3.23.

Waste water is brought to the supercritical pressure by a high-pressure pump before it enters the economiser, where the feed is preheated by the reactor effluent. At start-up, or if the organic concentration in the waste water is less than 4 %, the feed has to be heated further to reach the supercritical temperature range. When oxygen is added to the feed the temperature in the reactor will rise to about 600 °C.
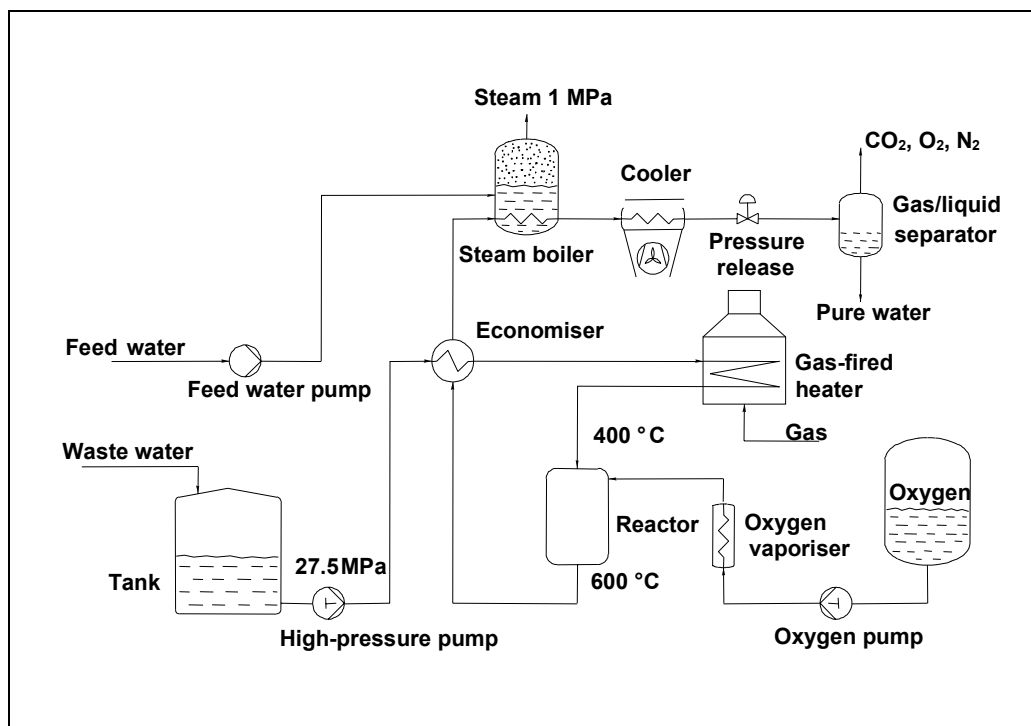
Figure 3.23: Simplified Flowsheet of the SCWO Process

The reactor effluent flows into the economiser, then through a heat recovery steam generator and through an effluent cooler. Finally a control valve drops the effluent pressure to atmospheric conditions and the liquid and gas phases are separated.

The organic waste water content is reduced to carbon dioxide, water and nitrogen.

Characteristics of SCWO are:

- complete solubility of organic compounds in supercritical water
- complete precipitation of inorganic solids, such as salts
- reaction time for complete destruction between 30 and 60 seconds, strongly dependent on the reaction temperature
- reaction at about 25 MPa and 400–600 °C
- complete conversion of the organic content, i.e.
  - organic carbon is converted to carbon dioxide
  - organic and inorganic nitrogen are converted to nitrogen gas
  - organic and inorganic halogens are converted to the corresponding acid
  - organic and inorganic sulphur are converted to sulphuric acid.
- destruction of volatile solids
- oxidation of heavy metals to their highest oxidation state
- separation of all inerts as fine, non-leachable ash.

Application

SCWO is applied to contaminants with low biodegradability and/or high toxicity in the chemical, petrochemical and pharmaceutical industry. It also destroys dioxins and PCB, whereas the relatively low temperature range of 400–600 °C makes it unlikely to produce NO_x (i.e. nitrogen oxides, excluding N_2O).

Another application field for SCWO is the treatment of industrial and municipal sludge to destroy toxic organic compounds, including dioxins.

Advantages / Disadvantages

Advantages	Disadvantages
• All organic content, irrespective of its properties, is destroyed. • Very high destruction efficiency at relatively low temperatures achieved, resulting in NO$_x$-free emissions. • No dioxins generated. • Very short reaction time necessary, resulting in short residence time and thus in low reactor volume. • Can be combined with other downstream treatments.	• Traces of laughing gas (N$_2$O) and acetic acid are likely to be found. • Inorganic solids precipitate and might cause corrosion.

Achievable Emission Levels / Performance Rates

Parameter	Performance rate [%]	Remarks
Organic compounds	>99	
1,2,4-Trichlorobenzene	99.99 [1]	495 °C, 3.6 min
4,4-Dichlorobiphenyl	>99.99 [1]	500 °C, 4.4 min
DDT	>99.99 [1]	505 °C, 3.7 min
PCB 1234	99.99 [1]	510 °C, 3.7 min
PCB 1254	99.99 [1]	510 °C, 3.7 min
Dioxin	>99.99 [1]	574 °C, 3.7 min
[1] [cww/tm/27]		

Cross-media Effects

Depending on the waste water influent, the gaseous effluent contains traces of laughing gas and acetic acid generated by the process, but also hydrogen halides as a degradation product of organic halides, which need to be treated in downstream waste gas facilities. Inorganic solids need to be discharged if they cannot be recycled or used elsewhere.

The installation is a source of noise, relating to the pressure generation. To abate noise the equipment needs to be closed.

Consumables are:

Consumable	Amount
Air, oxygen	
Energy [kWh/m^3]	

Monitoring

During the whole process a thorough monitoring of operating parameters such as pressure, temperature and oxygen content will inform about faultless working.

Economics

Type of costs	Costs	Remarks
Capital costs		
Operating costs		

3.3.4.2.6 Chemical Reduction

Description

Chemical reduction is the conversion of pollutants by chemical reduction agents to similar but less harmful or hazardous compounds. Common chemical reducing agents are, e.g.:

- sulphur dioxide
- sodium hydrogen sulphite/metabisulphite
- ferrous sulphate
- sodium sulphide and sodium hydrogen sulphide
- urea or amidosulphonic acid (at low pH).

They are brought into contact with the waste species under appropriate pH and concentration conditions. Chemical reduction normally results in products that can be treated more easily in downstream treatment facilities such as chemical precipitation.

The design of the treatment reactor depends on its special purpose. The basic facility is a continuously stirred tank reactor (CSTR), tailor-made according to the process requirements, e.g. corrosion- and pressure-resistant material or cover and ducts for gases arising. Additional installations should be provided to eliminate surplus reducing agent, e.g. hypochlorite or hydrogen peroxide to oxidise sulphite to sulphate. Adjustments to the design and operating parameters, e.g. by pH and redox potential (ORP) control, may alleviate this problem. Chemical reduction plants need not be especially sophisticated and costly. Where continuous / automatic processing is appropriate, the capital cost might be higher, but is normally compensated by lower operating costs. The process is performed in fully automatic units operated by monitoring a surrogate indicator parameter, typically the ORP.

Storage facilities need to be provided for the reduction agents, bearing in mind the hazardous potential of these substances.

Application

Chemical reduction is applied to waste water that contains contaminants that are not readily removable or have properties too harmful to allow them to be released into a common sewer system. The target contaminants are inorganic compounds: it is less effective with organic compounds.

Examples of such contaminants are:

- chromium(VI), which is reduced to chromium(III)
- chlorine or hypochlorite, which are reduced to chloride
- hydrogen peroxide, which is reduced to water and oxygen
- nitrite, using urea or amidosulphonic acid at low pH.

The frequent downstream operation in connection with chemical reduction is chemical precipitation.

Application limits and restrictions:

	Limits / restrictions
Substances	the number of affected inorganic substances is limited
pH, ORP	performance highly dependent on pH and ORP, thus strict control of these parameters essential
Reaction conditions	good stirring is required

Advantages and Disadvantages

Advantages	Disadvantages
• Waste water over a large concentration range can be treated (from some g/l down to less than 1 mg/l).	• Gas formation is common; with sulphide, the generation of hydrogen sulphide is possible.

Achievable Emissions Levels / Performance Rates

Reported removal efficiencies are very high.

Parameter	Performance rate [%]	Reduction agent	Remarks
Chromium(VI)			
Chlorine			
Hypochlorite			
Hydrogen peroxide			

Cross-media Effects

No particular environmental problems are to be considered. The arising gases are captured and ducted to downstream waste gas treatment facilities.

Consumables are:

Consumable	Amount
Reduction agent	
Chemical agent to destroy surplus reaction agents	
Energy [kWh/m^3]	

The consumption of reduction agent depends on the contaminant load; the consumption of chemicals to destroy surplus reactants depends on the processing quality.

Monitoring

The reaction is monitored and controlled by independent control loops:

• caustic/acid addition by pH control
• reducing agent addition by ORP control.

The effluent needs to be checked for surplus reduction agents.

Economics

Combined with high contaminant concentrations and the large amount of reducing agent there might be other treatment techniques that are more cost-effective.

Type of costs	Costs	Remarks
Capital costs		
Operating costs		

3.3.4.2.7   Chemical Hydrolysis

Description

Basically, hydrolysis is a destructive technology. It is a chemical reaction in which organic and inorganic constituents react with water, breaking into smaller compounds. In some cases, the reaction continues and other products – usually short-chained and easily biodegradable compounds – are formed. Downstream treatment of the chemically hydrolysed stream is generally required, e.g. in a central biological WWTP.

The design of a hydrolysis reactor depends on its purpose. Normally, hydrolysis processes are operated at ambient pressure and temperature. When high temperature is required, the reactor has to be fitted with a heat exchanger system with pre-heating facilities for the waste water input. In some cases, autoclaves may be required, thus ensuring temperatures well above 100 °C and pressures up to 0.5–1 MPa. Processes are batch-based and require staff to charge and empty the vessel. If low(er) boiling compounds are obtained from the chemical degradation of the pollutants, the plant may also be provided with vacuum facilities to remove contaminated liquid and vapour and enable the application of more than one temperature and pressure cycle without the need to open the vessel.

Since surplus acid or base has to be neutralised after the treatment operation, additional installations need to be provided. Safety requirements to handle strong acids and bases are strict. Their use entails special corrosion-resistant equipment.

Storage facilities need to be provided for acids and bases, bearing in mind the hazardous potential of these substances.

Application

Chemical hydrolysis is applied to waste water streams containing contaminants not readily biodegradable, or that might disturb the biological process in a downstream biological WWTP or have properties too harmful to allow them to be released into a common sewer system. Examples of such contaminants are:

- organic halides
- pesticides
- organic cyanides
- organic sulphides
- organophosphates
- carbamates
- esters
- amides.

Frequent operations in connection with chemical hydrolysis are:

- chemical neutralization
- chemical oxidation
- precipitation.

The reaction is highly dependent on chemical structure, pH and temperature:

- increase of temperature entails increase of hydrolysis rate
- low or high pH can increase the reaction rate, depending on the reagent, e.g. phosphoric acid esters and organic chlorides are preferably hydrolysed under alkaline conditions
- catalysts can increase the reaction rate.

Application limits and restrictions:

	Limits / restrictions
pH	either acidic or alkaline
Temperature	15–80 °C, up to 120 °C under pressure
Concentration range	1 mg/l–100 g/l
Substance properties	substances requiring too drastic operating conditions are unsuitable
Water solubility	low solubility in aqueous media can limit the applicability

Advantages and Disadvantages

Advantages	Disadvantages
• Waste water with a large range of refractory COD can be treated. • Process can be combined with many downstream treatment operations, such as GAC adsorption, air/vapour stripping, activated sludge biology.	• Chemical neutralisation of the hydrolysed stream is usually needed, thus entailing additional salt load to the recipient and/or additional sludge to be disposed of. • Gases and vapours may be released. • High pressure and / or heating are often needed, resulting in considerable energy consumption.

Achievable Emission Levels / Performance Rates

Removal efficiencies are strongly dependent on the compound's chemical structure, pH and temperature. Quantitative degradation can be achieved, but pilot studies are required to get the individual treatment conditions.

Parameter	Performance rate [%]	Reaction conditions	Remarks
COD			
AOX			

Since the elimination of refractory organic contents and/or inhibitors of subsequent biological treatment is the main goal, the performance evidence is not assessed by looking just at the efficiency of the hydrolysis process, but also by taking into account the efficiency of the subsequent biological process.

Cross-media Effects

Chemical hydrolysis with strong alkalis – NaOH and $Ca(OH)_2$ – or acids – H_2SO_4 – does not usually create cross-media transfer, e.g. from water to air and/or waste, to be disposed of.

Releases of odorous and/or volatile substances – if any are expected – are normally prevented by covering the vessel or operating in a closed tank and ducting the exhaust air to a waste gas abatement system.

Consumables are:

Consumable	Amount
Chemicals	
Steam / hot water for heating	
Energy [kWh/m^3]	

<u>**Monitoring**</u>

During the hydrolysis process a thorough monitoring of operating parameters, such as:

- temperature
- pH
- pressure
- residence time

is crucial. The effluent should be checked for specific compounds degraded and surplus acid / base agents.

<u>**Economics**</u>

The costs are:

Type of costs	Costs	Remarks
Capital costs		
Operating costs		

3.3.4.2.8   Nanofiltration (NF) and Reverse Osmosis (RO)

<u>**Description**</u>

A membrane process is the permeation of a liquid through a membrane, to be segregated into permeate that passes the membrane and concentrate that is retained. The driving force of this process is the pressure difference across the membrane.

NF and RO membranes can hold back all particles down to the size of organic molecules and even ions. Provided that the feed is particle-free, these membranes are mainly used when complete recycling of permeate and/or concentrate is desired.

The typical characteristics of NF and RO membranes are illustrated in Table 3.5.

Parameter	Nanofiltration	Reverse osmosis
Pore diameter [μm] [1]	0.01–0.001	<0.001
Operating pressure [MPa]	0.5-3 [2]	2-100 [3]
Cut-off size [nm] [2]	>1 200–1000 g/mol	<1000 g/mol
Permeate flow [l m^{-2} h^{-1}]	<100	10–35
Cross flow speed [m/s] [2]	1-2	<2
Membrane type	polymeric asymmetric or composite	polymeric asymmetric or composite
Membrane configuration	spiral-wound tubular	spiral-wound tubular

[1] [cww/tm/27]
[2] [cww/tm/132]
[3] [cww/tm/159]

Table 3.5: Characteristics of Nanofiltration (NF) and Reverse Osmosis (RO)

Membranes are available in several materials and configurations. The optimum modification for a particular application will depend on the nature of the waste water, since the different materials have varying resistances to dissolved substances. Membrane materials for NF are, e.g.:

- cellulose acetate
- polyamide.

Membrane materials for RO are organic polymers, such as:

- cellulose acetate
- polyamide
- polyimide
- polycarbonate
- polyvinylchloride
- polysulphone
- polyethersulphone
- polyacetal
- copolymers of acrylonitrile and vinyl chloride
- polyelectrolyte complexes
- cross-linked polyvinyl alcohol
- polyacrylates.

The polyamide-based membranes are normally superior to cellulose acetate-based membranes for the removal of trace organic molecules.

NF and RO processes are usually operated cross-flow, i.e. the permeate flow is directed perpendicular to the feed flow. The impurities remain in the feed which, reducing in volume, leaves the membrane system as a concentrated waste stream.

Even under the best pretreatment regimes and programmes, membranes will foul and deteriorate in performance if cleaning is not ensured. So membrane systems should be designed in such a way that those modules can be taken offline and cleaned mechanically or chemically.

An industrial membrane plant usually consists of three separate sections:

- the pretreatment section where the feed is treated by chemical clarification (precipitation, coagulation/flocculation or flotation) and subsequent filtration, or by filtration and subsequent UF
- the membrane section where high pressure is applied and the waste water cross-flowed across the membrane
- the post-treatment section where the permeate is prepared for re-use or discharge, and the concentrate brine collected for further work-up or disposal.

As an example a typical RO arrangement is illustrated in Figure 3.24 [cww/tm/4].

Membrane units are arranged as modules either in parallel – to provide the necessary hydraulic capacity – or in series – to increase the degree of efficiency.
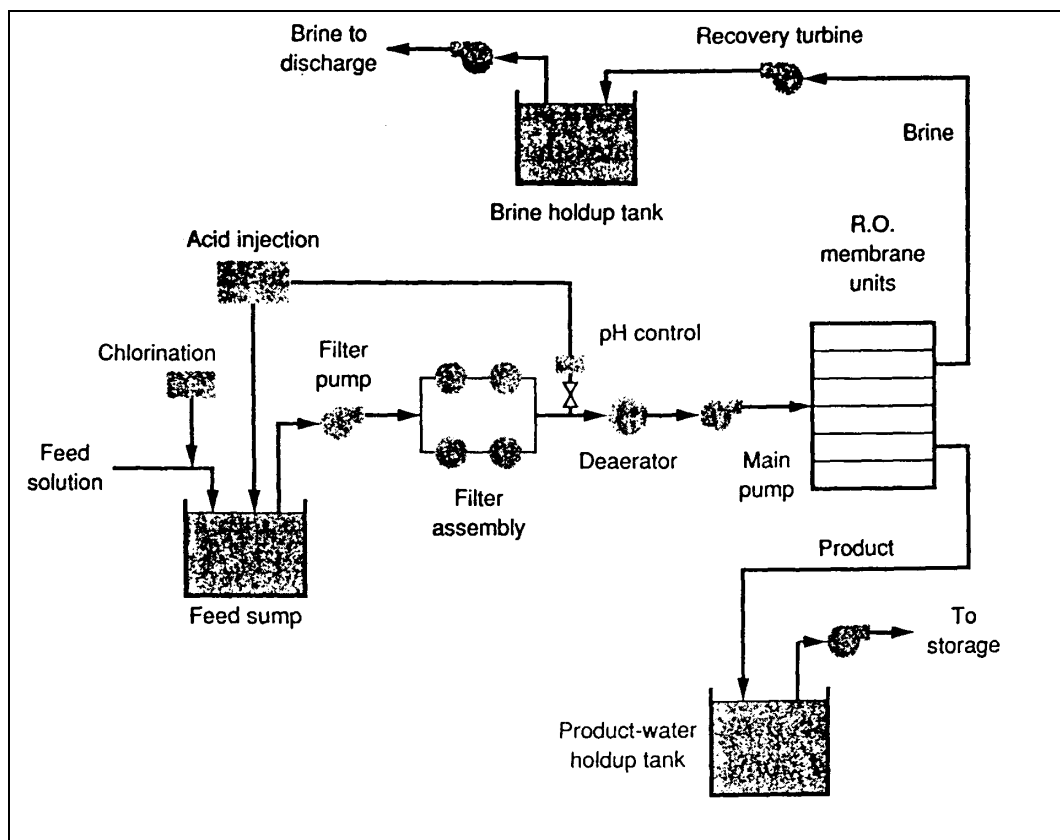
Figure 3.24: RO Arrangement

<u>Application</u>

NF and RO have different applications because of the different properties they exhibit in the migration of molecular particles through their surface.

NF is applied to remove larger organic molecules and multivalent ions in order to recycle and re-use the waste water or reduce its volume and simultaneously increase the concentration of contaminants to such an extent that subsequent destruction processes are feasible.

RO is a process to separate water and the dissolved constituents down to ionic species. It is applied when a high grade of purity is required. The segregated water phase is recycled and re-used. Examples are:

- desalination
- final removal of, e.g.:
    - degradable components if biological treatment is not available
    - heavy metals
    - toxic components
- segregation of pollutants with the aim of concentrating or further processing them.

NF and RO are often used in combination with post-treatment techniques for the permeate, e.g. ion exchange or GAC adsorption.

Application limits and restrictions:

		Limits / restrictions
NF	Particle size	restricted capacity to retain suspended particles with molecular weight <200
RO	Concentration	concentrated solutions with osmotic pressure so high that it either exceeds available operating pressure or is not economically viable
	Salt solubility	salt solutions with low solubility tend to precipitate and thus cause fouling
	Polymerisation monomers	contaminants tending to polymerisation cause fouling
Both	membrane material	low thermal and chemical resistance limits their application to a restricted pH and temperature range (18-30 °C)

Advantages and Disadvantages

Advantages	Disadvantages
• High separation efficiency. • Modular systems, i.e. flexible in usage. • Recycling of permeate and concentrate is possible. • Low operating temperatures. • Possibility of fully automatic operation.	• Clogging, plugging and fouling processes are possible. • Compaction in the presence of softening agents. • High pressures required. Low permeate fluxes.

Achievable Emission Levels / Performance Rates

Parameter	Performance rate [%]		Remarks
	NF	**RO**	
Inorganic mercury	>90 [1]		
Organic mercury	>90 [1]		
Cadmium compounds	>90 [1]		
Tetrachloromethane	96 [1]		
1,2-dichloroethane	71 [1]		
Trichlorobenzene	96 [1]		
Perchloroethene	90–92 [1]		
Atrazine	>70 [1]	84–97 [1]	
γ-Hexachlorocyclohexane		99 [1]	
DDT		100 [1]	
Aldrin		100 [1]	
Dieldrin		100 [1]	
Dichlorvos		98 [1]	
Simazine		95 [1]	
Trifluralin		99 [1]	
Fenitrothion		99 [1]	
Azinphos-methyl		98 [1]	
Malathion		99 [1]	
TOC	80-90 [2]		
[1] [cww/tm/27] [2] [cww/tm/160]			

Cross-media Effects

Membrane treatment produces a waste stream (concentrate) of approximately 10 % of the original feed volume, in which the target substances are present at levels approximately 10 times their concentration in the waste water. An assessment needs to be made as to whether this residue can be recycled, disposed of or needs further treatment, e.g. wet oxidation (concentrate from dye production [cww/tm/132]).

With organic substances the concentration increase might improve the conditions for subsequent oxidative destruction processes. With inorganic substances the concentration stage could be used as part of a recovery process. In both cases, the permeate water from a membrane process could potentially be re-used or recycled in the industrial process, thus reducing water input and discharge.

Consumables are:

Consumable	Amount	
	NF	**RO**
Membrane material		
Chemicals for cleaning		
Energy [kWh/m^3]	1-3 [a][1]	1-3 [a][1]
[a] low-pressure application, <2.5 MPa		
[1] [cww/tm/161]		

The energy consumption is directly related to the flow rate and pressure requirements. It is mainly associated with maintaining a minimum velocity of about 2 m/s across the membrane surface.

Monitoring

To ensure reliable operation, the pressure difference and flow across the membrane have to be monitored continuously.

Economics

	Flow rate [m^3/h]	Capital costs	Operating costs	Replacement costs
NF		GBP 350–1100 [1] per m^2 membrane [a]		GBP 60–140 [1] per m^2 membrane [a]
			EUR 3.3/kg TOC [2]	
RO		GBP 350–1100 [1] per m^2 membrane [a]		GBP 60–140 [1] per m^2 membrane [a]
		EUR 10–12 million per 1000 m^3/h waste water		
[a] for spiral and tubular membranes				
[1] [cww/tm/93]				
[2] [cww/tm/160]				

The capital costs, including automated cleaning facilities, can be broken down approximately as follows [cww/tm/93]:

pumps	30 %
replaceable membrane components	20 %
membrane modules (housings)	10 %
pipework, valves, framework	20 %
control system	15 %
other	5 %

The operating cost [cww/tm/93] is derived from:

- energy cost of maintaining the hydrostatic pressure and flow rate of the systems
- expected membrane life
- cleaning regime required
- site-specific factors, e.g. labour requirement.

They can be broken down approximately as follows [cww/tm/93]:

replaceable membrane components	35–50 %
cleaning	12–35 %
energy	15–20 %
labour	15–18 %

3.3.4.2.9   Adsorption

<u>Description</u>

Adsorption is the transfer of soluble substances (solutes) from the waste water phase to the surface of solid, highly porous, particles (the adsorbent). The adsorbent has a finite capacity for each compound to be removed. When this capacity is exhausted, the adsorbent is 'spent' and has to be replaced by fresh material. The spent adsorbent either has to be regenerated or incinerated.

Potential adsorbents for adsorptive waste water purification are listed in Table 3.6 [cww/tm/132].

Adsorbent	Form	Specific surface area [m²/g]	Pore volume [cm³/g]	Bulk density [g/l]
Activated carbon	granular	500–1000	0.3–0.8	300–550
	powder	600–1500	0.3-1.0	
Lignite coke	granular, powder	200–250	<0.1	about 500
γ-Aluminium oxide	granular, powder	300–350	0.4–0.5	700–800
Adsorber resins	granules	400-1500	porosity 35–65 v-%	650-700

Table 3.6: Commonly Used Adsorbents and their Properties

Adsorption processes are divided into [cww/tm/132]:

- mixing, usually used for batchwise treatment
- percolation, applicable to continuous treatment, normally with fixed-bed adsorber packed in two columns that are alternatively used on duty and backwashing
- pulse-bed or moving-bed process, as continuous percolation, waste water and adsorbent led in counter-current through the column.

Since the adsorbent active surface is often liable to clogging and blockage, the waste water needs to be free from solid content as completely as possible, which often makes an upstream filtration step necessary.

An example of the operating stages of a two-column fixed bed adsorber connected in series is illustrated in Figure 3.25 [cww/tm/132].

Adsorber vessels are usually built of corrosion-resistant material, e.g. lined carbon-steel, stainless steel or fibreglass-reinforced plastic (FRP).

Storage facilities for the adsorbent are necessary.
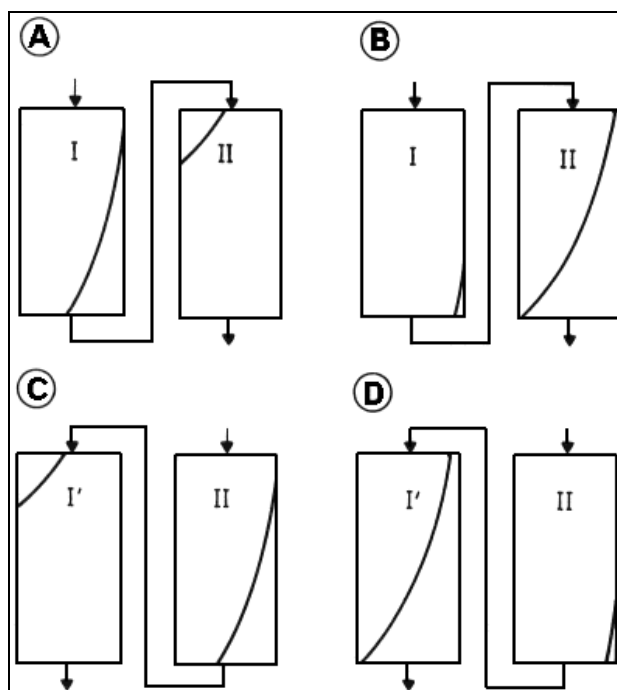
Figure 3.25: Operation of 2 Adsorption Columns Connected in Series
A) Sequence I → II, early in the process,
B) Sequence I → II, when filter I is due to be replaced,
C) Sequence II → I′, shortly after the replacement of I,
D) Sequence II → I′, when filter II is due for replacement

Application

The adsorbent most commonly used in the chemical sector is activated carbon. It is used as granulate (GAC) in columns or as powder (PAC) dosed to a treatment tank or basin. Other commonly used adsorbents are lignite coke, activated aluminium oxide, adsorber resins and zeolites.

- **GAC Adsorption** is applied to remove organic contaminants, mainly those with refractory, toxic, coloured and/or odorous characteristics, and residual amounts of inorganic contaminants, such as nitrogen compounds, sulphides and heavy metals. Granular medium filters, e.g. sand filters, are commonly used upstream of the GAC adsorber to remove the suspended solids present.

  Representative applications are [cww/tm/92]:

  - textiles and dyestuffs: removal of TOC, colour, dyes
  - oil refinery and petrochemical: removal of COD, BOD
  - detergents, resins, chemicals: removal of TOC, COD, xylene,
                                     alcohols, phenols, resin intermediates,
                                     resorcinol, nitrated aromatics, polyols
  - herbicides, insecticides: removal of chlorophenols, cresol
  - pharmaceuticals: removal of phenol
  - explosives: removal of nitrated phenols

  GAC is normally regenerated by thermal reactivation at temperatures of about 900-1000 °C.

- **PAC Adsorption** is applied to the same contaminants as GAC. It is dosed to the waste water to be treated as a slurry and subsequently removed by separation processes such as sedimentation and filtration. PAC can also be added to the waste water stream at the same point as the inorganic coagulants and removed by existing sedimentation and filtration devices. It is usually preferred where the requirement for adsorptive removal of organics is intermittent or variable. It can be dosed individually as and when it is needed. Another application is its use in emergency cases to remove refractory, hazardous or toxic substances that have escaped into a sedimentation tank, activated sludge tank or other vessel. PAC can also be added to the aeration basin of an activated sludge system, where the microbiological processes are enhanced by the adsorption process. PAC adsorbents are typically used with a mixer-settler or slurry adsorber arrangement in combination with coagulation/flocculation agents, with the PAC being added in the flocculation, sedimentation or filtration step.

  Normally PAC is not regenerated but becomes part of the sludge to be disposed of.

- **Lignite Coke** is processed and applied like GAC and might replace it when lower cleaning effects are sufficient. Its lower price is set against its lower adsorption efficiency, thus requiring larger amounts of adsorbent or more frequent regeneration cycles.

- **Activated aluminium oxide** is used to adsorb hydrophilic substances, e.g. fluoride and phosphate. When it is contaminated with organic substances, it is regenerated thermally at a temperature of about 750 °C. If it is contaminated with inorganic substances, it is regenerated chemically.

- **Adsorber resins** are applied for the targeted removal of both hydrophobic and hydrophilic organic contaminants, e.g. to facilitate the recovery of the organic compounds. The resins tend to swell in the course of time by taking up the organic compounds.

  Adsorber resins are regenerated chemically with solvents such as methanol or acetone.

- **Zeolites** are applied to remove ammonia or heavy metals, e.g. cadmium. When applied to ammonia removal, they are only effective on very weak streams (up to 40 mg/l). They are regenerated by elution with solutions of sodium chloride with caustic soda or lime.

Application limits and restrictions:

	Limits / restrictions
TSS	<20 mg/l with fixed bed adsorbers [1] <10 mg/l with moving bed adsorbers [2]
Pollutant concentration	<100 g/l (without adsorbent recovery) [2] <500 g/l (with adsorbent recovery) [2]
Molecular mass	decreased efficiency with low molecular mass
Length of carbon chain	decreased efficiency with increasing carbon chain
Branching of carbon chain	decreased efficiency with increasing branching
Polarity	decreased efficiency with high polarity
Solubility in water	decreased efficiency with high solubility
Degree of dissociation	decreased efficiency with increase of dissociation
Macromolecules	decreased efficiency with macromolecular structure
[1] [cww/tm/4] [2] [cww/tm/51]	

The influence of polarity is demonstrated in Table 3.7 [cww/tm/91]

Substance	Removal [%]	Capacity [mg/g]
Benzene	95	80
Ethylbenzene	84	19
Butyl acetate	84	169
Ethyl acetate	51	100
Phenol	81	161
Methyl ethyl ketone (MEK)	47	94
Acetone	22	43
Pyridine	47	95
Diethanol amine	28	57
Monoethanol amine	7	15
Acetaldehyde	12	22
Formaldehyde	9	18
Isopropyl alcohol	22	24
Methyl alcohol	4	7

Table 3.7: Typical Performance Characteristics of GAC Adsorption with Feed Concentrations of about 1000 mg/l

Advantages and Disadvantages

Advantages	Disadvantages
• High removal efficiency (not lignite coke). • Enables removal of refractory and/or toxic organic compounds (GAC, PAC, lignite coke, resins). • Usually low extra space requirement. • Systems automated. • Recovery of compounds possible (preferably with zeolites).	• Mixtures of organic compounds may cause a significantly reduced adsorption capacity. • High content of macromolecular compounds decreases efficiency and may cause irreversible blockage of active sites. • Scouring effect in the activated sludge unit causing major erosion problem (PAC). • Spent adsorbent has to be regenerated (high energy consumption) or disposed of (causing waste to be incinerated).

Achievable Emission Values / Performance Rates

The efficiency of adsorption processes varies widely with waste water composition and feed concentration, which should be borne in mind when references to achievable emissions or removal efficiencies are cited.

Achievable performance rates are:

Parameter	Performance Rate [%]						Remarks
	GAC	PAC	Lignite	Al$_2$O$_3$	Resin	Zeolite	
Inorganic Hg	80 [1]						feed 29 µg/l
Organic Hg	80 [1]						low feed
γ-Hexa-chloro-cyclo-hexane	93 [1]						feed 7.7 µg/l
		99 [1]					feed 10 µg/l PAC 85 mg/l
DDT	97 [1]-99.9						
Aldrin	88-93 [1]						
		90-99 [1]					PAC 5-20 mg/l
Dieldrin	86-98 [1]						
		99 [1] [0.1 µg/l]					feed 10 µg/l, PAC 126 mg/l
Atrazin	84 [1]						feed 0.61 µg/l

Parameter	Performance Rate [%]						Remarks
	GAC	**PAC**	**Lignite**	**Al$_2$O$_3$**	**Resin**	**Zeolite**	
Endrin		<0.1 µg/l [1]					feed 10 µg/l, PAC 70 mg/l
Dichlorvos		99 [1]					
TCB		70-93 [1]					feed 200 µg/l PAC 20 mg/l
Fenitrothion		99 [1]					
Azinphos-methyl		99 [1]					
Ammonia						98 [1] [0.5 mg/l]	feed 25 mg/l
COD	50 [2]						moving bed, feed 5 g/l
	67-75 [3] [<100 mg/l]						feed concentra-tion 300-400 mg/l
Phenols	75 [2]						moving bed, feed 70 mg/l
	60-80 [3] [1-2 mg/l]						feed concentra-tion 5 mg/l
AOX	>90 [2]						moving bed, feed 60 mg/l

[1] [cww/tm/27]
[2] [cww/tm/82]
[3] [cww/tm/96]

PAC treatment systems are reported [cww/tm/77] to treat waste water with a COD higher than 60000 mg/l, including toxic volatile organic compounds higher than 1000 mg/l with a reduction of specific toxic organic chemicals to below the detection limit, i.e. about 100 % reduction.

Cross-media Effects

When the adsorptive capacity of the adsorbent has been exhausted it will be replaced and subsequently regenerated (with the exception of PAC which is disposed of together with other waste water sludge). As mentioned above, the adsorbents have their own different regeneration methods. Common to these methods is, however, that they need energy and/or chemicals for their operation.

GAC, lignite and activated aluminium oxide (when carrying organic load) are thermally regenerated at temperatures up to 750–1000 °C. Resins, zeolites and activated aluminium oxide carrying inorganic load are eluted with chemicals, either organic solvents or inorganic solutions.

For example, the regeneration process of GAC releases off-gases that contain the thermal and chemical decomposition products of the adsorbed compounds. With each regeneration a proportion of about 10 % will be lost [cww/tm/27] and has to be replaced by fresh GAC. This continuous renewal should be adequate to maintain the overall quality of the GAC in the bed. The regeneration of GAC would normally be carried out by specialist companies, which operate regeneration furnaces. These companies will transport GAC from the consuming treatment plant to the regeneration furnaces and vice versa. As regeneration is relatively expensive, plants are usually designed to give a period of at least six months between regeneration cycles.

The generation of off-gases with regeneration causes subsequent waste gas treatment, if not at the chemical site itself, then at the site of the regenerating company.

If the GAC cannot be regenerated, it has to be disposed of as chemical waste and incinerated. This might be the case if the GAC is contaminated with PCBs, dioxins, heavy metals or dichlorobromopropane (DCBP) [cww/tm/77].

The regeneration of the zeolite adsorbent generates a concentrated stream of ammonia, which is ducted to a conventional waste water treatment plant for biological treatment or, alternatively,

undergoes a treatment comprised of air stripping to recover ammonia, followed by adsorption in dilute acid to form a fertiliser which can be sold.

Consumables are:

Consumable	GAC	PAC	Lignite	Al₂O₃	Resin	Zeolite
Adsorbent	10 % loss per regeneration	0.5-1.0 kg/m^3 waste water [1]				
Chemicals for regeneration						NaCl/NaOH or lime 10-30 bed volumes [2]
Energy [kWh/m^3]						
[1] [cww/tm/128] [2] [cww/tm/27]						

Further impacts on the environment are:

- the transport of spent GAC to and from regeneration
- the regeneration operation itself at the site of a specialist company
- the energy consumption for the regeneration process
- the release of contaminants to water and/or air during this regeneration process
- sources of noise, e.g. the pumps, which can be enclosed.

Monitoring

Input and output of the adsorber device has to be monitored according to the compounds in question. Normally a TOC measurement (for organic contaminants) or a conductivity measurement for inorganic contaminants would be the method of choice for a breakthrough warning.

Economics

Costs	GAC	PAC	Lignite	Al₂O₃	Resin	Zeolite
Capital	GBP 30000 [1] [14 m^3/h]					
	GBP 75000 [1] [60 m^3/h]					
	GBP 110000 [1] [120 m^3/h]					
	FIM 20-30 million [3] [350 m^3/h]					
Operating	GBP 1000-2000 [1] per tonne GAC [a]					
	BEF 200000 [2] per tonne GAC [b]					
	FIM 0.7/m^3 waste water [3]					
[a] regeneration cost of GAC [b] cost of GAC inclusive regeneration [1] [cww/tm/92] [2] [cww/tm/128] [3] [cww/tm 96]						

3.3.4.2.10   Ion Exchange

Description

Ion Exchange is the removal of undesired or hazardous ionic constituents of waste water and their replacement by more acceptable ions from an ion exchange resin, where they are temporarily retained and afterwards released into a regeneration or backwashing liquid.

The equipment of an ion exchanger usually consists of:

- a vertical cylindrical pressure vessel with corrosion-resistant linings that contains the resin, usually as a packed column with several possible configurations
- a control valves and piping system, directing the flow of waste water and regeneration solution to the proper locations
- a system to regenerate the resin, consisting of salt-dissolving and dilution control equipment.

An inlet distribution system is located at either the top or the bottom of the vessel and provides even distribution of the influent waste water, to prevent hollowing out flow channels in the resin bed. It also acts as collector for backwash water.

Ion exchangers commonly in use are macroporous granule resins with cationic or anionic functional groups, such as:

- strong acid cation exchangers (SAC), neutralising strong bases and converting neutral salts into their corresponding acids
- weak acid cation exchangers (WAC), able to neutralise strong bases and used for dealkalisation
- strong base anion exchangers (SBA), neutralising strong acids and converting neutral salts into their corresponding bases
- weak base anion exchangers (WBA), neutralising strong acids and used for partial demineralisation.

The ion exchange operation cycle comprises:

- the actual ion exchange operation
- the backwash stage, including removal of accumulated particles and reclassification of the ion exchange resin bed
- the regeneration stage, using a low volume/high concentration solution, reloading the ion exchange resin with the respective ion, and releasing the unwanted ion species to the regeneration solution
- the displacement, or slow rinse, with a slow water-flow displacing the regeneration solution through the bed
- the fast rinse, removing the remaining traces of the regeneration solution, including any residual hardness, from the resin bed.

Storage facilities for the regeneration chemicals are necessary.

Application

Ion exchange is applied to remove unwanted ionic and ionisable species from waste water, e.g.:

- heavy metal ions – cationic or anionic, e.g. Cr^{3+} or cadmium and its compounds, with low feed concentrations, CrO_4^{2-} also with high feed concentrations
- ionisable inorganic compounds, such as H_3BO_3
- soluble, ionic or ionisable organic compounds, e.g. carboxylic acids, sulphonic acids, some phenols, amines as acid salt, quaternary amines, alkylsulphates and organic mercury can be removed.

Ion exchange is feasible as an end-of-pipe treatment, but its greatest value lies in its recovery potential. It is commonly used as an integrated operation in waste water treatment, e.g. to recover rinse water and process chemicals. Typical influent concentrations are between 10 and 1000 mg/l. Suspended particles in the feed should be less than 50 mg/l to prevent plugging, thus gravity or membrane filtration are appropriate pretreatments.

Application limits and restrictions:

	Limits / restrictions
Ion concentration	high ionic strength can cause swelling of resin particles
Temperature	thermal limits of anion resins generally in the vicinity of about 60 °C
Corrosive agents	nitric acid, chromic acid, hydrogen peroxide, iron, manganese, copper can damage the resins
Interfering compounds	inorganic compounds such as iron precipitates, or organic compounds such as aromatics, can cause irreversible adsorption to the resin

Advantages and Disadvantages

Advantages	Disadvantages
• In principle all ions and ionisable species can be removed from aqueous liquids. • It operates on demand, relatively insensitive to flow variations. • High efficiency possible. • Recovery of valuable species is possible. • Water recovery possible. • A large variety of specific resins are available.	• Pre-filtration is required. • Bacteria growth on the resin surface and fouling caused by precipitation or adsorption. • Interference of competing ions in the waste water. • Attrition of resin particles, due to regeneration or mechanical impacts. • The brine and sludge resulting from regeneration has to be treated or disposed of.

Achievable Emission Levels / Performance Rates

Typical effluent ion concentrations that can be achieved are in the range of 0.1–10 mg/l with influent concentrations of 10–1000 mg/l.

Parameter	Concentration [mg/l]	Performance rate [%]	Remarks
Effluent ion	0.1–10	80–99 [1]	influent concentrations of 10–1000 mg/l
Copper			
Nickel			
Cobalt			
Zinc			
Chromium(III)			
Chromium(VI)			
Iron			
Sulphate			
Nitrate			
[1] [cww/tm/128]			

Cross-media Effects

The regeneration of ion exchange resins results in a small volume of concentrated acid or salt solution, containing the removed ions originating from the resin. This enriched liquid has to be treated separately to remove these ions, e.g. heavy metals by precipitation.

The rinsing water from regeneration contains the same ions as the brine, but in relatively low concentrations. Whether this part can be discharged directly or has to undergo treatment depends on the actual concentrations.

Consumables are:

Consumable	Amount
Ion exchange resin	
Regeneration liquid (hydrochloric acid, sulphuric acid, sodium chloride, sodium hydroxide, etc.	depends on amount of resin
Chemicals, e.g. microbiological fouling suppressors	
Backwash and rinsing water	
Energy [kWh/m^3]	

Sources of noise are the pumps, which can be enclosed.

Monitoring

Influent and effluent of the ion exchange vessel have to be carefully monitored for the occurrence of breakthrough. The parameters that need to be controlled are:

- pressure drop
- electrical conductivity
- pH
- effluent concentration of the ion(s) to be controlled.

Economics

Capital and operating costs depend on the nature of the feed stream.

Type of costs	Costs	Remarks
Capital costs	GBP 60000 [1] + GBP 20000 [1]	packed height of 1 m and diameter of 1 m, vessel, valves and resin included; for additional 0.5 m of diameter
	BEF 80000/m^3 [2]	cationic ion exchanger
	BEF 200000/m^3 [2]	anionic ion exchanger
Operating costs	BEF 200/m^3 [2]	
[1] [cww/tm/92] [2] [cww/tm/128]		

3.3.4.2.11   Extraction

Description

Extraction means transferring soluble contaminants from the waste water phase into a solvent. Desirable properties for suitable solvents are:

- low solubility and miscibility in water; examples are light crude oil, toluene, pentane and hexane
- greater dissolution capacity of the contaminant than water
- easy separation of solvent and waste water, e.g. because of large density difference

- easy separation of contaminants, e.g. because of low evaporation heat when distillation is applied
- low toxicity
- thermal stability.

Extraction is operated in columns where the waste water is brought into contact with the organic solvent in different ways, e.g.:

- counter-current cascades
- mixer-settler contactors
- sieve plate columns
- packed columns
- spray towers
- rotating disc contactors
- centrifugal contactors for low density differences.

Downstream facilities are operated for liquid/liquid separation and distillation of the solvent fraction. The remaining waste water phase normally has to get rid of the dissolved extraction solvent, e.g. by stripping or GAC adsorption.

Storage facilities for the extraction solvent and the residue have to be provided for, equipped with the necessary safety items to prevent emissions to air and soil.

Application

Solvent extraction is used with a variety of organic contaminants and metal complexes, when a suitable solvent is available and if the contaminant concentration is not too low. At low concentrations, extraction is not compatible with adsorption or biological treatment. It is often used as a pretreatment to adsorption and/or biological treatment units.

Examples are [cww/tm/82]:

- removal of phenol (phenosolvan process)
- recycling of metals, such as zinc
- recycling of substances from mother liquors
- removal of phosphoric acid esters
- removal of chloro-aromatics
- pretreatment concentration of aromatic sulphonic acids.

Application limits and restrictions:

	Limits / restrictions
Suspended solids	waste water should preferably be almost free of suspended solids and/or emulsions
Solvent	suitability of the solvent (see above); solvent loss entails costs and environmental impact; solvent regeneration can be very complicated and cost-intensive

Advantages and Disadvantages

Advantages	Disadvantages
- Enables removal and recycling of refractory and/or toxic organic compounds and some metals.	- Residues have to be disposed of or incinerated. - Limited application because of solvent characteristics.

Achievable Emission Levels / Performance Rates

Parameter	Performance rate [%]	Emission level [mg/l]	Remarks
Phenols	99	<1	feed 10 g/l
COD			
AOX			
Zinc			
Phosphoric acid esters			

Cross-media Effects

The loss of organic solvent during operation causes emissions of waste gas or of solvent residue to waste water. The latter usually requires additional treatment, e.g. stripping, the former a ducted removal to, e.g., thermal/catalytic oxidation or adsorption.

After solvent recovery (distillation or rectification) the bottom residue that contains the extracted contaminants has to be disposed of as chemical waste, normally by incineration.

Consumables are:

Consumable	Amount
Solvent, replacement of losses	
Energy [kWh/m^3]	
Energy of subsequent treatment [kWh/m^3]	

Monitoring

The input to the extraction unit has to be checked to prevent unwanted solids entering, which might cause disturbance to the process or destruction to the plant. Regular maintenance is necessary in order to prevent or detect solvent losses to the environment.

Economics

The costs are:

Type of costs	Costs	Remarks
Capital costs		
Operating costs		

3.3.4.2.12   Distillation / Rectification

Description

Distillation or rectification is the separation of waste water from its contaminants by transferring them into the vapour phase. The enriched vapour phase is condensed afterwards.

Operating the process under vacuum conditions lowers the boiling temperature and allows the separation of vulnerable substances.

Distillation and rectification are performed in columns, equipped with plates or packing material, and a downstream condenser device. The heating is often done by direct steam injection to avoid local overheating.

Storage facilities equipped with the necessary safety items have to be provided for distillate and residue.

Application

Waste water distillation or rectification has a limited application. It is often used as a process-integrated measure to recover starting material and/or product from mother liquors. As a waste water treatment operation it is applied, e.g.:

- to recover solvent after waste water extraction
- to recover solvent from waste water, e.g. separation of alcohols from methyl cellulose production
- to treat oil emulsions
- as a pretreatment to remove the main contaminant content from the waste water stream to recover it and afterwards discharge the waste water to further downstream treatment
- to recover organics from scrubbing liquors.

Application limits and restrictions:

	Limits / restrictions
Feed concentration	needs to be large enough for distillation to become economically feasible
Boiling temperature	sufficient difference between boiling temperatures of waste water and contaminants; azeotropic mixtures need auxiliaries, or distillative separation is not possible

Advantages and Disadvantages

Advantages	Disadvantages
- Material recovery is possible. - Enables removal of refractory and/or toxic organic compounds.	- Residues have to be disposed of, usually by incineration. - High energy consumption.

Achievable Emission Levels / Performance Rates

Parameter	Performance rate [%]	Emission level [mg/l]	Remarks
Phenols	96 [1]	2000	feed 50 g/l
Methanol	97.5 [1]	2000	feed 80 g/l
Epichlorohydrine (ECH)	90 [1]	700	feed 7 g/l
Aniline	97.5 [1]	100	feed 4 g/l
Chlorobenzene	90 [1]	10	feed 100 mg/l
[1] [cww/tm/82]			

Cross-media Effects

Consumables are:

Consumable	Amount
Steam (for heating)	
Energy [kWh/m^3]	
Energy of subsequent treatment [kWh/m^3]	

Monitoring

The input to the distillation/rectification unit has to be checked to prevent the entrance of unwanted solids that might cause disturbance to the process or damage to the plant. Regular maintenance is necessary so that solvent losses to the environment do not occur or can be detected in time.

Economics

The costs are:

Type of costs	Costs	Remarks
Capital costs		
Operating costs		

3.3.4.2.13   Evaporation

Description

Evaporation of waste water is a distillation process where water is the volatile substance, leaving the concentrate as bottom residue to be disposed of. The aim of this operation is to reduce the volume of waste water or to concentrate mother liquors. The volatile steam is collected in a condenser and the condensed water is, if needed after subsequent treatment, recycled.

Operating under vacuum decreases the boiling temperature and enables recycling of substances that would otherwise decompose.

There are many types of evaporators. Their suitability depends on the individual requirements. Examples of evaporators are:

- natural-circulation evaporators, suitable for material not sensitive to heat
- short-tube vertical evaporators, suitable for non-corrosive or non-crystallising liquors
- basket-type evaporators, same application as short-tube evaporators
- falling film evaporators, used in fertiliser industry to concentrate urea, phosphoric acid, ammonium nitrate etc.
- agitated thin film evaporators, used for concentrating, fractionating, deodorizing and stripping in the production of pharmaceuticals, polymers, organic and inorganic chemicals.

Evaporators are usually operated in series, where the condensation heat of one stage heats the condensate (i.e. waste water) of the preceding stage. Operation under vacuum minimises energy demand. Normal operation conditions are 12–20 kPa and 50–60 °C.

Storage facilities have to be provided for residues before their disposal (or recycling).

Application

Evaporation is applied when concentrated waste water streams are wanted or recommended, e.g.:

- to concentrate mother liquors and liquors from waste gas scrubbing to recycle valuable substances
- to evaporate and crystallise solids, either to recover or remove them from the waste water effluent
- as pretreatment in order to concentrate the waste stream before thermal exploitation, waste water incineration or disposal as hazardous waste.

Evaporation units should be operated in such a way that the necessary thermal energy is delivered by exploiting the waste heat of production processes [cww/tm/82].

When material recovery is the main purpose, a pretreatment operation is required before evaporation can be started. Examples of pretreatment are:

- addition of acids, bases etc. to lower the volatility of molecular compounds
- separation of insoluble, free liquid phases, e.g. oil
- chemical/physical operations to separate heavy metals and/or other solids.

Further treatment, e.g. incineration, after evaporation is required, if the concentrate is not recycled.

Application limits and restrictions:

	Limits / restrictions
Fouling	heat exchangers tend to fouling
Corrosion	the evaporator body and the heat exchanger(s) are vulnerable to corrosive substances
Substances	foam generating substances and colloidal and suspended particles disturb the process; volatile inorganic / organic substances evaporate as well

Advantages and Disadvantages

Advantages	**Disadvantages**
- Material recovery possible. - Enables removal of refractory and/or toxic organic compounds from waste water. - Reduces waste water amount. - Reduces amount and volume of hazardous waste.	- Residues have to be disposed of, normally by incineration, if not suitable for recycling. - Volatile contaminants pollute the condensate (entailing subsequent treatment) or are emitted as waste gas. - Vulnerable to fouling, corrosion and foaming. - High energy consumption.

Achievable Emission Levels / Performance Rates

Parameter	**Performance rate [%]**	**Remarks**
Contaminants	99 [1]	condensate not recycled

[1] [cww/tm/128]

Cross-media Effects

Evaporation is normally a 'waste water-free' process, because the condensate will be recycled – with or without further treatment – and the concentrate will be recycled or disposed of as waste, e.g. by incineration.

Consumables are:

Consumable	**Amount**
Chemicals for pretreatment	
Steam (for heating)	5–16 kg water/kg steam
Energy [kWh/m^3]	

Monitoring

Proper maintenance of the heat exchangers is a crucial point. Encrustations, fouling and corrosion disturb the heat transfer to the liquid and decrease the energy efficiency. The concentration of contaminants, or surrogate parameters (TOC, pH, conductivity etc.) in the condensate need continuous monitoring to prevent the transfer of pollutants.

<u>**Economics**</u>

The costs are:

Type of costs	Costs	Remarks
Capital costs		
Operating costs	BEF 100-2000 per m^3 condensate [1]	

[1] [cww/tm/128]

3.3.4.2.14   Stripping

<u>**Description**</u>

Waste water stripping is an operation in which waste water is brought into contact with a high flow of a gas current in order to transfer volatile pollutants from the water phase to the gas phase. The pollutants are removed from the stripping gas so it can be recycled into the process and re-used. Volatile organics and inorganics are transferred from waste water to waste gas, greatly increasing the surface area of the contaminated water exposed. Water evaporation, however, decreases the temperature of the waste water, thus decreasing the volatility of the contaminants.

The gases in use are air and steam:

- air stripping can be operated with or without heating the stripping column, the latter used with highly volatile or vulnerable compounds. The necessary heating energy is usually supplied by exploiting process heat.
- steam stripping as an alternative to air stripping is applied to compounds that are less volatile and/or less vulnerable. Steam is normally delivered by the steam generation equipment already existing on the site or by exploited waste heat. If there is no existing steam generation equipment, steam stripping might not be economically feasible.

The most common stripping facilities are:

- packed tower stripper, with spray nozzles at the top to distribute waste water over the packing, the stripping gas led counter-current through the packing, a sump at the bottom to collect the decontaminated water, additionally equipped with an air heater (for air stripping), automated control system and air emission control system (GAC unit, catalytic oxidiser or incinerator)
- stripping tank, in which volatile compounds are stripped by bubbling gas (air, steam) into a waste water ducting tank.

The equipment consists of:

- a buffer tank for waste water
- a pretreatment tank for pH adjustment
- stripping column(s), operated counter-flow
- feed preheater, recovering heat from the subsequent strip steam condenser
- condenser, air or water cooled
- downstream facilities for gas treatment.

Strippers can be operated continuously or batchwise, the latter ensuring consistent performance and higher energy efficiency than continuously operated units.

The subsequent removal of the volatile pollutants from the gas phase can be accomplished by:

- adsorption on GAC, zeolite or synthetic resins
- absorption by non-aqueous solvent and subsequent desorption
- absorption by aqueous solutions, such as strong acids (to absorb ammonia)
- condensation or partial condensation and subsequent further treatment
- thermal or catalytic oxidation.

An example of a stripping process, the air / steam stripping of ammonia, is illustrated in Figure 3.26 [cww/tm/78].
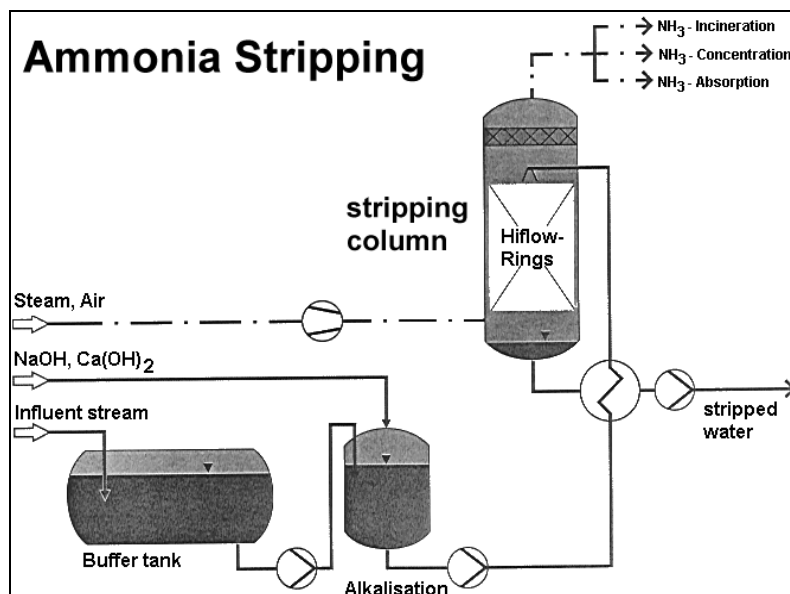
Figure 3.26: Stripping of Ammonia, Air and Steam Stripping

Application

Stripping is applied to separate volatile contaminants from water, e.g.:

- chlorinated hydrocarbons, such as trichloroethene, perchloroethene, trichloromethane, dichloroethane, trichloroethane
- ammonia and hydrogen sulphide, their volatility strongly dependent on temperature and pH, thus pH control is essential (pH >9.5 with ammonia, pH 2-3 with hydrogen sulphide)
- ammonia and hydrogen sulphide together in a two-stage steam stripping unit [cww/tm/149]
- organic solvents, petrol, diesel fuel, low aromatics, phenol, mercaptanes.

Whether air stripping or steam stripping is applied depends on:

- the vulnerability of the contaminants
- whether the contaminants are to be recovered
- the availability of steam
- safety conditions (only an issue for high loads of VOCs), etc.

Application limits and restrictions:

	Limits / restrictions
Fouling	heat exchangers tend to fouling
Suspended solids	<5 ppm

Advantages and Disadvantages

Advantages	Disadvantages
• High removal efficiency. • Material recovery is possible. • Low pressure drop. • Low energy consumption.	• Under certain conditions (iron >5 mg/l, water hardness >800 mg/l) high capacity for fouling (e.g. sour water strippers in refineries) and therefore injection of anti-fouling agents necessary. • Stripping gas has to be treated. • Frequent column cleaning required.

Achievable Emission Levels / Performance Rates

Parameter	Performance rate [%]		Emission level [mg/l]		Remarks
	Air	Steam	Air	Steam	
Ammonia			<5 [1]		refinery: low feed concentrations and optimum conditions (examples: sour water stripping)
		99 [2]		<50 [2]	feed 10 g/l
	>92 [4]		70 [4]		filtrate from treatment of activated sludge, feed 500-1200 mg/l, feed rate 19-24 m³/h
NH₄-N				5 [3]	refinery: 2-stage process, feed 1372 mg/l NH₄-N [a]
Total inorganic N				7 [3]	refinery: 2-stage process, feed 1373 mg/l total inorg. N
Volatile organics	99 [1]				feed rate 1 m³/h, concentration 2 g/l (dichloromethane, trichloro-methane, benzene, toluene, xylene, esters, ethers
Methanol		97			feed rate 3.4 m³/h, concentration 36 g/l
Chloromethane				<1 [1]	feed rate 6 m³/h, concentration >200 mg/l
Dichloromethane		99 [1]			feed rate 4 m³/h, concentration 5 g/l
Tetrachloromethane	90-98 [2]				packed tower, air/water 5-35:1
1,2-Dichloroethane	65 [2]				packed tower, air/water 35:1
Trichloroethene	69-92 [2]				packed tower, air/water 4-30:1
	90 [2]				spray aeration
Perchloroethene	95 [2]				packed tower, air/water 5:1
	90 [2]				spray aeration
Methylal		99 [1]			feed rate 4 m³/h, concentration 30 g/l
Hydrocarbons				1.1 [3]	refinery: 2-stage process, feed 98 mg/l hydrocarbons
BTX		>99 [1]			feed 400 m³/h, concentration 500-1000 mg/l BTX
Hydrogen sulphide			<20		refinery: sour gas stripping
Mercaptans			<20		refinery: sour gas stripping
Phenols		99-99.6 [5]		50-200 [5]	feed 7-8 m³/h, concentration 20-40 g/l
				0.1 [3]	refinery: 2-stage process, feed 182 mg/l phenols
Sulphide				0.5 [3]	refinery: 2-stage process, feed 1323 mg/l sulphide
COD				37 [3]	refinery: 2-stage process, feed 14400 mg/l COD

[a] stripped ammonia concentrated to 10 % solution and used for de-NOₓ process in another plant
[1] [cww/tm/82]
[2] [cww/tm/27]
[3] [cww/tm/149]
[4] [cww/tm/146]
[5] [cww/tm/96]

Cross-media Effects

Stripping is not used as an individual process. It needs at least downstream gas treatment. The removed volatiles are either recycled to a production process or treated (scrubbing, adsorption, thermal or catalytic oxidation). Generally speaking, the treatment of the stripping gas is an essential process step and sometimes more complicated than the stripping operation itself. To obtain an efficient treatment in total, both the stripping stage and the stripping gas treatment have to be carefully adjusted to each other.

If the achieved emission level for waste water is not sufficient (see the achievable emission levels), further treatment downstream needs to be available.

Consumables are:

Consumable	Amount	
	Air stripping	**Steam stripping**
Chemicals to adjust pH (acid, caustic soda, lime)	stoichiometric	stoichiometric
Anti-fouling agents		
Steam		0.1-0.3 tonne/m^3 [3 1,2,]
Energy [kWh/m^3]		680 [3 b]
electrical	1.8 [4 a]	
gas (heating) [m^3 gas/m^3 water]	0.5 [4]	
[a] engine driven equipment such as pumps and vents [b] including steam generation [1] [cww/tm/27] [2] [cww/tm/82] [3] [cww/tm/96] [4] [cww/tm/146]		

Monitoring

The parameters to control are:

- pH, in particular if ammonia or hydrogen sulphide is involved
- feed
- pressure
- temperature
- liquid level control
- column reflux ratio.

Economics

Type of costs	Costs		Remarks
	Air	**Steam**	
Capital cost	BEF 4 million [1]		100 m^3/h
		BEF 80 million [1]	50 m^3/h
	EUR 4.0–5.3 million[2]		refinery sour water stripper, 30-32 m^3/h
		GBP 200–300 thousand [3]	50 m^3/h
Operating cost	BEF 200/m^3 [1]	BEF 200/m^3 [1]	
[1] [cww/tm/128] [2] [cww/tm/48] [3] [cww/tm/92]			

3.3.4.2.15   Waste Water Incineration

Description

Waste water incineration is the oxidation with air of organic and inorganic waste water contaminants and the simultaneous evaporation of the aqueous part at normal pressure and a temperature range between 730 and 1200 ºC, or below that range when catalysts are used. In the chemical industry, waste water incineration is often operated centrally or, as co-incineration, in waste combustion plants. Reaction products are carbon dioxide, water and other inorganic compounds (nitrogen oxides, sulphur oxides, hydrogen halides, phosphates, heavy metal compounds), depending on the contaminants present.

Waste water incineration is only self-sustaining if the organic load is sufficient to ensure adequate energy support for vaporisation and heating of the water (COD >50 g/l). With a low organic load the incineration plant needs to be operated with supporting fuel. The amount of additional energy is reduced by lowering the water content, e.g. by upstream evaporation (see Section 3.3.4.2.13), making use of waste heat. The installation of a boiler may be a convenient way of generating steam from the heat of combustion, which might be used for evaporation [cww/tm/132].

Devices for waste water incineration can be constructed as ordinary combustion chambers or fluidised-bed incinerators. There is a high demand on the stability and corrosion resistance of the plant material. Combustion chambers are often built in ceramics.

Waste water incineration can also be operated in an ordinary waste combustion plant, with waste water as an additional input. Pretreatment might be necessary to eliminate particulates exceeding a maximum size to prevent jet blockage.

Application

Incineration is applied to waste water containing compounds that are either not readily biodegradable or might disturb the biological process in a downstream biological WWTP, or that have properties too harmful to be released into an ordinary sewer system. Such contents are e.g.:

- aqueous residues from dye production
- aqueous residues from rubber production, containing extremely large loads of salt
- aqueous extracts from pesticide productions
- aqueous residues from polyester production.

Waste water incineration is preferred to other treatment techniques that serve the same purpose when these fail or prove to be uneconomic. It is particularly suitable, when [cww/tm/132]:

- the organic constituents cannot be re-used or when recycling them is unprofitable
- the contaminants constitute a multi-component mixture in which both the concentration and the mixing ratio vary continuously
- apart from the organic content, there is a considerable amount of inorganic material
- waste water is poorly biodegradable or toxic
- the salt content is too high for biological treatment, or only after considerable dilution
- incineration allows the recycling of indestructible feed material, e.g. salts, or produces valuable products.

Waste water streams suitable to be incinerated generally cover a range between 2 and 30 m³/h with COD concentrations between 50000 and 100000 mg/l. Lower concentrations require supporting fuel.

Waste water of low combustion heat can be injected into rotary kilns for co-combustion with waste.

Application limits and restrictions:

	Limits / restrictions
Halogens, sulphur	halogens and sulphur content requires special flue gas treatment
Combustion temperature	increase of nitrogen oxides with increasing combustion temperature
Solids, salts	can block the injectors, thus adequate equipment is needed

Advantages and Disadvantages

Advantages	**Disadvantages**
• High organic content will be nearly completely removed. • Elimination of pollutants also possible with high salt concentration. • Waste heat can be used.	• Low organic concentrations need supporting fuel. • Solid waste (bottom and fly ashes) to be disposed of. • Incineration of sulphur and/or halide compounds might demand flue gas treatment causing waste water and solid waste.

Achievable Emission Levels / Performance Rates

Parameter	Performance rate [%]	Emission level [mg/l]	Remarks
TOC	>99 [1]		
VOC	92 [2]	30 [2]	feed 375 mg/l, catalytic incineration
[1] [cww/tm/82] [2] [cww/tm/96]			

The achievable emission levels and performance rates in the table are related to the waste water stream that is treated by incineration. Emissions to air and the discharges of waste water from the cleaning of exhaust gases are regulated by the Waste Incineration Directive 2000/76/EC [cww/tm/155] in Annex II, IV and V. Further information might be expected from the BREF on waste incineration.

Cross-media Effects

Waste water incineration results in waste gas (combustion exhaust gas potentially containing HCl, SO_x, NO_x etc.) which, depending on its content, can need further treatment resulting in additional waste water and solid waste. When the process cannot be operated autothermally, supporting fuel is required. On the other hand, when the waste heat cannot be recovered or re-used, some heat is released into the environment.

Consumables are:

Consumable	Amount
Supporting fuel (low TOC content) [a]	4.5 kg/m^3 waste water 12.5 kg/kg VOC [1]
Energy [kWh/m^3] [b]	0.09 [1]
[a] light fuel oil, organic content 375 mg/l, catalytic incineration [b] electric energy for pumps, burners, etc. [1] [cww/tm/96]	

Monitoring

Throughout the process, thorough monitoring is needed of operating parameters, such as oxygen content, temperature, content of sulphur oxides, nitrogen oxides, hydrogen halides, dust to ensure faultless working.

Economics

Type of costs	Costs	Remarks
Capital costs		
Operating costs	FIM 2.4/m^3 FIM 6.6/kg VOC [1]	8 m^3/h, VOC concentration 375 mg/l, catalytic incineration
[1] [cww/tm/96]		

3.3.4.3 Soluble Biodegradable Contaminants / Biological Treatment

The main production line in the chemical industry is the production and handling of organic substances. Thus the major part of chemical industry waste water is loaded with organic contaminants which are more or less biodegradable and suitable for biological treatment techniques. Substances that can disturb biological degradation need to be removed earlier (see Section 3.3.4.2).

Biological treatment is the degradation of dissolved organic substances with micro-organisms – bacteria – as oxidation agents. Organic nitrogen and phosphorous transform into ammonium and phosphate respectively. The biodegradability of a waste water stream can, by rule of thumb, be estimated by its BOD/COD ratio (before treatment):

- BOD/COD <0.2   relatively undegradable waste water
- BOD/COD 0.2–0.4   well-to-moderately degradable
- BOD/COD >0.4   well degradable

There are three types of metabolic processes:

- aerobic processes, using dissolved oxygen
- anoxic processes, using the biological reduction of oxygen donors
- anaerobic processes without oxygen supply.

The main properties of these three metabolic processes in connection with waste water treatment are listed in Table 3.8 [cww/tm/132].

Parameter	Anaerobic	Anoxic	Aerobic
Dissolved oxygen (DO) [mg/l]	0	0	>0
Energy consumption	low	low	high
Sludge production	low	high	high
Sensitivity to toxic substances	high	low	low
COD removal efficiency	<85 % [a]	varying, depending on denitrification	>85 %
Nitrogen removal efficiency	0	45-90 % (nitrification required as first stage)	0
Suitability as pretreatment	yes	yes	yes
Suitability for last stage treatment	no	no	yes
[a] normal value, can be higher for special applications (see Section 3.3.4.3.1, Achievable emission levels / performance rates)			

Table 3.8: Specific Process Parameters normally associated with Anaerobic, Anoxic and Aerobic Biology

A comparison of carbon balance of aerobic and anaerobic processes is illustrated in Figure 3.27 [cww/tm/132].
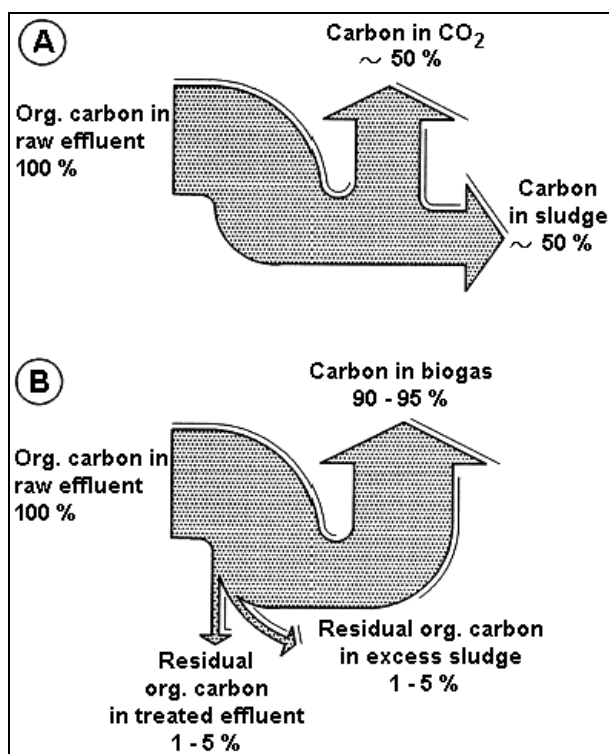
Figure 3.27: Carbon Balances in the Aerobic (A) and Anaerobic (B) Microbiological Degradation of Organic Compounds

One advantage of biological waste water treatment – independent of the kind of metabolic process – is the more or less rapid adaptability of microorganisms to a wide variety of nutrient media.

Biological treatment techniques common in the chemical industry are dealt with in the following sections.

3.3.4.3.1   Anaerobic Treatment

Description

Anaerobic waste water treatment converts the organic content of waste water, with the help of microorganisms and without entry of air, to a variety of products such as methane, carbon dioxide, sulphide etc. The biogas consists of about 70 % methane, 30 % carbon dioxide and other gases such as hydrogen and hydrogen sulphide [cww/tm/128]. The process is carried out in an airtight stirred tank reactor, the microorganisms retained in the tank as biomass (sludge).

There are several reactor types available. The most commonly used are:

- anaerobic contact reactor (ACR)
- upflow anaerobic sludge blanket (UASB)
- fixed-bed reactor
- expanded-bed reactor.

In the **anaerobic contact process** (ACP) waste water is mixed with recycled sludge and digested in a sealed reactor, the waste water / sludge mixture externally separated (sedimentation, Section 3.3.4.1.2, or vacuum flotation 3.3.4.1.3) and the supernatant discharged for further downstream treatment. The anaerobic sludge is recycled to the reactor. [cww/tm/4]. A schematic overview is given in Figure 3.28.
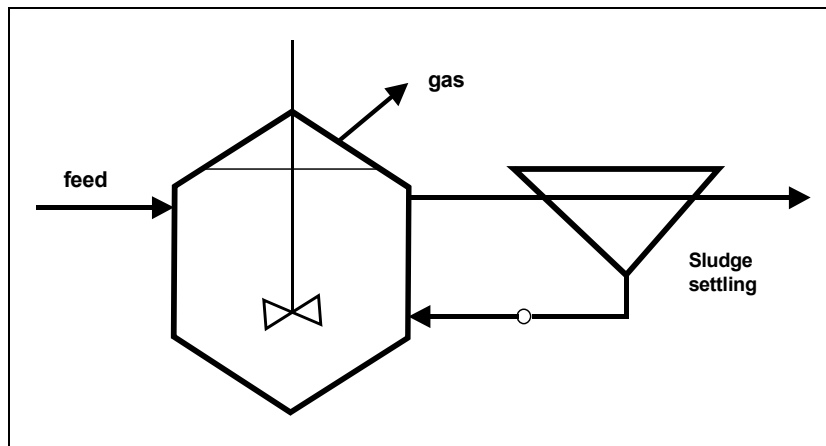
Figure 3.28: Anaerobic Contact Process

In the **UASB process,** waste water is introduced at the bottom of the reactor, from where it flows upward through a sludge blanket composed of biologically formed granules or particles. The produced gases cause mixing of the bulk waste water. The waste water phase passes into a settling chamber where the solid content is separated; the gases are collected in domes in the top of the reactor [cww/tm/4]. The principle is illustrated in Figure 3.29 [cww/tm/132].
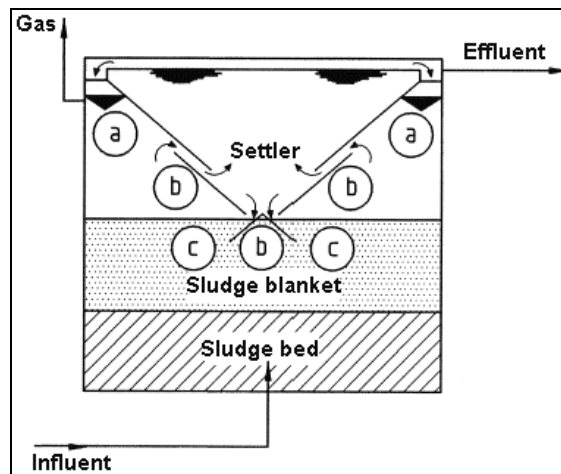
Figure 3.29: Schematic Representation of the UASB Process
a) sludge – liquid inlet
b) gas screens
c) settled sludge return opening

In the **fixed-bed** or **anaerobic filter process,** waste water flows upward or downward (depending on the solids content of the influent) through a column with various types of solid media on which anaerobic micro-organisms grow and are retained. [cww/tm/4].

In the **expanded-bed process,** waste water is pumped upward through a bed of an appropriate medium (sand, coal, polythene, etc.) on which a biological growth has been developed in a biofilm. The effluent is recycled to dilute the incoming waste water and to provide an adequate flow to maintain the bed in the expanded condition [cww/tm/4].

Excess biomass is worn off from the surface and treated after the bioreactor. There is no sludge recirculation needed, the biofilm carrier ensuring a high biomass concentration inside the reactor. The advantage of this version of anaerobic treatment is the reduced space requirement with the same performance. The system is more resistant to temporary load peaks, which otherwise might cause toxic discharges.

To increase the efficiency of anaerobic treatment, a two-stage variant is introduced as shown in Figure 3.30.
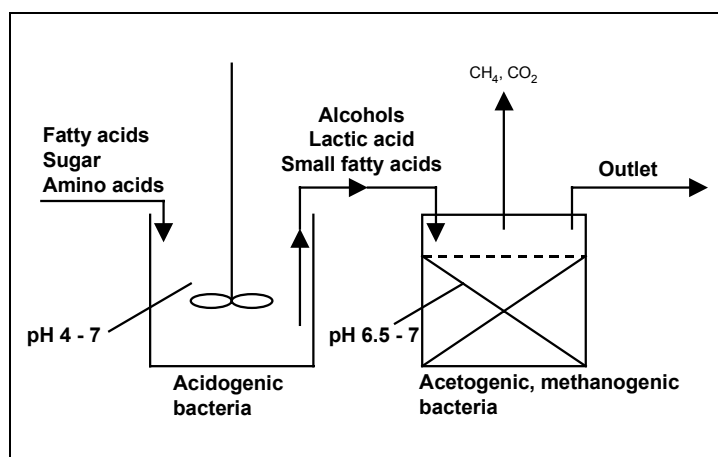
Figure 3.30: Schematic Presentation of a Two-Stage Anaerobic Treatment Process

<u>**Application**</u>

Anaerobic waste water treatment is essentially used only as pretreatment for waste water, which is characterised by a high organic load (>2 g/l) and a more or less constant quality [cww/tm/132]. It is applicable mostly in sectors with consistent effluents of high BOD loads.

The anaerobic treatment of industrial waste water has become increasingly important in recent years as a result of rising energy costs and problems with the disposal of excess sludge formed in aerobic treatment processes. Efforts are now being made to remove organic contaminants as far as possible without external sources of energy, taking advantage of the biogas produced, where the desired level of purity is ultimately achieved with the aid of a subsequent aerobic biological clarification step [cww/tm/132].

Application limits and restrictions are:

	Limits / restrictions
Temperature	20–40 °C
pH	6.5–7.5, pH >8 stops methane-forming process
Toxic substances	prevention of toxic substances, because process is sensitive

Advantages and Disadvantages

Advantages	Disadvantages
• Low energy consumption, compared to aerobic process. • Production of an energy-rich gas, probably amenable to further use as a low-quality fuel reserved for local use. • Comparatively (to aerobic process) low amount of clarification sludge (one tenth of the aerobic process) (see Figure 3.27). • In the presence of sulphate or organic sulphur compounds, heavy metal compounds are converted to sulphides and precipitated. • No aerosol formation and stripping of volatile substances (compared to aerobic process).	• High sensitivity to toxic substances, which might lead to an increased discharge of activated sludge, when toxic substances enter. • Production of toxic, flammable and odorous off-gases possible. • Very slow start-up. • Performance rate not sufficient for final treatment stage (COD removal normally <85 %), thus requiring further treatment.

Achievable Emission Levels / Performance Rates

Process	Input COD [g/l]	Detention time [h]	Organic loading [kg/(m^3 d)]	COD removal [%]
ACP [1]	1.5–5	2–10	0.48–2.40	75–90
UASB [1]	5–15	4–12	4.00–12.0	75–85
Fixed-bed [1]	10–20	24–48	0.96–4.81	75–85
Expanded-bed [1]	5-10	5-10	4.81–9.62	80–85
[1] [cww/tm/4]				

The performance rate of COD removal is highly dependent on the biodegradability of the organic substances responsible for the COD content. Thus the main requirement for anaerobic treatment – and for all biological treatment – is to avoid the introduction of undegradable waste water streams as far as possible.

In combination with downstream aerobic treatment the total performance rates are:

Parameter	Performance rate [%]
BOD	99–99.8
COD	95–97

Cross-media Effects

Normally anaerobic processes are run as biological high load stages that need an additional downstream biological (aerobic) treatment. The advantage of anaerobic pretreatment is the low amount of excess activated sludge produced during the process, about 10 % in comparison to the aerobic activated sludge process. In this way the main part of degradable organic load (75-85 %) is removed with one tenth of the normal (i.e. aerobic) formation of excess sludge, i.e. compared with aerobic techniques only 10 % of waste needs to be disposed of.

The anaerobic degradation process results in a mixture of methane and carbon dioxide in a ratio of 1-3 : 1, thus producing a combustible gas of high energy content which is normally used for fuel replacement or other energy supply facilities. Compared with aerobic processes the energy consumption is considerably less, because there is no energy need for air or oxygen supply to the reactor, but only for efficient stirring. Overall, it contributes to the reduction of carbon dioxide.

The arising of combustible gases and the formation of metabolites such as low chain carboxylic acids make the use of closed equipment unavoidable to prevent the efflux of odour. Odour abatement is an essential downstream treatment necessity.

Consumables are:

Consumable	Amount
Auxiliaries (for sedimentation, flotation, etc.)	
Energy [kWh/m^3]	

Monitoring

Monitoring of a biological waste water treatment plant is illustrated in Annex 7.3.

Economics

Type of costs	Costs	Remarks
Capital costs	BEF 120 million [1]	UASB reactor, 25 m^3/h, raw COD 30 g/l
	NLG 3.5 million [2]	206 m^3/d, raw COD load 7300 kg/d or 35 g/l
Operating costs	BEF 40/m^3 [1]	UASB reactor, 25 m^3/h, raw COD 30 g/l
	NLG 0.3/m^3 [2] [NLG 20000/yr]	206 m^3/d, raw COD load 7300 kg/d or 35 g/l
Benefit (biogas)	NLG 210000/yr [2]	206 m^3/d, raw COD load 7300 kg/d or 35 g/l
	NLG 1.5 million/yr [2]	compared to incineration of excess sludge
[1] [cww/tm/128]		
[2] [cww/tm/100]		

The effective reduction of organic contaminants goes together with the production of biogas – usable as fuel – and a considerable reduction of excess activated sludge. Provided that the biogas can be used, ecology and economics become mutually interdependent, i.e. a win-win situation over a longer period of time, when anaerobic treatment / final low-load aerobic treatment is compared with high-load final aerobic treatment and its associated costs (sludge incineration or landfilling).

3.3.4.3.2   Biological Removal of Sulphur Compounds / Heavy Metals

Description

Biological removal of heavy metals and sulphur compounds is a special application of anaerobic treatment. It is a three-step process that consists of:

- the biological reaction of sulphate or other oxidised sulphur compounds to sulphide by means of sulphate-reducing bacteria
- the subsequent reaction of heavy metal ions with sulphide and the precipitation of the heavy metal sulphides
- a second biological reaction to remove excess sulphide and convert it to sulphur.

The process takes advantage of the much lower solubility of metal sulphides compared to their hydroxides.

An example of a treatment installation is given in Figure 3.31.
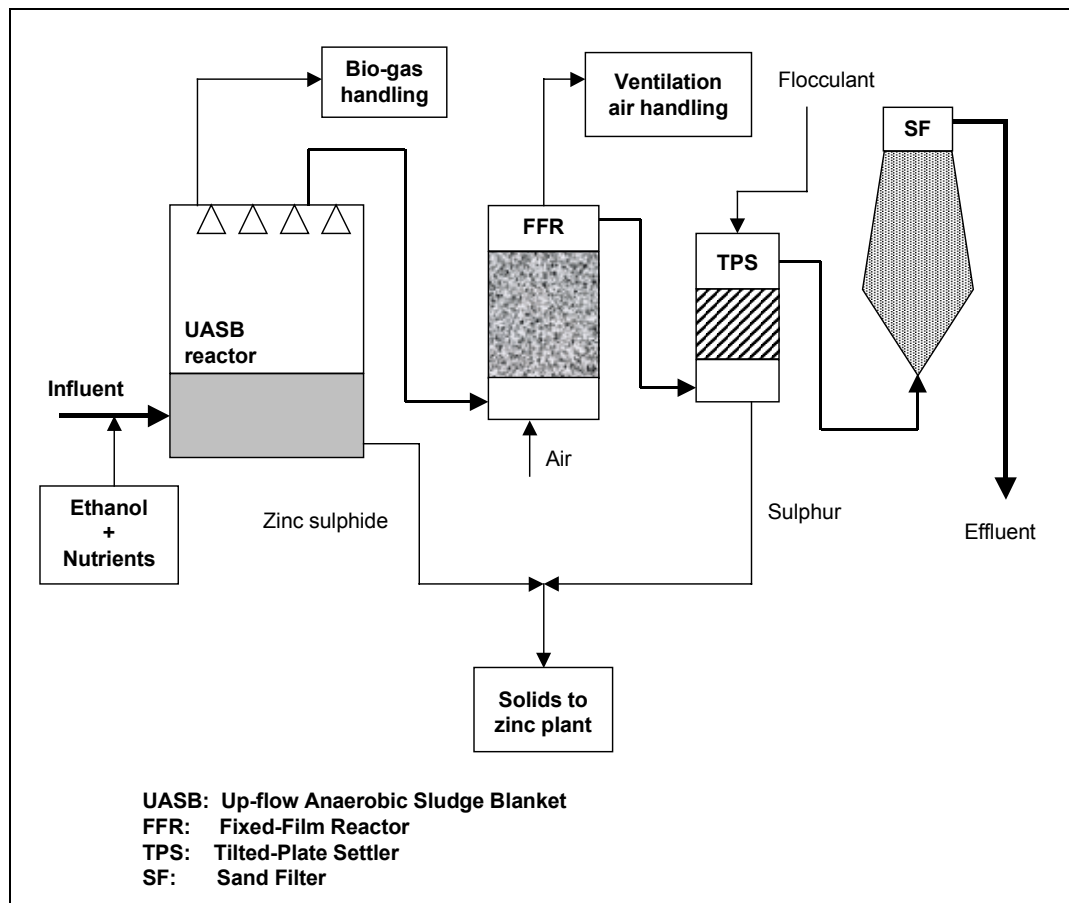
Figure 3.31: Process Diagram of Biological Metal and Sulphate Reducing Plant

The main components are:

- the UASB reactor, where the biological reduction of sulphate into sulphide takes place
- the bio-gas handling system to use or control the waste gas originating from the UASB
- the fixed-film reactor, where sulphide is aerobically converted into sulphur, the bacteria attached to a carrier material
- the tilted-plate settler to separate the sulphur
- the final polishing facility, e.g. a continuously cleaned sand filter.

The biological process needs electron donors, which are normally provided by the COD content in the waste water. If the COD content is not sufficient, electron donors have to be added. Possible electron donors are, e.g.:

- hydrogen
- starch
- ethanol
- formic acid
- acetate esters or salts
- propionate esters or salts
- lactate.

Besides these chemical substances, residues can be used as electron donors, such as:

- wood dust
- molasses.

If the influent requires neutralisation, a part of the waste water behind the tilted-plate settler or the sand filter can be recirculated, since the conversion of sulphide into sulphur increases the alkalinity.

The handling of bio-gas from the UASB reactor and of ventilation air from the fixed-film reactor enable odourless operation.

Application

This biological treatment operation is applicable to all waste water streams that contain a considerable amount of sulphate. While the removal of sulphate is possible without the presence of heavy metal compounds, the abatement of heavy metals needs enough sulphate to deliver the necessary amount of sulphide for the precipitation reaction. The presence of sufficient COD content favours the performance. A possible application is, for example, waste water from viscose fibre production, where zinc, sulphate and sulphide are the main pollutants.

Application limits and restrictions are:

	Limits / restrictions
Residence time	6 h for UASB reactor [1]
COD/sulphate rate	1 : 1, if COD content is too low, electron donor needs to be added
Flocculant dosage in the tilted-plate settler (removal of sulphur)	flocculant dosage needs to be optimally adjusted to the settler to achieve stable operation
[1] [cww/tm/101]	

Advantages and Disadvantages

Advantages	**Disadvantages**
• Treatment of sulphate without addition of precipitant chemicals. • Simultaneous removal of heavy metals and sulphate possible. • Heavy metals are separated from waste water as sulphides that may be re-used. • Metal sulphides have lower solubility than the respective hydroxides, so higher demands on effluent can be met. • At the end of the chain is sulphur that can be used as starting material in productions (e.g. production of sulphuric acid) or for recovery. • COD and nitrate can also be removed. • Stable process, so fluctuations and disturbances in the waste water stream hardly influence the efficiency.	• Often additional COD content is necessary as electron donor, which enlarges the operational costs. • Metal sulphides mix with the biological sludge in the UASB reactor. • Removal of heavy metals without sulphate is not possible.

Achievable Emission Levels / Performance Rates

Parameter	**Performance rate [%]**	**Emission level [mg/l]**	**Remarks**
Zinc	99.8 [1]	0.05-0.15	influent 100 mg/l
Cadmium	>99 [1]	<0.01	influent 1 mg/l
Sulphate	94 [2]	75	influent 1170 mg/l, presence of heavy metals
[1] [cww/tm/102] [2] [cww/tm/101]			

Cross-media Effects

Residues of the treatment process are:

- heavy metal sulphides, if heavy metals are present in the waste water stream, mixed with excess sludge from the UASB reactor
- sulphur, probably mixed with solid matter, from the tilted-plate settler.

The sulphides can, depending on the type of metal, be re-used to recover the metal. The sulphur fraction, when recovered separately, is produced as a sulphur cake, consisting of 60 % dry solids with a purity up to 95 %. It can be used for the production of sulphuric acid at sulphuric acid plants with the facilities for burning 'waste-acid' or slurries.

Because of the bio-gas and ventilation air handling, which is necessary for safety reasons, the process operates without odour emissions. As far as noise generation is concerned, the regular sources are pumps and vents that are enclosed.

Consumables are:

Consumable	Amount
Neutralising agents	
Electron donor	
Flocculant	
Energy [kWh/m^3]	

Monitoring

The right alkalinity and optimum COD/sulphate ratio (minimum 1 : 1) influence the efficiency of the treatment process, so monitoring the influent waste water stream for pH and COD content is an important issue. It is also essential that the influent be free of substances that can destroy the sulphur-active bacteria or inhibit their growth. So the influent has to be protected from such substances. The effluent is monitored for the pollutants treated, such as heavy metals, sulphate, COD, etc.

Economics

Type of costs	Costs	Remarks
Capital costs		
Operating costs		

3.3.4.3.3   Aerobic Treatment

Description

Aerobic treatment is the biological oxidation of dissolved organic substances with oxygen using the metabolism of microorganisms. In the presence of dissolved oxygen – injected as air or pure oxygen – the organic components are converted (mineralised) into carbon dioxide, water or other metabolites and biomass, the activated sludge.

Toxic waste water content can inhibit the biological process. Some of these toxic substances are shown in Table 3.9 [cww/tm/132].

Substance	Inhibiting concentration [mg/l]
Cadmium (Cd^{2+})	2–5
Bichromate (CrO$_4^{2-}$)	3–10
Copper (Cu^{2+})	1–5
Nickel (Ni^{2+})	2–10
Zinc (Zn^{2+})	5–20
Chlorine (Cl$_2$)	0.2–1
Cyanide (CN$^-$)	0.3–2
Mineral oils	>25
Phenols	200–1000
Hydrogen sulphide / sulphide	5–30

Table 3.9: Threshold Concentration of Representative Substances Toxic to Activated Sludge

The potential toxicity of a substance within a biological WWTP is not a predetermined constant but a function of the exposure conditions and the organisms present. The term toxicity refers to an interaction between substance and organism. With continuous feeding of low concentrations of toxic substances, the inhibitory effect soon diminishes due to adaptation, leading to the growth of micro-organisms displaying increased resistance and a higher degradation potential [cww/tm/132].

Common aerobic biological treatment techniques are:

* complete-mix activated sludge process
* membrane bioreactor process
* trickling or percolating filter process
* the expanded-bed process
* biofilter fixed-bed process.

Today the **complete-mix activated sludge process** is a method often used within the chemical industry and as such the most common treatment technique for biodegradable waste water. The micro-organisms are maintained as suspension in the waste water and the whole mixture is mechanically aerated. The activated sludge mixture is ducted to a separation facility from which the sludge is recycled to the aeration tank. The separation facility can be:

* sedimentation or settling tank
* air flotation facility
* MF or UF membrane (membrane bioreactor, see paragraph below).

The complete-mix process is operated with several variants, depending on the amount of waste water, the availability of space, the air emissions requirements etc. Examples of variants are:

* the oxidant agent: air or pure oxygen, the latter having the advantage of less stripping effects and less odorous release, because less gas is blown through the waste water, and of faster and more effective biological reaction
* the aeration chamber: a more or less flat tank biology or a tower biology, the latter taking into account the higher degradation efficiency because of smaller air bubbles ascending in a high column of waste water and thus considerably increasing the air / waste water mass transfer, see Figure 3.32 [cww/tm/132]
* the clarification step: sedimentation or membrane filtration (membrane bioreactor, see below), the latter with less space requirement, the former probably supported by a final flotation stage
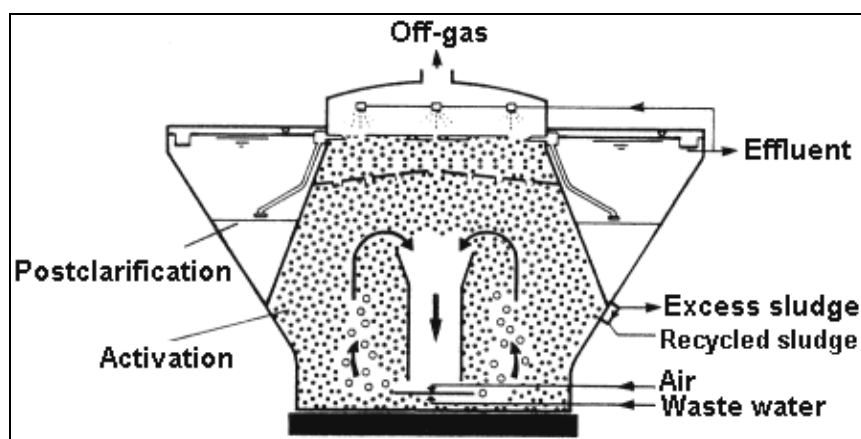
Figure 3.32: Example of Tower Biology

The membrane bioreactor process, as a combination of biological activated sludge treatment and membrane separation, is a biological treatment process used for urban and industrial waste water. The different variations of this process are:

- external recirculation loop between activated sludge tank and membrane module
- immersion of the membrane module in the aerated activated sludge tank, where the effluent is filtered through the hollow fibre membrane, the biomass remaining in the tank; this variant is less energy consuming and resulting in more compact plants.

These variants together with the conventional activated sludge process are shown in Figure 3.33.

Fouling, as a major problem for membranes, is diminished by:

- aeration
- backwashing of the membrane,

with the specific conditions being adapted for each treatment facility.

As a physical barrier, membranes allow the biomass in the tank to be maintained, resulting in:

- high sludge concentrations (TSS 10-20 g/l)
- high sludge age (or mean cell residence time, MCRT).

A membrane bioreactor is a compact facility (up to 5 times more compact than a conventional activated sludge plant, the membrane module replacing the clarification tank) that produces significantly less excess sludge. On the other hand, however, may the energy consumption, because of pumping, be significantly higher than with a conventional activated sludge process.

In the **trickling or percolating filter process** the microorganisms are attached to a highly permeable medium through which the waste water is trickled – or percolated. The filter medium normally consists of rock or various types of plastic. A schematic view is given in Figure 3.34 [cww/tm/132].

The liquid is collected in an underdrain system and passed to a settling tank and part of the liquid is recycled to dilute the strength of the incoming waste water.

The **expanded-bed process** is operated as described for anaerobic treatment (see Section 3.3.4.3.1) with the distinction that air or oxygen is introduced and aerobic instead of

anaerobic bacteria are fixed in the biofilm. The advantage of this version of aerobic treatment is the reduced space requirement with the same performance.
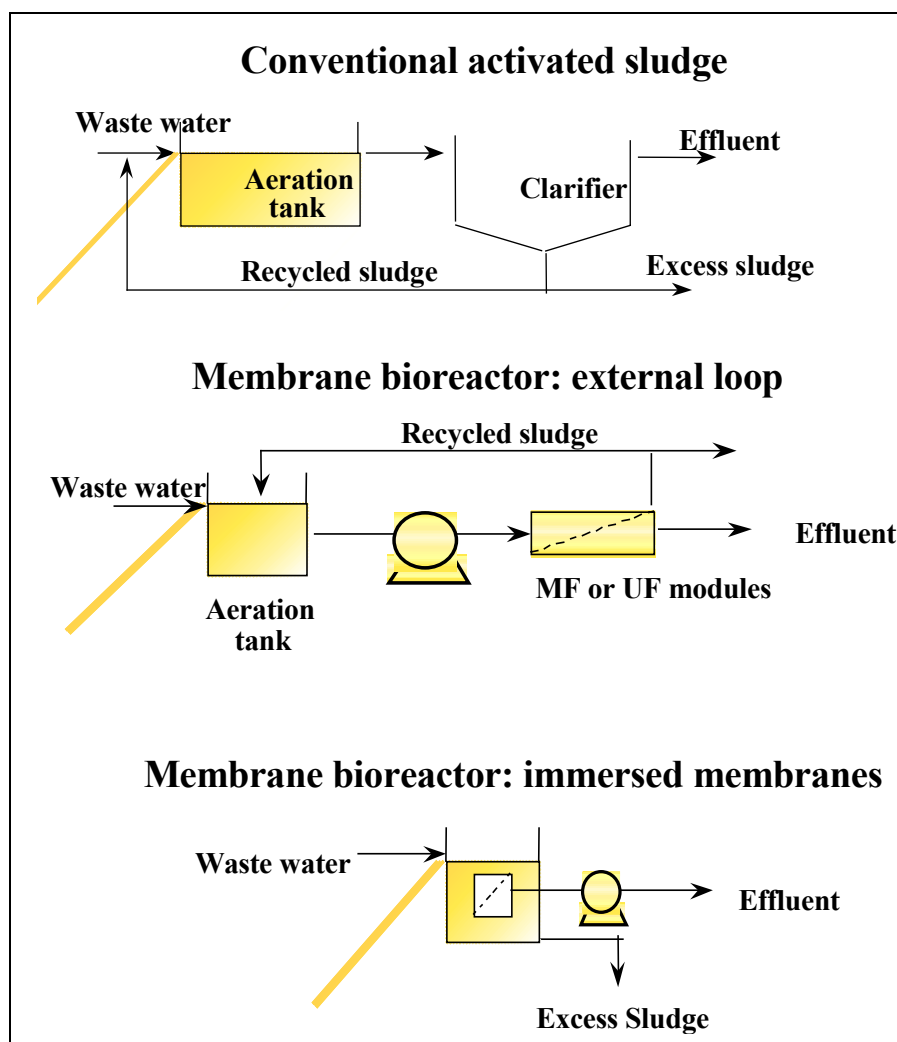
Figure 3.33: Variants of Membrane Bioreactor, compared with Conventional Activated Sludge Process
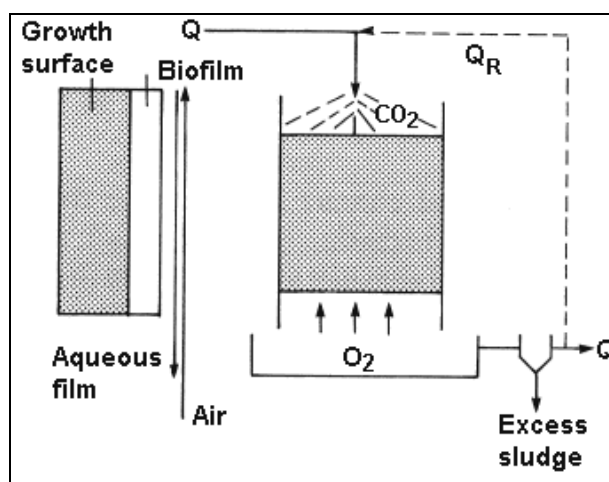
Figure 3.34: Schematic View of a Trickling Filter
Q: Waste water
Q_R: Recycle water

In the **biofilter fixed-bed process** the biofilm is maintained at the surface of a carrier. The waste water stream is treated when passing through this biofilm; suspended solids are retained in the filter, from where they are backwashed regularly. This technology has been developed as a compact (high turnover rate per volume and omission of a secondary clarifier) and odourless alternative to the conventional activated sludge process (see Figure 3.35).
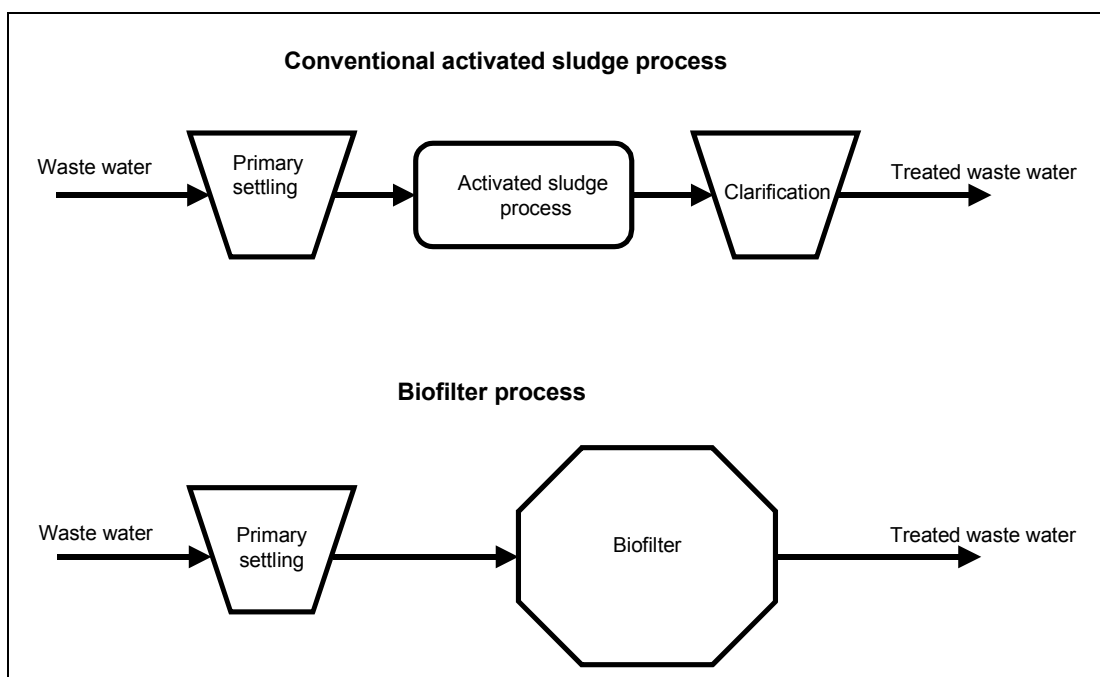
Figure 3.35: Biofilter Process in Comparison to Conventional Activated Sludge Process

Most submerged biofilters are based on one single filter medium. The water flow in a filter is upflow or downflow and with either sinking or floating medium. Biofilters can have mono or multilayer construction. Whereas multilayer biofilters are fed with raw water without primary settling, monolayer filters are usually used after a primary treatment to remove suspended solids.

The backwash frequency depends on the characteristics of the effluent. A normal frequency is flushing once a day with a large amount of water, but this has to be adapted on a case-by-case basis. The backwash operates with different steps:

- water only
- air only
- water and air.

A variation of carrier material is lignite coke because of its ability to adsorb in its pores the organic contaminants, the oxygen and the bacteria material, which extends the reaction time far longer than the normal residence time. Thus, refractory COD is more reduced than in a complete-mix activated sludge process, as result of a combination of enhanced biodegradation and adsorption on the carrier material. The lignite coke covers the surface of the tank and serves as an exhaust air filter which considerably reduces the odorous emissions.

Application

Aerobic waste water treatment generally represents the final biological step. It offers the advantage of a high rate of sludge growth that not only enables the handling of the various components of toxic waste water but also provides an efficiency of COD removal that is normally superior to anaerobic treatment.

In general, the **complete-mix activated sludge process** is applicable to all biodegradable waste water streams, be it as high load pretreatment of tributary streams or as the main part of a central WWTP.

The **membrane bioreactor** is used to treat municipal and industrial waste water, the latter originating, for example, from the chemical industry, the food processing industry or the pulp and paper industry, as well as landfill leachate. It is particularly suitable for:

- effluents with high COD and/or ammonium loads
- recycling of waste water
- stringent discharge regulations
- sensitive receiving water bodies
- sludges which are hard to settle
- upgrading existing plants
- compact installations
- nuisance (e.g. odour) problems
- disinfection of water.

When **trickling filters** are used in the chemical industry they are operated as part of a central WWTP to reduce the most easily degradable contaminants and to improve the sludge quality in the subsequent aeration stage.

Biofilters are used to treat urban and some industrial waste water (e.g. effluent highly loaded with COD in the pulp and paper industry), but also to upgrade an existing activated sludge plant (which is also the case with expanded-bed reactors). The advantage of the fixed biofilm on carrier material is the lower vulnerability to high salt contents and the better conditions for slow-growing bacteria because of the long-term retention in the system. Biofilters are also used as a direct pretreatment or final polishing step to an activated sludge process.

Biofilters can be loaded 2 to 3 times higher than a high-loaded activated sludge plant and still remove 90 % of the COD [cww/tm/164]. A comparison of the loads treated by different biosystems is shown in Table 3.10 [cww/tm/164]. Biofiltration achieves the same performance with nitrification / denitrification, but with a higher load.

	COD [kg/(m^3/d)]	BOD [kg/(m^3/d)]	NH$_4$-N [kg/(m^3/d)]	NO$_3$-N [kg/(m^3/d)]
Activated sludge	0.4-6	0.35-3 [a]	0.04-0.1	0.24-0.72
Activated sludge with oxygen enriched aeration		2-5 [b]		
Biofilter	3-25	1.3-10 [a]	0.4-1.5	0.7-6
Trickling filter (with plastic support)		1-5 [b]		
Membrane bioreactor [c]	2-3 [d 1]		0.9 [e 1]	

[a] BOD$_5$
[b] BOD$_7$
[c] sludge concentration 11-25 g/l [1]
[d] peaks between 1.6 and 8.5 kg COD/(m^3/d)
[e] from thermal treatment liquor
[1] [cww/tm/163]

Table 3.10: Comparison of the Volumetric Loads Treated by Various Aerobic Processes

Application limits and restrictions are:

	Limits / restrictions
Nutrients	BOD:N:P should be 100:5:1; critical ratios that should not be exceeded to ensure adequate operation are BOD:N 32:1 and BOD:P 150:1
Concentration	high substance concentrations (even of non-toxic substances) need to be avoided
Inhibitors	see Table 3.9
Temperature	waste water temperatures >35 °C can be critical for microorganisms
Salt load	high salt loads (>30 g/l) can disturb the biological process by damaging the micro-organisms; fixed-film techniques are less vulnerable

Advantages and Disadvantages

Advantages	Disadvantages
• Cost-effective treatment of organic contaminants. • Environmental impact lower than with other treatment processes. • Large amount of waste water can be treated. • Relatively high energy efficiency compared with non-biological treatment systems. Energy is mostly produced by sustainable methods (metabolism of micro-organisms with air and water). • Degradation mainly into harmless compounds.	• High energy consumption to supply oxygen to the water. • Production of a considerable amount of clarification sludge (except with membrane bioreactor or fixed-bed biofilters). • The aeration process causes stripping effects for volatile compounds resulting in fugitive releases, often the cause for odour and aerosols. • Complete-mix processes can cause bulking, resulting in excess discharge of activated floc. • Biological processes can be inhibited by contaminants. • With membrane bioreactors: fouling of membranes can be a problem. • High pressure drop, equivalent with increase in electric energy consumption.

Achievable Emission Levels / Performance Rates

The main parameter to check the performance rate or efficiency of biological treatment is BOD, whereas the degradation of COD depends on the degree of upstream pretreatment and the content of hardly degradable contaminants. Since refractory COD (or contaminant concentrations that act as refractory COD) is not suitable for biological treatment, and should therefore be left out as far as possible from a biological WWTP, it makes sense to list achievable COD levels.

Parameter	Performance rates [%]				
	Complete-mix activated sludge	Membrane bioreactor	Trickling filter	Expanded-bed	Biofilter fixed-bed
TSS		99 [5]			
Turbidity		99 [5]			
BOD	97–99.5 [1]	97 [5]	40–90 [2] 85–95 [a 2]	>98 [1]	
COD (TOC)	76–96 [c 1]	>90-96 [5]		90 [b 1]	26–68 [d 3]
Phenol index	>99 [e 4]				75–98 [3]
AOX					55–98 [3]
total inorganic N		82 [5]			4–50 [3]
NH₄-N		96-98 [5]			

[a] two stage
[b] 3 bioreactors in series, subsequent GAC adsorption results in TOC reduction of 98 %, COD reduction of 99 %
[c] 96 % with pure oxygen
[d] degradation of refractory COD, plant operates as polisher behind activated sludge WWTP
[e] input phenol 30 mg/l, 2200 m^3/d waste water
[1] [cww/tm/132]
[2] [cww/tm/4]
[3] [cww/tm/151]
[4] [cww/tm/96]
[5] [cww/tm/163]

Cross-media Effects

The main environmental issues of aerobic biological treatment are:

- the introduction of oxygen into the system and its effects
- the arising of activated sludge as a result of the biological process.

Oxygen is introduced by aeration, which calls for high energy input and stripping the volatile waste water content into the atmosphere, giving cause to odour. This impact can be controlled by various means:

- replacement of air by pure oxygen or oxygen enriched air, the gas injection reduced to about 20 % of the necessary air injection and by this reducing the stripping effect as well as the energy need; the advantage of this process variant, however, needs to be assessed carefully in comparison with the impact(s) of oxygen production, e.g. energy consumption, safety issues, difficulties to strip out CO_2, etc.
- covering the aeration tanks and ducting the captured exhaust air to a downstream abatement system (such as GAC adsorber, incinerator, biofilter or wet scrubber)
- use of carrier-based biological treatment techniques (fixed-bed biofilter) either with the equipment covered or the carrier material (lignite coke) serves as gas adsorbent.

Aerobic biological treatment produces a relatively large amount of excess activated sludge that needs to be disposed of. Special activated sludge treatment is involved with aerobic biological waste water treatment techniques, either on site or off site, which is detailed in Section 3.4.

Consumables are:

Consumable	Complete-mix activated sludge	Membrane bioreactor	Trickling filter	Expanded-bed	Biofilter fixed-bed
Oxygen (air or pure gas)					
Neutralisation chemicals					
Flocculants	300-550 kg/tonne COD [a][1]				
Nutrients	23-42 kg/tonne COD [b][1]				
Carrier					
Energy [kWh/m^3]	9.5 [c][1] 0.1 kWh per p.e. [2]				
[a] flocculant: ferrosulphate [b] o-phosphoric acid [c] including sludge incineration [1] [cww/tm/96] [2] [cww/tm/128]					

Monitoring

Monitoring of a biological waste water treatment plant is illustrated in Annex 7.3

Economics

	Costs				
	Complete-mix activated sludge	Membrane bioreactor	Trickling filter	Expanded-bed	Biofilter fixed-bed
Capital costs	FIM 15-20 million [a][1]				
Operating costs	about 2 % of capital costs [2]				DEM 0.2/m^3 [3]
	FIM 0.60/m^3 [a][1]				
[a] about 90 m^3/h, COD 500-900 mg/l [1] [cww/tm/96] [2] [cww/tm/128] [3] [cww/tm/151]					

Capital and operating costs are highly dependent on hydraulic and contaminant load, necessary implemented facilities such as API, neutralisation step, sludge separation equipment etc. Thus cost information at this stage can only be a rough guide and needs further refining in the light of the equipment and load of the plant in question.

3.3.4.3.4   Biological Nitrogen Elimination

Description

Nitrogen, or more precisely ammonium, is removed by a special biological treatment that consists of two steps:

- the aerobic nitrification, where special micro-organisms oxidise ammonium (NH_4^+) to the intermediate nitrite (NO_2^-) that is further converted to nitrate (NO_3^-)
- the anoxic denitrification, where micro-organisms convert nitrate to nitrogen gas.

Like all biological processes, nitrification/denitrification is vulnerable to toxic or inhibiting substances. However, as already mentioned above, cautious feeding of low concentrations of these toxic substances can lead to adaptation of the microorganisms and thus to the complete loss of inhibiting effects, if the concentration is not considerably increased. Substances with inhibiting effects are listed in Table 3.11 [cww/tm/27].

Compound	Inhibition concentration [mg/l] dissolved	Reduction in rate [%]
Thiourea	1	50
Thiosemicarbazide	1	50
Sodium methyldithiocarbamate	1	50
Methyl isocyanate	1	50
Allyl isothiocyanate	1	50
1,1-Dichloroethane	125	starting point
1,1-Dichloroethene	75	
1,2-trans-Dichloroethene	75	
1-Naphthylamine	15	50
2,2-Bipyridine	16 / 20	50
Ammonia-N	200	50
Benzene	500	
Benzidine dihydrochloride	20-100	50
Benzocaine	>100	50
Benzylamine	>100	50
Tetrachloromethane	50	
Chlorobenzene	100	
Trichloromethane	18	75
Dimethylgloxime	>100	50
Dimethylphthalate	100	
Dodecylamine	<1	50
Ethylendiamine	17	50
Hexamethyldiamine	85	50
Monoethanolamine	>100	50
Methylamine	<1	50
Methyl thiouronium sulphate	10	50
Skatole	10	50
Sodium dimethyldithiocarbamate	20	50
Sodium cyclopentamethylene-thiocarbamate	20	50
Guanidine carbonate	20	50
Allyl alcohol	20	50
Benzyl thiouronium chloride	20–100	50
Diguanide	20–100	50
Allylthiourea	1	50
Thioacetamide	1	50
Dithio-oxamide	1	50
Mercaptobenzthiazole	1	50
N-Methylalanine	1	50
Naphthalene	50	
Naphthylethylene diamine dihydrochloride	23	50
Ninhydrin	>100	50
p-Aminopropiophenone	43	50
p-Nitroaniline	31	50
p-Nitrobenzaldehyde	87	50
p-Phenylazoaniline	72	50
Phenol	3	30
Tannic acid	>100	50
Toluene	350	starting point
Triethylamine	127	50
Zinc	0.08–0.5	
Copper	0.005–0.5	starting point
Cyanide	0.34	starting point
Chromium(VI)	0.25	starting point
Lead	0.5	starting point
Mercury	1	starting point
Quinoline	10	50
p-Benzoquinone	10	50
Tetramethylthiuramthiocarbamate	20	50
Pyridine	20	50
Cresols	20	50
Cetyl trimethyl ammonium	20	50
Tetramethylthiuram disulphide	20–100	50

Compound	Inhibition concentration [mg/l] dissolved	Reduction in rate [%]
Hydrazine	20–100	50
8-Hydroxy-quinoline	20–100	50
Diallyl ether	20–100	50
Carbon disulphide	20–100	50
Dicyandiamide	>100	50
Strychnine hydrochloride	>100	50
Potassium thiocyanate	300	50
EDTA (Ethylene diamine tetra acetate)	350	50
N-Methylalanine hydro-chloride	550	
Cetyl pyridinium chloride	20–100	50
Sodium azide	20–100	50
Dichlorophen	20–100	50
Trimethylamine hydrochloride	>100	50
2,4,6-Tribromophenol	>100	50
Methylene blue	100	50
Streptomycin	400	50

Table 3.11: Substantial Inhibitors to Nitrification

When nitrification/denitrification is operated, it can typically be incorporated in a central biological WWTP. A vital factor for denitrification is the ratio of oxygenated nitrogen (nitrate/nitrite) and BOD (as reducing agent). There are two major layout options:

- nitrification stage as part of the aerated section; if necessary the N/BOD ratio is improved by addition of easily biodegradable TOC, e.g. methanol, to the subsequent denitrification stage (see Figure 3.36)
- denitrification as first stage, using the BOD-rich untreated waste water for energy supply, followed by the aeration (nitrification) section, a large part of nitrated waste water to be recycled to the denitrification zone (see Figure 3.37).

When only single tributary streams need nitrification/denitrification treatment it is recommendable to operate it separately from central treatment.

Nitrification/denitrification might be suitably retrofitted in existing biological WWTP by constructional alterations, such as:

- installation of separation walls
- installation of return pipes for nitrate containing waste water
- re-using of existent tank volume
- usage of existing clarifier or
- adjusting or adapting process control.
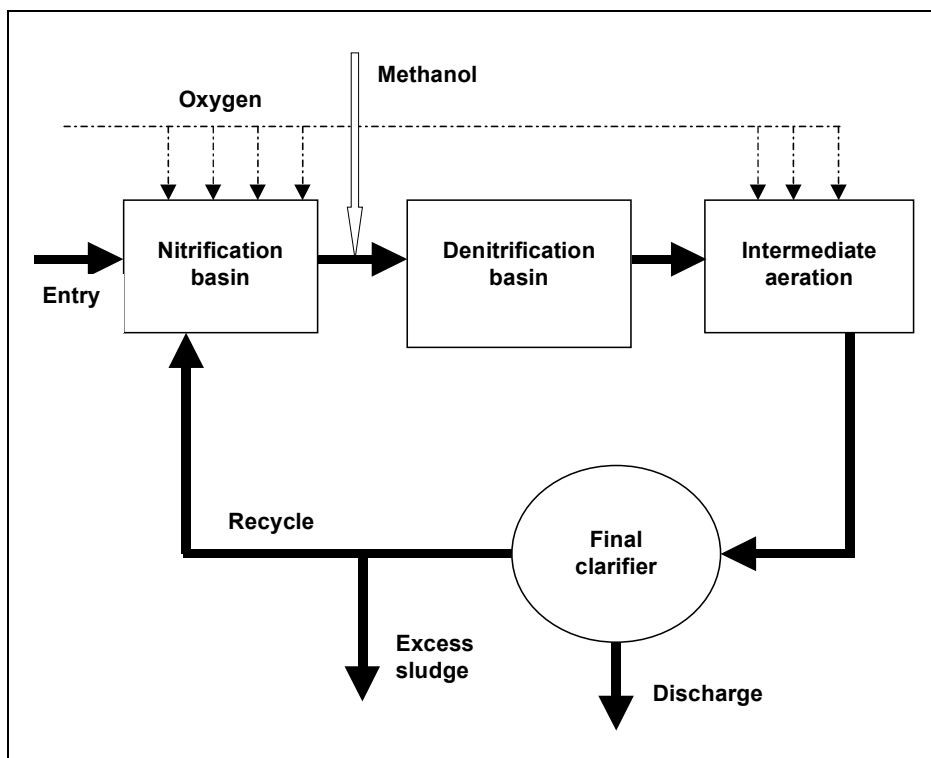
Figure 3.36: Nitrification/Denitrification in Series
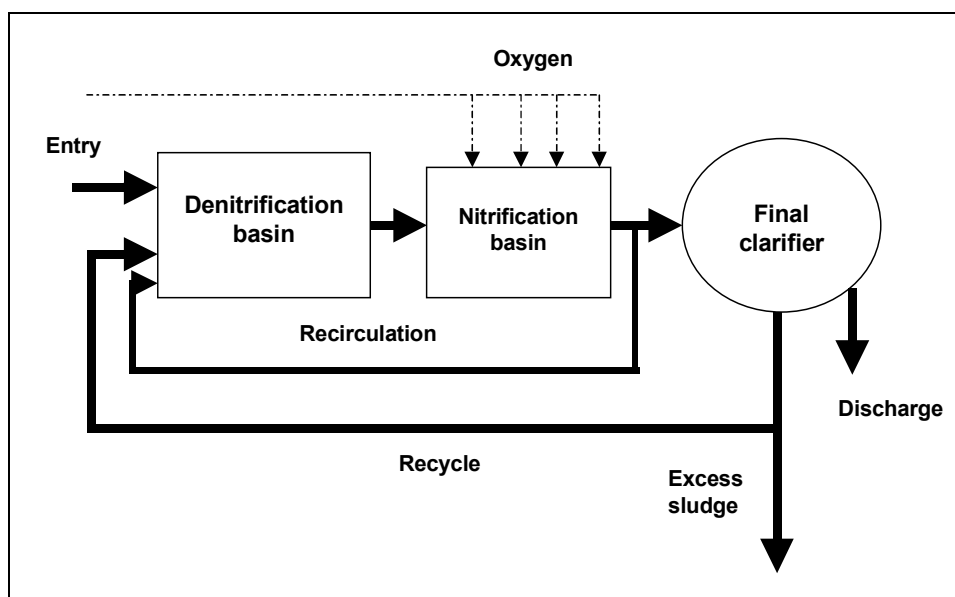
Figure 3.37: Nitrification/Denitrification with Denitrification as First Stage

Application

Nitrification/denitrification is applied to waste water streams that contain a considerable amount of nitrogen compounds, in particular amines and ammonium compounds. The control of ammonium discharge is an important measure to protect the quality of surface water (e.g. rivers), because the conversion of ammonium to ammonia, dependent on pH, results in fish toxicity.

Application limits and restrictions:

	Limits / restrictions
Temperature	>12–15 °C, lower temperatures restrain the growth of bacteria in the nitrification step
Toxic substances	certain substances act as inhibitors (see Table 3.11)
BOD/N ratio	in the range of 12 : 1 [1]
TOC/N ratio	in the range of 10 : 1 [1]
Chloride concentration	<5 g/l [1]

[1] [cww/tm/160]

Advantages and Disadvantages

Advantages	Disadvantages
• Effective elimination of nitrogen compounds. • Process can be integrated in the existing biological treatment, e.g. in the CWTP. • Existing plants can easily be retrofitted.	• Operation sensitive to varying conditions, pH, temperature, inhibitors (see Table 3.11), waste water contents. • Gaseous releases to air.

Achievable Emission Levels / Performance Rates

Parameter	Performance rate [%]	Emission level [mg/l]	Remarks
total inorganic N	70–80 [1]	10–20 [2]	

[1] [cww/tm/128]
[2] [cww/tm/160]

Cross-media Effects

When the nitrification/denitrification stage is part of the central WWTP, it contributes to the release of odorous and volatile substances. The other emissions are those normally expected from biological treatment facilities, which means it may be necessary to cover the equipment, if not operated in closed vessels, and abate the arising gases.

Consumables are:

Consumable	Amount
Carbon feed	
Energy [kWh/m^3]	

The common noise sources such as pumps, jets and mixers should be considered and appropriate measures taken, e.g. enclosure of equipment.

Monitoring

Monitoring of a biological waste water treatment plant is illustrated in Annex 7.3.

Economics

Type of costs	Costs		Remarks
	nitri/denitri series	denitri/nitri series	
Capital costs			
Operating costs			

3.3.4.3.5   Central Biological Waste Water Treatment

Description

The main part of the central WWTP is the aerobic biological activated sludge process (see Section 3.3.4.3.3). Around this central facility are grouped a complex of preparatory and subsequent separation operations. The central waste water plant is normally equipped with:

- buffer or equalisation volumes, if not already provided by other upstream facilities
- mixing station, where neutralisation and flocculation chemicals are added and mixed (usually lime milk and/or mineral acids, ferrous sulphate); enclosed or covered if necessary to prevent releases of odorous substances, the captured exhaust air ducted to an abatement system
- primary clarifier, where the floc is removed; enclosed or covered if necessary to prevent fugitive releases of odorous substances, the captured exhaust air ducted to an abatement system
- activated sludge part, e.g.
    - aeration basin with nutrient feed at the entry, enclosed or covered if necessary with exhaust air ducts to an abatement system
    - or closed reaction tank (e.g. tower biology) with gas duct, connected to a gas abatement system
    - nitri/denitrification stage (optionally) and phosphate elimination
- optional intermediate clarifier, when a second aerobic biological stage is operated, with sludge recycling
- optional second activated sludge part, for low load biology
- final clarifier with sludge recycling and transfer to sludge treatment; alternative sandfilter, MF or UF equipment
- optionally further special treatment facilities to eliminate the rest of refractory COD, e.g. biofilter (see Section 3.3.4.3.3)
- optionally further treatment facilities after the final clarifier, e.g. air flotation (see Section 3.3.4.1.3)
- optionally sludge treatment facilities, such as:
    - digesters (see Section 3.4.2)
    - sludge thickeners (see Section 3.4.1)
    - sludge dewaterers (see Section 3.4.1)
    - sludge incinerators (see Section 3.4.3)
- waste gas (exhaust air) abatement facilities such as:
    - GAC adsorbers (see Section 3.5.1.3)
    - thermal or catalytic oxidiser (see Section 3.5.2.4 and Section 3.5.2.5)
    - flares (see Section 3.5.2.6).

An example is illustrated in Figure 3.38 [cww/tm/81]

Application

Central biological waste water treatment is applied to complex waste water originating from the production and handling of organic chemicals, provided the content is biodegradable. Thus central WWTP are common end-of-pipe facilities in the chemical industry. Some illustrative examples are given in Annex 7.6.1.

According to the description given above, the central biological WWTP is able to remove two kinds of contaminants:

- suspended solids
- biodegradable compounds.

Waste water with a considerable amount of contaminants not belonging to these groups needs either pretreatment before being discharged into the central plant or special treatment (see Section 3.3.4.2) and by-passing of the central plant. Waste water containing an exceedingly high biodegradable load is also normally pretreated (see Sections 3.3.4.3.1 to 3.3.4.3.4).

For application limits and restrictions, see Sections 3.3.4.3.3 and 3.3.4.3.4:
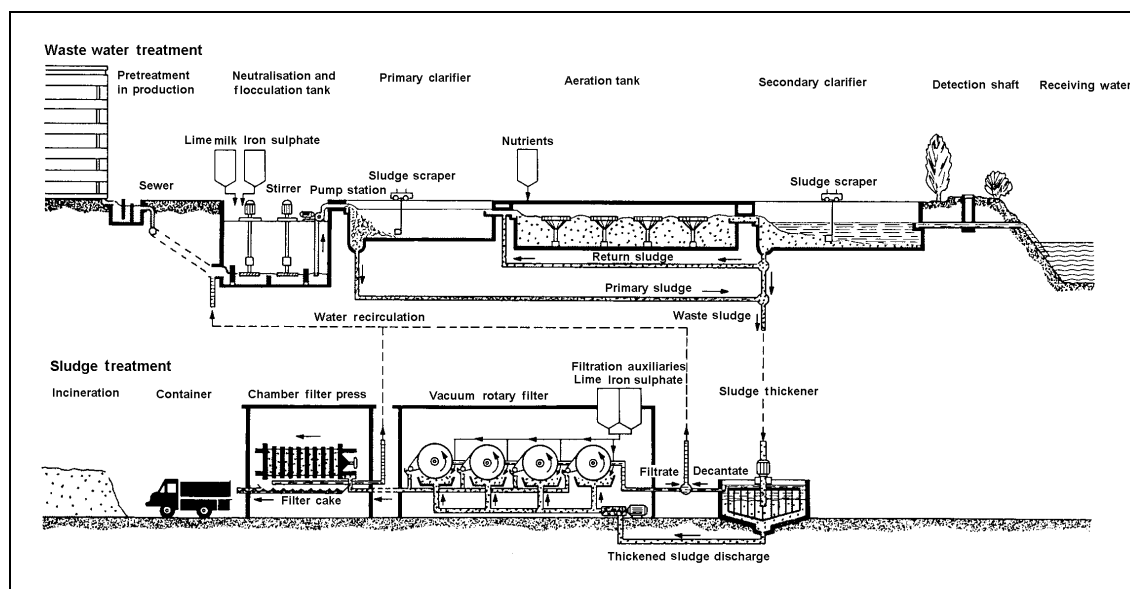
Figure 3.38: Example of a Central WWTP (Mechanical-Biological-Chemical)

Advantages and Disadvantages

Advantages	Disadvantages
• Large amount of waste water is treated. • Synergetic effects can increase efficiency. • Energy efficiency is high compared to processes such as GAC adsorption, incineration, wet oxidation. Energy is mainly supplied by sustainable methods (metabolism of micro-organisms with air and water). • Degradation normally into less harmful compounds (some exceptions when degradation products react to new compounds are known in pharmaceutical and pesticide production).	• Biological processes can be inhibited by contaminants or temperatures that are too high (>35 °) or too low (<12 °C). • High amount of excess sludge has to be disposed of. • The aeration process causes stripping effects for volatile compounds resulting in fugitive odorous and/or aerosol releases.

Achievable Emission Levels / Performance Rates

The main parameter to check the performance rate or efficiency of biological treatment is BOD, whereas the degradation of COD depends on the degree of upstream pretreatment and the content of hardly degradable contaminants. Since refractory COD (or contaminant concentrations that act as refractory COD) is not suitable for biological treatment, and should therefore be left out as far as possible from a biological WWTP, it makes sense to list achievable COD levels.

Parameter	Performance rate [%]	Achievable emission level [mg/l]	Remarks
TSS		10 [4]	
BOD	97–99.5 [1,4]	7-10 [4]	
	99–99.8		anaerobic pretreatment
COD (TOC) [a]	60–98 [1,2,4]		98 % with oxygen gas
	95–97		anaerobic pretreatment
AOX		<1 [4]	
Total inorganic N	70–80 [3]	10–20 [4]	
Phenol	>99 [5]		waste water rate 2200 m^3/d, input 30 mg/l phenol
T_F		2-3 [b 6]	measurements in Germany [c] (outliers up to 24)
T_D		2-4 [b 6]	Measurements in Germany [c] (outliers up to 768)
T_A		1-16 [b 6]	Measurements in Germany [c] (outliers up to 1024)
T_L		2-12 [b 6]	measurements in Germany [c] (outliers up to 1024)
T_M		1.5 [b]	measurements in Germany

[a] considering that refractory COD is removed upstream
[b] dimensionless numbers
[c] higher value is 90 percentile
[1] [cww/tm/132]
[2] [cww/tm/105]
[3] [cww/tm/128]
[4] [cww/tm/160]
[5] [cww/tm/96]
[6] [cww/tm/162, 165]

Cross-media Effects

As already described in Section 3.3.4.3.3 the main impact of aerobic biological treatment is the energy need for aeration combined with mixing in the aeration basin, the arising of a considerable amount of excess sludge that needs to be disposed of and treated, the stripping effect of aeration giving cause to the release of aerosols and volatile odorous substances and the noise generated by the treatment facilities. Action against the releases is enclosing or covering the sensitive areas such as mixing station, primary clarifier and aeration basin and ducting the exhaust air stream to a gas abatement system. A control measure against noise is the enclosure of equipment such as pumps.

Consumables are:

Consumable	Amount
Air or oxygen	
Neutralisation chemicals	
Flocculants	300-550 kg/tonne COD [a 1] 0.5-1.9 kg/tonne COD [b 2]
Nutrients	23-42 kg/tonne COD [c 1] 3-5 kg/tonne COD [c 2]
Energy [kWh/m^3]	9.5 [d 1] 0.7–4.0 [2] 0.1 kWh per p.e. [3]

[a] flocculant: ferrosulphate
[b] only waste water treatment part
[c] o-phosphoric acid
[d] including sludge incineration
[1] [cww/tm/96]
[2] [cww/tm/105]
[3] [cww/tm/128]

The amount of sludge arising during central treatment is not easy to quantify in relation to the contaminant load. It encompasses a large region between 34 and 2000 kg dry solid per tonne eliminated COD, averaging in the range of 250–720 kg dry solid per tonne eliminated COD [cww/tm/105].

Monitoring

Monitoring of a biological waste water treatment plant is illustrated in Annex 7.3.

Economics

Type of costs	Costs	Remarks
Capital costs per m^3		
Operating costs per m^3		

Capital and operating costs depend strongly on the facilities surrounding the biological part.

3.3.4.4 Rain and Fire-fighting Water Control

An essential point for industrial activities is the prevention of uncontrolled effluents from the site. For this purpose the drainage system of an industrial site can be divided into a production surface part, e.g.

- non-roofed production plant surfaces
- areas of storage tanks
- roofs exposed to effluent fallout,

and a normal traffic surface part, e.g.:

- roads inside the site
- administration area
- uncontaminated roof surfaces
- parking areas.

Rainwater from production areas and fire-fighting water are collected either in sumps on the spot or in other central facilities to allow inspection and then a decision to be made on whether to discharge them directly to the receiving water or to a waste treatment facility. Care needs to be taken to prevent the collection of fire-fighting water from causing fire to spread.

The drainage system of normal traffic areas is, where appropriate, connected to extra discharge facilities that are, e.g., installed to

- protect the receiving river against the hydraulic load of heavy rainfall from large paved areas
- remove flushed contaminant fallout accumulated during dry periods
- prevent the unintentional discharge of accidental spillage on roads or parking areas.

These facilities often include a first-flush compartment and hold-up for rainwater, to cater for the effluent which occurs as a result of the first rain after a relatively dry period, and further compartments for subsequent rainfall.

3.3.4.4.1   Retention Ponds

Description

A retention pond retains a permanent pool of water within a designated area, and relies on physical, biological and chemical processes to remove pollutants from rainwater run-off. Additionally, they control the rainwater flow to prevent downstream strain of the receiving river. When the pond is full the incoming rainwater displaces the existing content. The size of the pond depends on the necessary hydraulic residence time. Depending on the kind of contaminants and the hydraulic residence time, eutrophication might occur. From time to time it will be necessary to remove the sediment.

The water within the pond is discharged through an outlet that consists of a vertical riser attached to a horizontal barrel that conveys the rainwater flow beneath the embankment to a recipient. The outlet is designed to let excess water pass while maintaining a permanent pool. Risers are typically placed in, or on the edge of, the embankment and are capped with a rubbish rack to prevent clogging.

To prevent diffuse pollution from surface run-off or accidental spillage, retention ponds are equipped with oil separation / interception facilities.

Application

A retention pond is used to avoid hydraulic overload of downstream facilities and to separate solid pollutants from rainwater. These pollutants can include sediment, organic matter and, under certain circumstances, dissolved metal compounds and nutrients. It can be applied to industrial sites with lightly contaminated surfaces.

There are no application limits and restrictions.

Advantages and Disadvantages

Advantages	Disadvantages
• For dischargers into weak recipients retention ponds decrease the potential for downstream flooding and riverbank erosion.	• First flush systems provide no spillage containment, i.e. space required for sufficient volumes.

Achievable Emission Levels / Performance Rates

The achievable pollutant removal depends on special conditions, such as hydraulic residence times (HRT) and the kind of pollutant. Thus sedimentation and biological degradation inside the pond can occur to a certain degree.

Cross-media Effects

Sedimented sludge has normally to be disposed of. Easily biodegradable substances collected within the retention pond can cause odour discharge.

Consumables are:

Consumable	Amount
Energy [kWh/m^3]	

Monitoring

Proper maintenance will ensure continued accurate functioning of the retention pond. This includes [cww/tm/77]:

- clearing rubbish and debris
- conducting routine inspections of the embankment and spillway to check structural integrity and look for signs of erosion or animal habitation
- conducting periodic repairs on the embankment, emergency spillway, inlet and outlet
- removing sediment and algae
- removing woody vegetation or trees from the embankment that could potentially weaken the embankment
- maintaining the outfall area.

Economics

Type of costs	Costs	Remarks
Capital costs		
Operating costs		labour costs 3 h/month

3.3.4.4.2   Sand Filters

Description

A special application of sand filters is their function to treat rainwater run-off and remove undissolved pollutants such as suspended solids, undissolved phosphate and solid BOD. They provide a highly effective instrument to remove pollutants from rainwater while remaining flexible in application to allow for modifications in basic design structure to accommodate site-specific criteria. From time to time the filter is backwashed to remove its load of contaminants.

Sand filters for rainwater treatment are usually composed of two components:

- a sedimentation chamber, to remove floatables and heavy sediments
- a filtration chamber, to remove additional pollutants.

Examples are:

- the surface sand filter basin
- the underground vault sand filter
- the double trench sand filter
- the stone reservoir trench sand filter
- the peat sand filter.

Application

The sand filter is often applied where there is not enough space to incorporate a retention pond on an industrial site. It is used to treat rainwater from lightly contaminated surfaces.

There are no application limits and restrictions.

Advantages and Disadvantages

Advantages	Disadvantages
- High removal efficiencies achievable. - Low space requirement.	- Substances dissolved in water are not removed, unless by adsorption.

Achievable Emission Levels / Performance Rates

Parameter	Performance rate [%]	Remarks
TSS	80–83 [1]	

[1] [cww/tm/77]

Cross-media Effects

Backwashed sludge has to be disposed of as waste.

Consumables are:

Consumable	Amount
Energy [kWh/m^3]	

Monitoring

Performance of sand filters may be sustained through frequent inspections and regular replacement of the filter media. Accumulated rubbish and debris should be removed from the sand filter whenever necessary.

Economics

The capital costs are dependent on the chosen sand filter system and vary widely

Type of costs	Costs	Remarks
Capital costs		
Operating costs		

3.4 Sludge Treatment Techniques

Most waste water treatment processes result in sludge, although the amount, consistency and content depend on the waste water content and treatment technique. It is usually a liquid, or semi-solid liquid, with solid contents between 0.25-12 wt-% [cww/tm/4] and contains primarily the pollutants removed from the waste water. Excess activated sludge from a biological WWTP consists mostly of degradation (mineralisation) products and bacterial tissue as well as attached pollutants such as heavy metals.

Untreated sludge is not suitable to discharge or dispose of, because:

- its content of pollutants offensive to air prevents its deposition
- its content of pollutants offensive to water bodies prevents its being discharged into a receiving river
- the large amount of water it contains makes incineration an unattractive option because of the energy needed.

Sludge originating from chemical industry waste water is in general not suitable for agricultural purposes, but this depends on Member State legislation. A critical aspect is the content of heavy metals, AOX/EOX and other persistent sludge components.

The treatment operations for WWTP sludge are:

- preliminary operations (not described in this document), such as
  - grinding
  - blending or mixing
  - storage
  - degritting

- sludge thickening operations (see Section 3.4.1), such as
  - gravity thickening
  - centrifugal thickening
  - flotation thickening (DAF)
  - gravity belt thickening
  - rotary drum thickening

- sludge stabilisation (see Section 3.4.2), such as
  - chemical stabilisation (lime)
  - thermal stabilisation
  - anaerobic digestion
  - aerobic digestion
  - dual sludge stabilisation

- sludge conditioning (see Section 3.4.2), such as
  - chemical conditioning
  - thermal conditioning

- sludge dewatering techniques (see Section 3.4.1), such as
  - centrifugal dewatering
  - belt filter presses
  - filter presses

- drying operations (see Section 3.4.3), such as
  - rotary drying
  - spray drying
  - flash drying
  - evaporation
  - multiple hearth drying.

- thermal sludge oxidation (see Section 3.4.3), using techniques such as
  - fluidised-bed incineration
  - wet air oxidation
  - deep shaft oxidation
  - incineration with other (e.g. solid) waste.

- landfilling of sludge on site (not described in this document).

The treatment operations and disposal routes can be seen as single options or as a combination of single options. The listing mainly follows the path of degree of reduction and is not meant in any case as a ranking. It needs to be mentioned that the availability (or non-availability) of a disposal route can be a strong driver, at least at a local level, for the choice of the waste water treatment technique.

3.4.1 Sludge Thickening and Dewatering

<u>Description</u>

Sludge thickening and sludge dewatering are operations to increase the solid content of sludge and remove a part of the water fraction. Their benefit is a manifold (about five fold or more) decrease in volume to facilitate subsequent treatment operations as well as decrease the necessary size and capacity of treatment equipment. Both treatments differ only in the extent of water removal.

Common techniques are:

- gravity thickening, or sedimentation, using a settling tank
- centrifugal thickening (also as dewatering technique), ideal for high solid capture, operated either as solid bowl centrifuge or imperforate basket centrifuge, illustrated in Figure 3.39
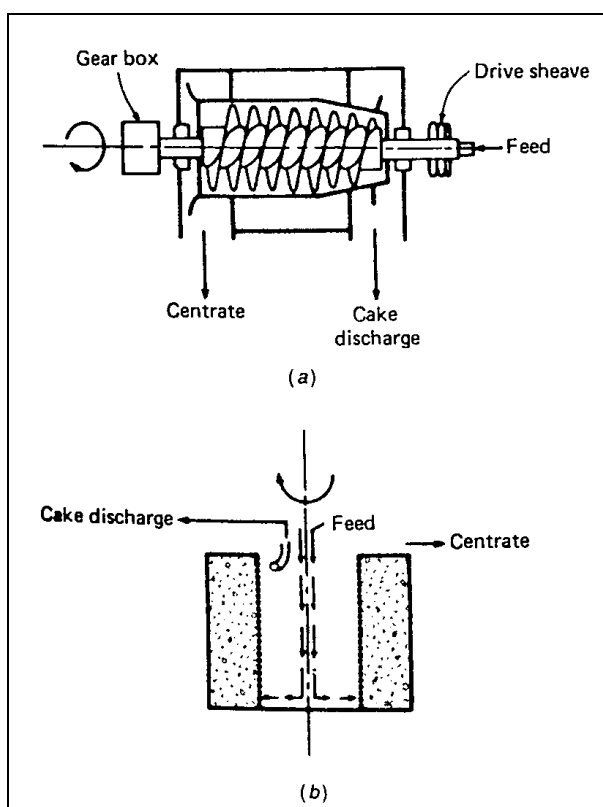
Figure 3.39: Centrifugal Sludge Thickener
(a) Solid Bowl Centrifuge, (b) Imperforate Basket Centrifuge

- flotation thickening, using DAF equipment as illustrated in Figure 3.40
- gravity belt thickening, using a gravity belt moving over driven rollers, the conditioned sludge added at one end into a feed/distribution box, the sludge ridged and furrowed by a series of plough blades, allowing the released water to pass through the belt
- rotary drum thickening, the unit consisting of a sludge conditioning system with polymer feed and rotating cylindrical screens where the polymer and thin sludge are mixed to flocculate and then separated from the water in the rotating screen drums
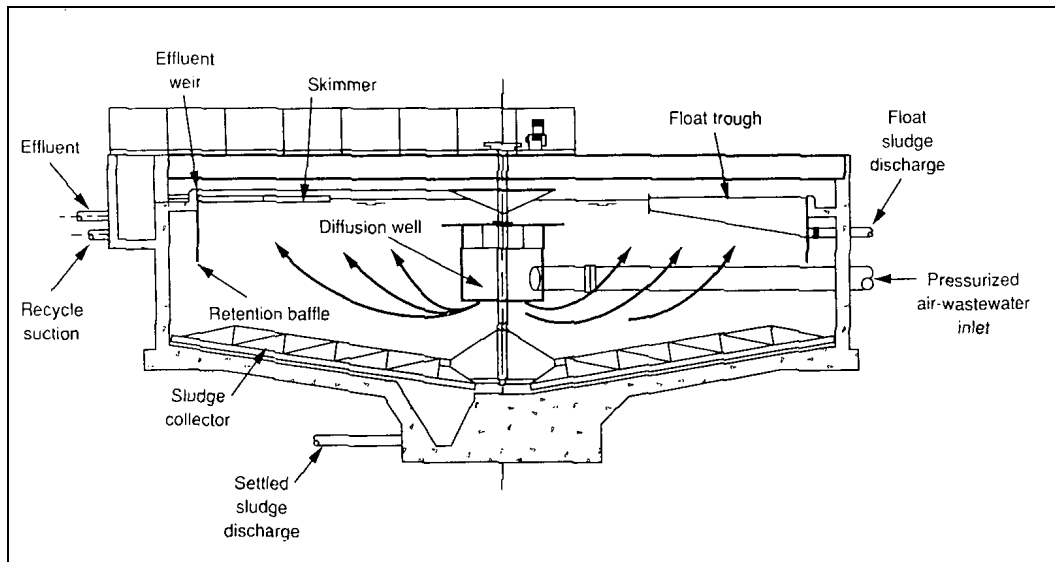
Figure 3.40: DAF Thickener for Waste Activated Sludge

- belt filter press dewatering, where the conditioned sludge is introduced to a gravity drainage section to thicken and separate from the water because of gravity, this operation assisted by vacuum which simultaneously enhances drainage and reduces odour; then pressure applied in a low-pressure sector, where the sludge is squeezed between opposing porous belts to release additional water (see Figure 3.41)
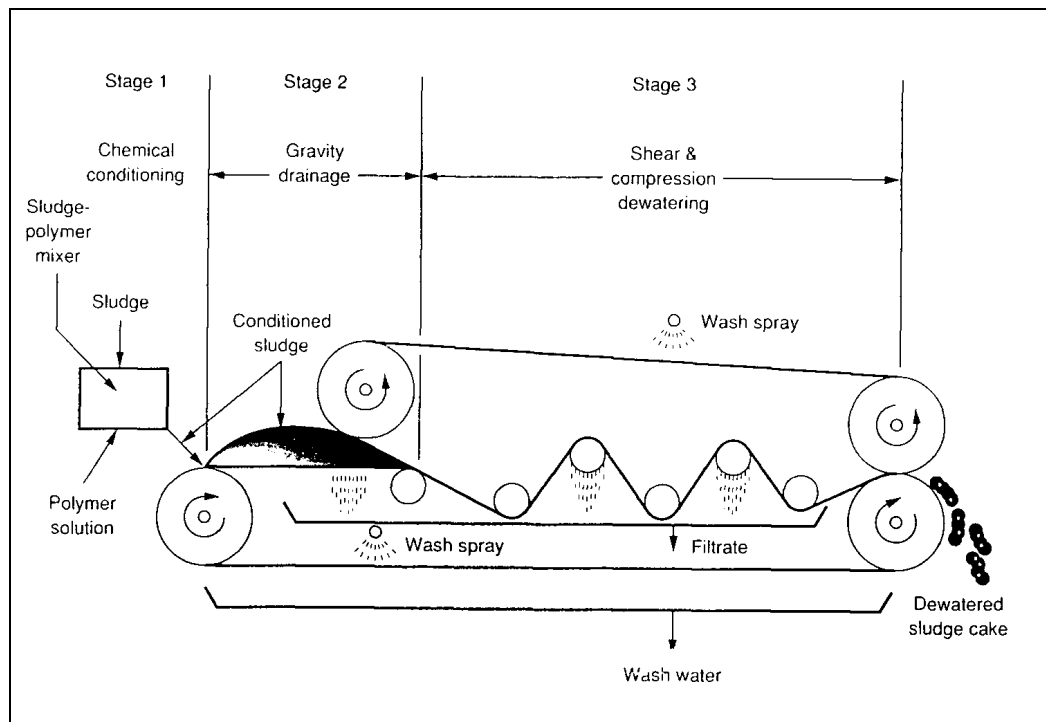
Figure 3.41: Belt Filter Press

- filter press dewatering, where the solid/liquid separation takes place at high pressure (0.7-1.5 MPa) [cww/tm/4], the sludge forced through a series of filter cloths to retain the particulates as filter cake and the filtrate recycled to the waste water treatment plant (see Figure 3.42).
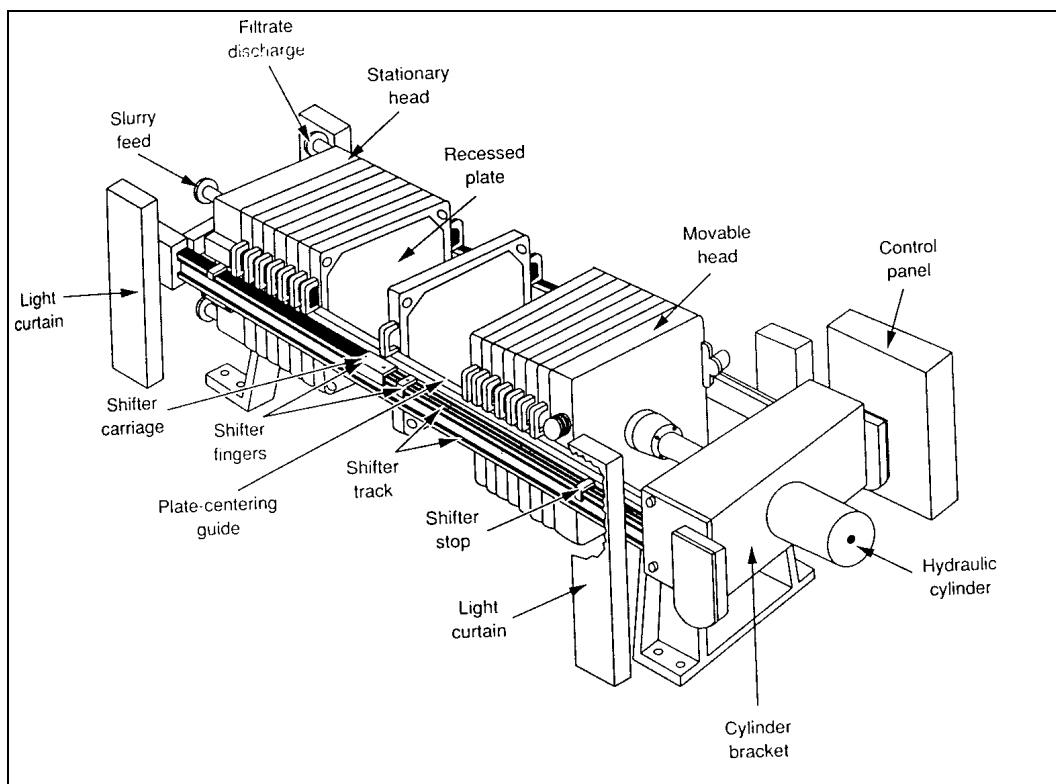
Figure 3.42: Fixed Volume Recessed Plate Filter Press

<u>Application</u>

The various techniques and their application to sludge properties are:

Gravity	Centrifugal	DAF	Gravity belt	Rotary drum
untreated primary sludge waste activated sludge mixture of untreated primary sludge and waste activated sludge	waste activated sludge, addition of flocculant and polymers necessary	waste activated sludge mixture of untreated primary sludge and waste activated sludge, addition of polymers necessary	waste activated sludge, particularly to solids concentration < 2 %	waste activated sludge

Belt Filter Press	Filter Press
all types of sludge, addition of flocculants and polymers necessary	all types of sludge, flocculants and polymers needed, used when low content of suspended solids in the filtrate is required

Advantages and Disadvantages

Advantages	Disadvantages
Gravity Thickening: • Excellent results with untreated primary sludge. • Gravity thickening gets generally satisfactory results with small plants and sludge concentrations between 4 and 6 %. • Low energy consumption.	Gravity Thickening: • Only marginal results with large plants. • For waste activated sludge only poor solids concentration.
Centrifugal Thickening: • Efficient production of dry sludge cake and good capture of solids that are difficult to filter. • Space requirements relatively low compared with other dewatering systems. • Easy installation. • Minimal odour problems.	Centrifugal Thickening • High consumption of energy per sludge unit dewatered. • Produces lowest cake solids concentration of the dewatering systems. • Vibrations and noise generation. • Skilled maintenance personnel required.
DAF Thickening: • Good efficiency for waste sludge from biological treatment processes.	DAF Thickening: • Vulnerable to freezing (blocking of air jets). • Release of odorous substances (stripping effect).
Gravity Belt Thickening: • Good results for raw and digested sludge.	
Rotary Drum Thickening: • Low maintenance, energy and space requirements.	
Belt Filter Presses: • High dewatering efficiency. • Easy maintenance.	Belt Filter Presses: • Hydraulic limitations. • Very sensitive to incoming sludge feed characteristics. • Short media life compared to other dewatering devices.
Filter Presses: • High dewatering efficiency and low suspended solids concentration in filtrate.	Filter Presses: • Batch operation. • Special requirements for support structure, floor area, personnel skill. • Limited filter cloth life.

Achievable Emission Levels / Performance Rates

Technique	Sludge concentration [%]	Solids capture [%]	Remarks
Gravity thickening	2–10 [1,2]	80–92 [1]	depending on sludge quality
Centrifugal thickening	3–8 [1]	80–98 [1]	
Centrifugal dewatering	10–35 [1,2]	85–98 [1]	with chemicals
DAF thickening	2–10 [2]	80–98 [1]	
Gravity belt thickening	4–6 [2]		
Rotary drum thickening	3–4 [1]		
	15–30 [1,2]	90–98 [1]	with vacuum
Belt filter press dewatering	15–30 [1,2]	85–98 [1]	with chemicals
Filter press dewatering	20–50 [1]	90–98 [1]	with chemicals
[1] [cww/tm/4] [2] [cww/tm/128]			

Cross-media Effects

Sludge thickening and dewatering are pretreatments for sludge to be handled more easily for further treatment, i.e. the resulting sludge after thickening and dewatering needs either final treatment or is disposed of in engineered landfills. The aqueous effluent (supernatant, filtrate) is recirculated back to the WWTP.

Noise and odour are controlled by enclosure and/or housing of the equipment.

Consumables are:

Consumable	Amount	Remarks
Conditioning chemicals	polymer 0–4 kg/tonne dry solid [1]	solid bowl centrifuge
	polymer 1–3 kg/tonne dry solid [1]	basket centrifuge
	polymer 2–5 kg/tonne dry solid [1]	DAF
	polymer 3–7 kg/tonne dry solid [1]	gravity belt
Washing water		for filter backwashing
Energy [kWh/m^3]	2-6	solid bowl centrifuge
	2-3	belt filter press
	4-5	filter press

[1] [cww/tm/4]

Monitoring

To prevent disturbances the thickening process has to be examined at least visually. Sludge input and its consistency as well as turbidity measurements of the water discharge should be frequently monitored. The appearance of bulking sludge has to be detected to prevent its release.

When sensitive equipment such as filter cloth is concerned, the input needs to be controlled to prevent the entrance of oversized or otherwise critical solids.

Economics

Technique	Cost	
	Capital	Operating
Gravity thickening	BEF 15 million [a 1]	BEF 8400/m^3 [a 1]
Centrifugal thickening		BEF 6-8000/tonne dry solid [1]
DAF thickening	BEF 40 million [a 1] BEF 4 million [b 1]	
Gravity belt thickening		
Rotary drum thickening		BEF 6-8000/tonne dry solid [1]
Belt filter press dewatering		BEF 6-8000/tonne dry solid [1]
Filter press dewatering		BEF 7-10000/tonne dry solid [1]

[a] capacity 100 m^3/h
[b] capacity 100 m^3/d
[1] [cww/tm/128]

3.4.2 Stabilisation and Conditioning

Description

Stabilisation of sewage sludge is a treatment operation to [cww/tm/132]:

- reduce or eliminate the amount of odorous constituents
- reduce the quantity of biodegradable sludge solids
- improve dewatering
- reduce pathogens
- reduce or eliminate the potential for putrefaction.

Stabilisation techniques are [cww/tm/132]:

- chemical stabilisation, using chiefly lime either as pretreatment, i.e. before dewatering, or as post-treatment, i.e. after dewatering, to raise the pH to >12 and thus kill pathogens
- thermal stabilisation, by heating the sludge in a pressure vessel at temperatures up to 260 °C and pressures up to 2.8 MPa during approximately 30 minutes, also used as a conditioning technique
- aerobic digestion, working in a tank – similar to the aerobic activated-sludge process for waste water treatment – with air or pure oxygen and adequate stirring, resulting in a 75-80 % reduction of the activated sludge content [cww/tm/4]; the technique is an attractive option when separate sludge digestion is considered
- anaerobic digestion, working in a tank under exclusion of air either in the mesophilic (30-38 °C) or the thermophilic (49–57 °C) range and producing a combustible gas mixture (65–70 % methane, 25–30 % carbon dioxide, small amounts of nitrogen, hydrogen, hydrogen sulphide etc.) of a low heating value of about 22 MJ/Nm^3
- dual sludge stabilisation, combining an upstream aerobic thermophilic and a downstream anaerobic mesophilic digestion.

The purpose of sludge **conditioning** is to improve the conditions for thickening and/or dewatering. Conditioning techniques are:

- chemical conditioning, using e.g. ferric chloride, lime, alum and organic polymers (coagulants and flocculants)
- thermal conditioning, by heating the sludge in a pressure vessel at temperatures of 60-80 °C (low thermal conditioning) or 180–230 °C and 1–2.5 MPa (high thermal conditioning).

Application

Stabilisation and conditioning is applied to sludge with organic content which is going to be thickened and/or dewatered. The suitability of the various techniques depends on the specific conditions at a site, e.g.:

- available space for digester tanks
- availability of energy, an important issue for thermal techniques
- the amount of sludge generated
- some techniques being viable only for larger plants.

Advantages and Disadvantages

Advantages	Disadvantages
Chemical stabilisation and conditioning: • Standard technique without high technological requirements. • Effective method to improve downstream filtration (conditioning) and to abate odorous substances and pathogens (stabilisation).	Chemical stabilisation and conditioning: • Considerable solid increase (except polymer conditioning).
Thermal stabilisation and conditioning: • Only limited space requirements. • Effective treatment without use of additional chemicals, both rendering the sludge capable of being dewatered and bacteria of being destroyed. • Most applicable to biological sludges that may be difficult to stabilise or condition by other means.	Thermal stabilisation and conditioning: • High capital costs compared to other techniques. • High energy requirements. • Release of odorous substances is an important issue.
Aerobic digestion: • Comparatively high volatile solids reduction, comparable to anaerobic digestion. • Production of an odourless, humus-like, biologically stable product. • Relatively easy operation. • Lower capital cost than with anaerobic digestion.	Aerobic digestion: • High energy need for stirring and air or oxygen supply. • Production of digested sludge with poor mechanical dewatering characteristics. • Process significantly affected by temperature, location and tank material.
Anaerobic digestion: • The arising gas can be used, after treatment, e.g. with dry or wet scrubbers, as fuel for combustion processes. • Effective use without use of additional chemicals. • Because of long residence time, efficient mineralisation of the sludge.	Anaerobic digestion: • Large space requirements are an issue for small sites.

Cross-media Effects

Chemical stabilisation and conditioning result in a considerable rise of solids content to be disposed of, with the exception of polymer conditioning. Because lime stabilisation does not destroy the organics necessary for bacterial growth, the sludge must be treated with an excess of lime or disposed of before the pH drops significantly. An excess dosage of lime may range up to 1.5 times the amount needed to maintain the initial pH of 12 [cww/tm/4].

The necessary amount of lime for sludge stabilisation is detailed in Table 3.12 [cww/tm/4], the amount of polymer for sludge conditioning in Table 3.13 [cww/tm/4].

Sludge	Solids concentration [%]	Lime dosage [a] [kg lime/kg dry solid]
Primary sludge	3–6	120–340
Waste activated sludge	1–5	420–860
Aerobically digested mixed sludge	6–7	280–500
Septage sludge	1–4.5	180–1020
[a] amount of lime required to maintain a pH of 12 for 30 minutes		

Table 3.12: Typical Lime Dosages for Stabilising Liquid Sludge

Sludge	kg dry polymer/tonne dry solids		
	Vacuum rotary drum filter	Belt filter press	Solid bowl centrifuge
Primary sludge	1–5	1–4	0.5–2.5
Primary and waste activated sludge	5–10	2–8	2–5
Primary and trickling filter sludge	1.3–2.5	2–8	-
Waste activated sludge	7.5–15	4–10	5–8
Anaerobically digested primary sludge	3.5–7	2–5	3–5
Anaerobically digested primary and air waste activated sludge	1.5–8.5	1.5–8.5	2–5
Aerobically digested primary sludge and air wasted activated sludge	7.5–10	2–8	-

Table 3.13: Typical Levels of Polymer Addition for Various Types of Sludge and for Various Methods of Dewatering

The main issue for aerobic sludge digestion is its air or oxygen need, which is about 2.3 kg O_2 per kg of degraded solid.

Anaerobic digestion results in a combustible gas that can be used as fuel, but because of the content of particulates and hydrogen sulphide it has to be cleaned before use. Appropriate waste gas treatment techniques are dry or wet scrubbing. In large plants it can be used as fuel for boiler and internal combustion engines.

Thermal stabilising and conditioning is an energy-intensive process which has to be assessed on its merits in the particular circumstances. During operation, odorous substances are generated or can be released which have to be abated accordingly.

Economics

Technique	Cost	
	Capital	Operating
Chemical stabilisation		
Thermal stabilisation / conditioning		
Anaerobic digestion		
Chemical conditioning		

3.4.3 Thermal Sludge Reduction

Description

Thermal sludge reduction is divided into two kinds of application:

- heat drying, reducing the water content by vaporisation of water
- oxidation of the dried sludge, mineralising the organic content.

Drying facilities normally used are:

- rotary dryers
- spray dryers
- flash dryers
- evaporators
- multiple hearth driers.

The subsequent oxidation of dried sludge converts the organic solid content into oxidised end-products, primarily carbon dioxide and water discharged as gas, and leaving a reduced volume of mostly inorganic solid. Sludges processed by thermal reduction are usually dewatered and

untreated, i.e. unstabilised, sludges. Stabilisation processes, e.g. anaerobic digestion, decrease the volatile content of the sludge and consequently increase the requirement for an auxiliary fuel. An exception is heat stabilisation ahead of incineration. Heat treated sludges dewater very well, the sludge becoming autocombustible. [cww/tm/4]

The techniques commonly used for thermal sludge oxidation (or incineration) are:

* fluidised-bed incineration (see Figure 3.43), used for sludge incineration, consisting of a cylindrically shaped steel shell, containing a sand bed and fluidising air orifices; the bed fluidised by air at a pressure of 20–35 kPa, the temperature of the sand bed controlled between 760 and 820 °C [cww/tm/4]; if the process is operated continuously or with shutdowns of short duration, there is no need for auxiliary fuel after start-up [cww/tm/4]. This technique is expected to be dealt with in the BREF on waste incineration yet to be written.
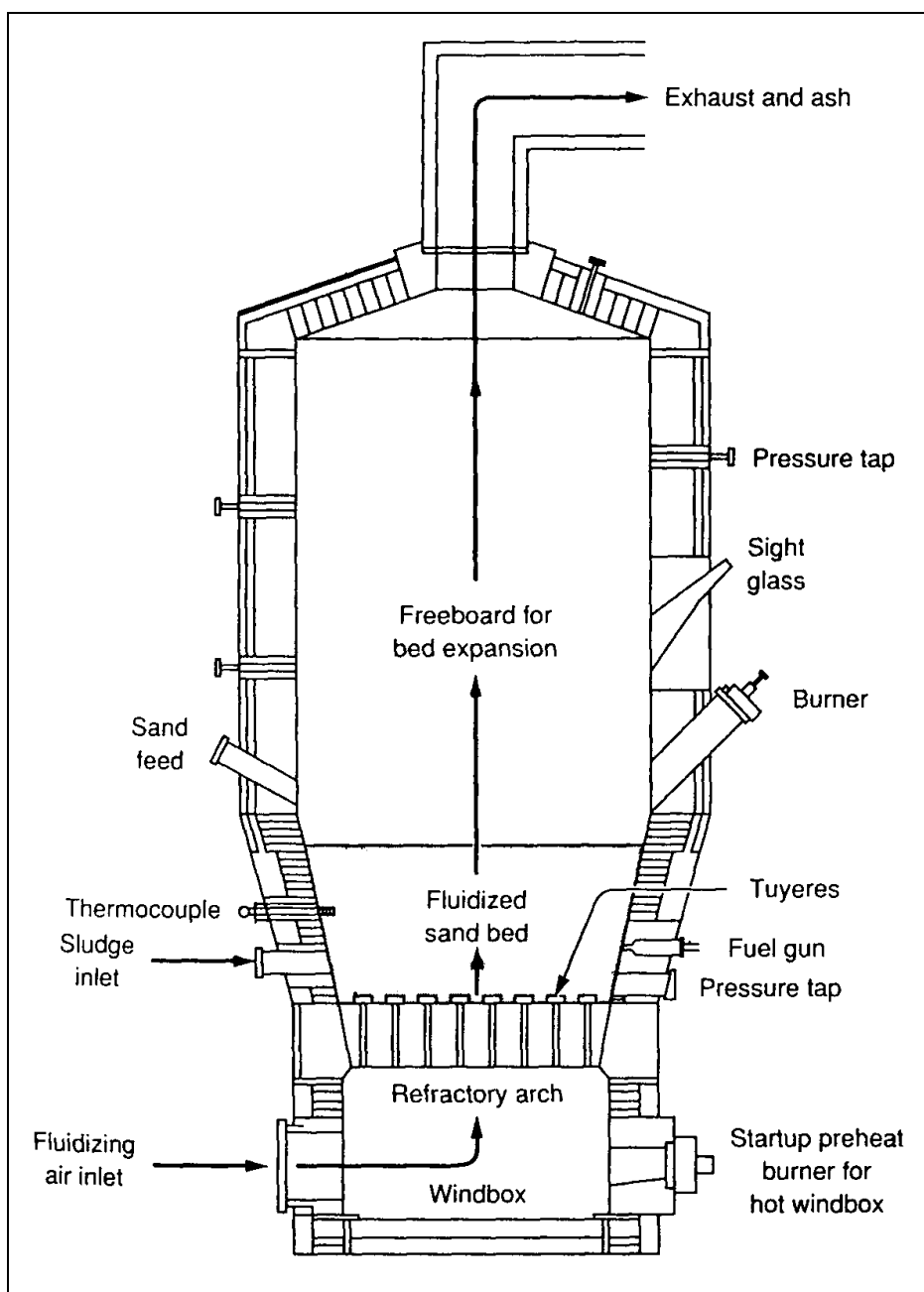
Figure 3.43: Fluidised-Bed Incinerator [cww/tm/4]

- wet air oxidation, the system already described in Section 3.3.4.2.4, used for untreated sludge, temperature range 175–315 °C and pressures up to 20 MPa; gases, liquid and ash leaving the reactor, the gases can be expanded to recover power
- deep-shaft oxidation (see Figure 3.44), i.e. discharging liquid sludge in the pressure and temperature controlled environment of a tube-and-shell reactor suspended within a deep well, oxygen or air injected into the waste sludge stream, temperature of about 290 °C, pressure range at bottom between 10–14 MPa (hydrostatic pressure); it is a special application of wet air oxidation
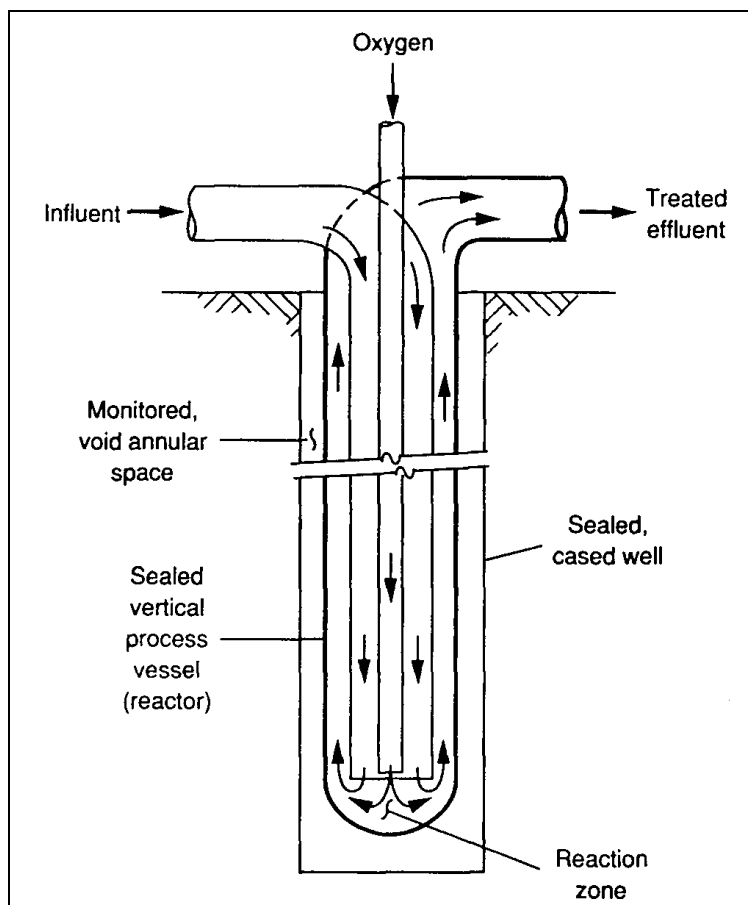
Figure 3.44: Deep-Shaft Oxidation Reactor [cww/tm/4]

- incineration with other waste, reducing the costs by using the same facility and taking advantage of the heat produced by waste incineration for the evaporation of the sludge water content. This issue can be expected to be dealt with in the BREF on waste incineration.

All techniques need further treatment of the released gases and liquids.

<u>Application</u>

Thermal sludge reduction is not necessarily a technology to perform at a chemical production site. Normally only larger sites operate sludge treatment to such an extent, others commission their sludge to external discharge. The reasons are that skilled personnel are needed, the capital and maintenance costs are considerable and the benefits from generated heat are normally relevant only to larger plants or where equipment is already available.

Incineration with other waste, for example, is an option for sites where waste incineration is already operated – provided the incinerator is appropriately equipped – or where the construction of an incinerator is planned.

Advantages and Disadvantages

Advantages	Disadvantages
Incineration: • Efficient destruction of organic content in sludge.	Incineration: • Complex process requires skilled personnel. • Addition of auxiliary fuel is common. • Gaseous emissions and odour.
Incineration with other waste: • The heat for water evaporation and sludge incineration is delivered by the incineration of solid waste, no auxiliary fuel required.	Incineration with other waste: • May lead to high emissions of PCDD/PCDF and heavy metals, when combustion conditions and flue gas cleaning system are not adapted to the mixture (e.g. primary measures for dioxin reduction, secondary measures for reduction of both dioxins and heavy metals).
Wet air oxidation: • Process can be designed to be thermally self-sufficient, recovering of power is sometimes available.	Wet air oxidation: • Production of high-strength recycle liquor. • Complex process needs skilled personnel.
Deep-shaft reactor: • Small space requirements. • High removal efficiency of suspended solids and organic matter. • Process completely exothermal. • Little odour or objectionable air emissions.	Deep-shaft reactor • Skilled personnel required for process control.

Cross-media Effects

The main environmental issues raised by thermal sludge reduction are the gaseous and liquid emissions generated during the process.

The gaseous emissions from the fluidised-bed incinerators consist of particulates (ashes), nitrogen oxides, acid gases, hydrocarbons, heavy metals, depending on the sludge content and the auxiliary fuel. Wet scrubbing techniques (details in Section 3.5.1.4) are used to abate the air contaminants. The aqueous releases from wet scrubbing contain the suspended solids and dissolved waste gases that need to undergo waste water treatment. The emissions to air and the waste water releases need to follow the requirements of the Waste Incineration Directive 2000/76/EC [cww/tm/155] Annexes II, IV and V.

With the fluidised-bed incinerator no dry ash exists at the bottom of the reactor; it is entrained in the combustion gases.

With the wet air oxidation process, gases, liquid and ash leave the reactor. The liquid and ash are returned through heat exchangers to preheat the incoming sludge, the gases are separated from particulates and liquid drops in a cyclone and then released. In large installations it can be economical to expand the gases through a turbine to recover power [cww/tm/4]. The liquid phase is separated from the solid content and returned to the settling tank or clarifier. The recycled liquid represents a considerable organic load. Typically ranges for COD are 10–15 g/l.

The deep-shaft oxidation process requires subsequent gas-liquid and solids-liquid separation as well as post-treatment of the supernatant. These treatments reduce the COD content of the sludge >80 % [cww/tm/4].

The energy requirement of thermal sludge reduction techniques depends greatly on the heat value of the sludge, i.e. the water content and the heat value of the dry solid.

<u>Monitoring</u>

The incineration process (furnace) is normally operated by a process control system and monitored by means of

- volume measurement
- temperature measurement
- pressure measurement
- analyses.

Regulation mechanisms ensure that the specified temperature is maintained in the incineration zone and the flue gas obtains the exact oxygen concentration, By ensuring optimum residence time, excess air and temperature, a complete ash incineration is available.

Furthermore, monitoring needs to follow Articles 10 and 11 and Annex III of Directive 2000/76/EC on the incineration of waste [cww/tm/155].

<u>Economics</u>

Technique	Capital costs	Operating costs
Fluidised-bed incineration		
Wet air oxidation		
Deep-shaft oxidation		
Incineration with other waste		

3.5 Waste Gas End-of-pipe Treatment Techniques

Waste gas end-of-pipe treatment techniques are described here in a similar order to that used for waste water end-of-pipe techniques. The relationship between pollutant and typical treatment, as pointed out in Section 1.3.2.2, is illustrated in Figure 3.45.
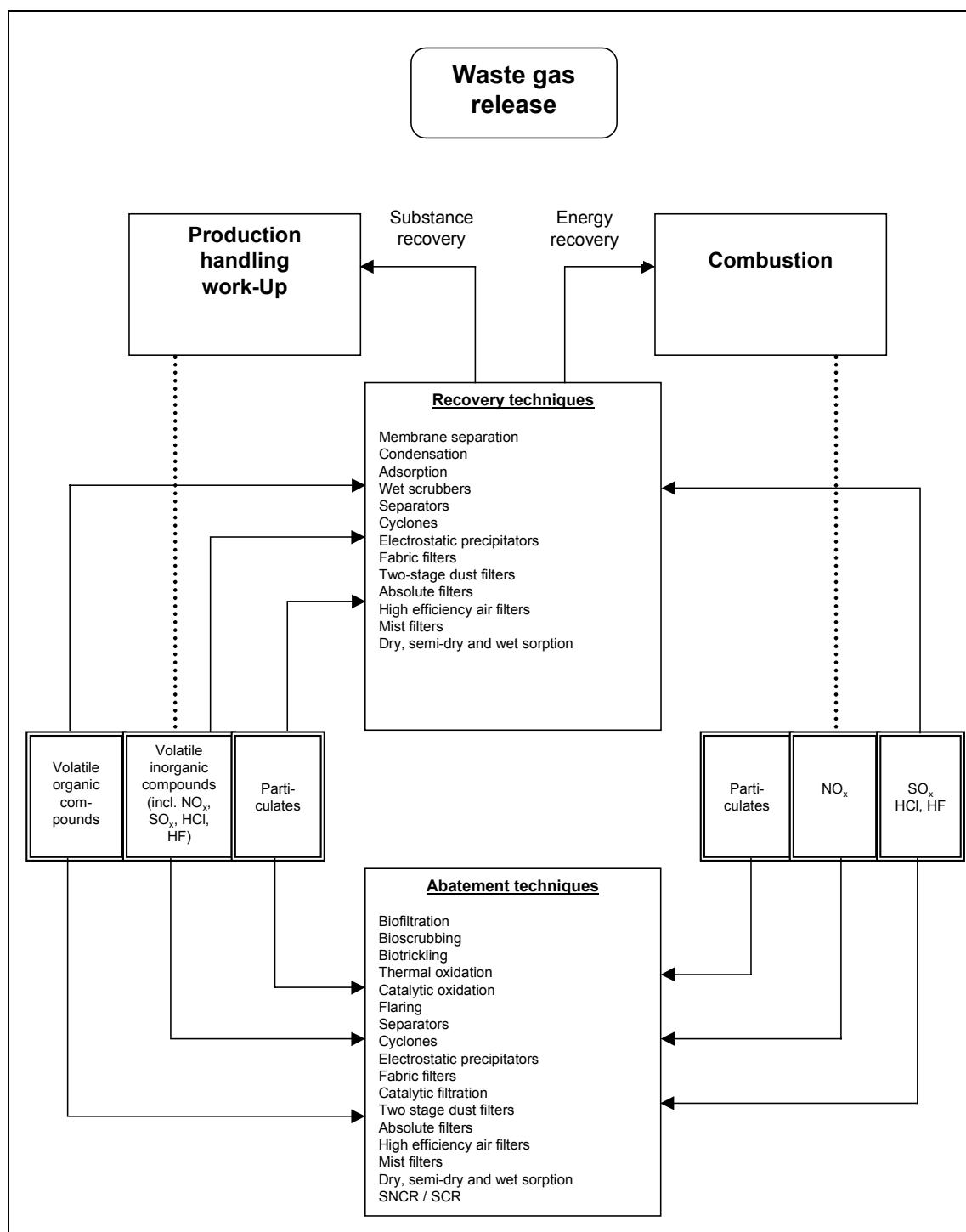
Figure 3.45: Range of Waste Gas End-of-pipe Treatment Techniques in Relation to Type of Contaminants

The sources of waste gases to be treated are:

- "normal" temperature processes, such as production, handling or work-up processes, with the main contaminants:
    - volatile organic compounds, such as solvents
    - inorganic compounds, such as hydrogen halides, hydrogen sulphide, ammonia, carbon monoxide
    - particulates in the form of dust
- incineration processes, with main contaminants:
    - particulates in the form of ashes and dust, containing soot, metal oxides
    - flue gases such as carbon monoxide, hydrogen halides, sulphur-oxygen compounds (SO_x), nitrogen-oxygen compounds (NO_x).

Arising waste gases are treated by techniques where:

- the waste gas content is recovered and either recycled to the original process or used in another process as raw product or energy carrier or
- the contaminants are abated.

Compounds, which are normally economically feasible to recover, include:

- VOC, recovered from solvent vapours or vapours of low-boiling products
- VOC used as energy carrier in incinerators or boilers
- hydrogen chloride, transferred into hydrochloric acid
- ammonia to recycle into the production process
- sulphur dioxide, transferred into sulphuric acid, sulphur or gypsum
- dust containing higher amounts of solid raw products or end products.

The treatment techniques are – following Figure 3.45 – classified as:

- recovery techniques for VOC and inorganic compounds:
    - membrane separation (see Section 3.5.1.1)
    - condensation (see Section 3.5.1.2)
    - adsorption (see Section 3.5.1.3)
    - wet scrubbing (see Section 3.5.1.4).

- abatement techniques for VOC and inorganic compounds:
    - biofiltration (see Section 3.5.2.1)
    - bioscrubbing (see Section 3.5.2.2)
    - biotrickling (see Section 3.5.2.3)
    - thermal oxidation (see Section 3.5.2.4)
    - catalytic oxidation (see Section 3.5.2.5)
    - flaring (see Section 3.5.2.6).

- recovery and abatement techniques for particulates, using:
    - separator (see Section 3.5.3.1)
    - cyclone (see Section 3.5.3.2)
    - electrostatic precipitator (see Section 3.5.3.3)
    - wet dust scrubber (see Section 3.5.3.4)
    - fabric filter, including ceramic filter (see Section 3.5.3.5)
    - catalytic filter (see Section 3.5.3.6)
    - two stage dust filter (see Section 3.5.3.7)
    - absolute filter (HEPA filter) (see Section 3.5.3.8)
    - high efficiency air filter (HEAF) (see Section 3.5.3.9)
    - mist filter (see Section 3.5.3.10).

- recovery and abatement techniques for combustion exhaust gases:
  - dry sorbent injection (see Section 3.5.4.1)
  - semi-dry sorbent injection (see Section 3.5.4.1)
  - wet sorbent injection (see Section 3.5.4.1)
  - selective non-catalytic reduction of NO_x (SNCR) (see Section 3.5.4.2)
  - selective catalytic reduction of NO_x (SCR) (see Section 3.5.4.2).

The majority of treatment techniques cannot simply be classified as recovery or abatement techniques, because whether the contaminants are recovered depends on the application of additional separation stages.

Some of the described techniques are individual operations and/or processes, others are only used as secondary pretreatment methods to avoid damage to the main treatment facilities or just take the role of a pre-filter, or they are used as a final polishing step. Others can be used as both – individual or secondary technology. Examples will be given in the paragraphs that follow.

Most waste gas treatment techniques require further downstream treatment, either for arising waste water or waste gas generated during the process, and/or disposal of solid waste. This issue will be discussed in the relevant chapters below.

3.5.1 Recovery Techniques for VOC and Inorganic Compounds

3.5.1.1 Membrane Separation

Description

Membrane separation of gases takes into account the selective permeability of organic vapours when permeating through a membrane. Organic vapours have a considerably higher permeation rate than oxygen, nitrogen, hydrogen or carbon dioxide (10 to 100 times higher [cww/tm/74]). The waste gas stream is compressed and passed over the membrane. The enriched permeate can be recovered by methods such as condensation (see Section 3.5.1.2) or adsorption (see Section 3.5.1.3), or it can be abated, e.g. by catalytic oxidation (see Section 3.5.2.5). The process is most appropriate to higher vapour concentrations. Additional treatment is in most cases needed to achieve concentration levels low enough to discharge [cww/tm/80].

Membrane separators are designed as modules, e.g. as capillary modules (see Figure 3.46) [cww/tm/64], manufactured as a polymer layer.
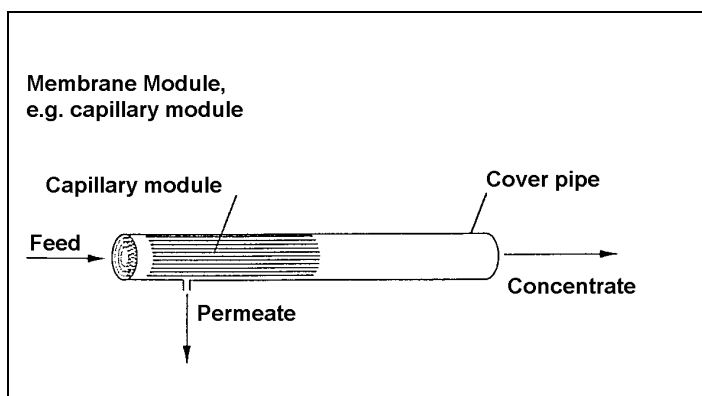
Figure 3.46: Typical Membrane Capillary Module

A membrane separation system consists of (see Figure 3.47):

- the membrane modules
- a compressor
- a recovery unit (e.g. condenser, adsorber)
- vents and ducts
- possibly a second stage for further treatment.
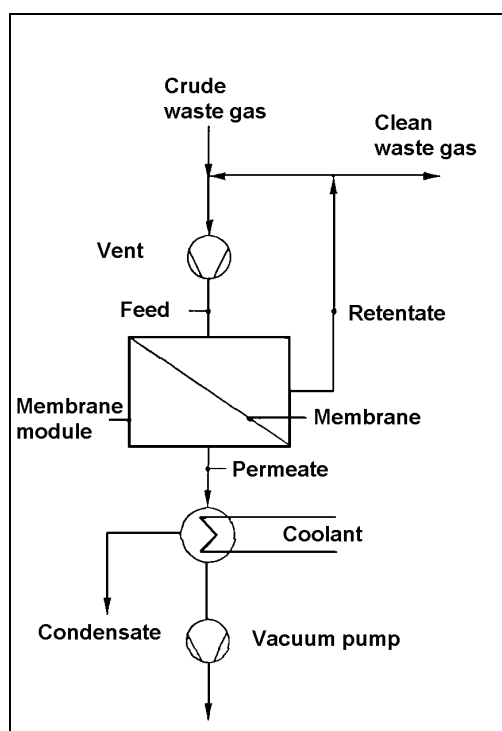
Figure 3.47: Schematic Sketch of a Common Membrane Separation Facility

To create the necessary pressure difference between feed and permeate sides of the membrane (0.1–1 MPa), the system works either by means of excess pressure on the feed side and vacuum (about 0.2 kPa) on the permeate side or both [cww/tm/64].

During the rise of vapour concentration within the membrane unit, the concentration level can climb from lower to higher than explosive limit and thus develop an explosive mixture. Safety is therefore a crucial issue and steps have to be taken to avoid these situations or to handle the risk.

An example of a membrane separation process as vapour recovery unit (VRU) is illustrated in Figure 3.48. Here a second treatment stage (PSA, see Section 3.5.1.3) improves the emission, according to the defined emission requirements.

Application

Membrane separation is applied, e.g., in the chemical industry, the petrochemical industry, refineries and the pharmaceutical industry to recover solvent vapours or fuel vapours (gasoline) from waste gas or exhaust air. Examples are [cww/tm/74] the recovery of:

- olefin monomers from polyolefin resin degassing streams
- vinyl chloride from PVC manufacturing
- solvent and hydrocarbon vapours from tank-filling
- hydrocarbon feedstocks from refinery vent and fuel gas streams
- hydrogen from refinery offgas.
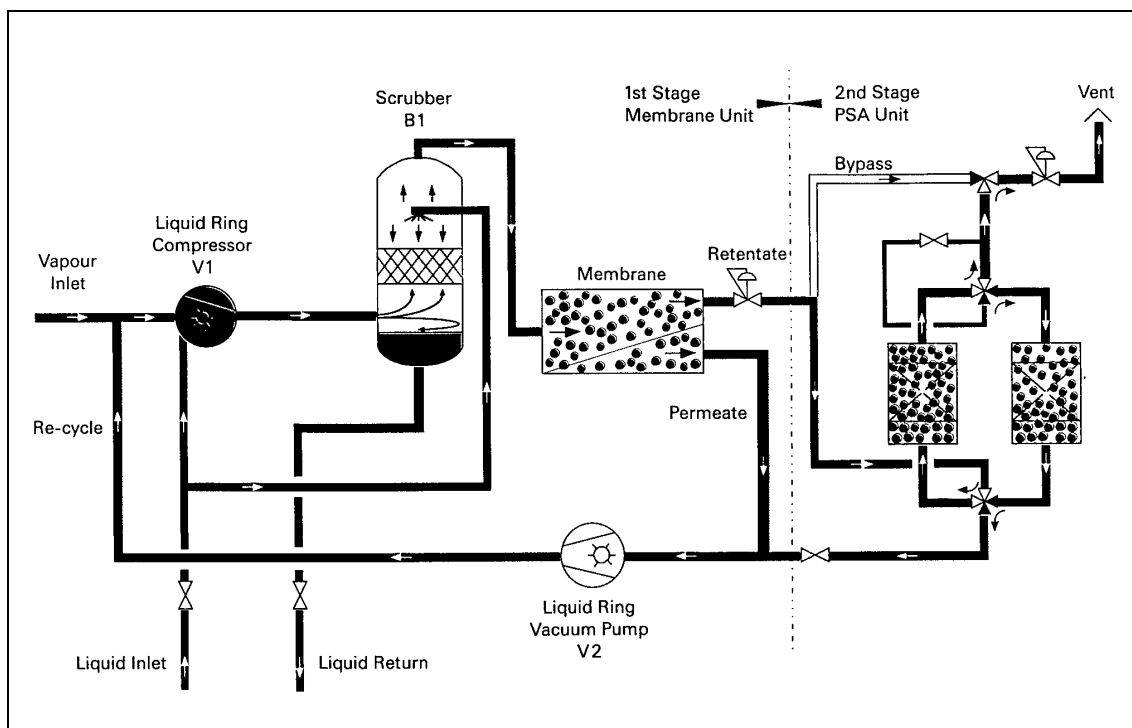
Figure 3.48: Application of a Membrane Separation Process as Vapour Recovery Unit (VRU)

Recoverable compounds include:

- alkanes
- olefins
- aromatics
- chlorinated hydrocarbons
- alcohols
- ethers
- ketones
- esters.

Application limits and restrictions:

	Limits / restrictions
Waste gas flow	dependent on membrane surface area, capacities of 2100–3000 Nm^3/h are known
Temperature	ambient temperature, dependent on membrane material
Pressure	dependent on membrane material
Dust content	very low, dust can damage the membrane surface, thus very low dust concentrations have to be achieved in advance
VOC concentration	up to 90 %

Advantages/Disadvantages

Advantages	**Disadvantages**
• The re-use of raw material is possible. • The operation in itself is simple. • No waste generated by the process.	• Subsequent work-up and/or treatment step necessary. • Explosion risk.

Achievable Emission Limits / Performance Rates

Parameter	Performance rate [%]	Remarks
Hydrocarbon	90–99 [1,a]	process for hydrocarbon recovery, upstream condensation unit
VOC	up to 99.9 [1,a]	VOC recovery, upstream and downstream condensation unit
[a] for solution membranes [1] [cww/tm/74]		

Cross-media Effects

Consumable	Amount	Remark
Membrane material		
Cooling medium		
Energy [kWh/1000 Nm^3]	250 [1]	electric energy for fan included
Pressure drop [MPa]	0.1–1 [2]	
[1] [cww/tm/70] [2] [cww/tm/64]		

Membrane separation is frequently used as a concentration step to facilitate further recovery or treatment, e.g.:

- enrichment of VOC in the gas phase increases the dew point of the waste gas stream, so that subsequent condensation occurs more readily, thereby saving money
- incinerating an enriched waste gas stream reduces the need for additional fuel.

VOCs from membrane separation processes are usually recycled and no residues result from the actual membrane process. It can, however, cause waste in a subsequent treatment step, depending on the technique used. Residual emissions can arise from cooling water or the treated waste gas stream. These gas streams are released either to the atmosphere via stack or to a subsequent waste gas treatment step, such as adsorption or incineration.

Monitoring

The efficiency of the membrane separation system is determined by monitoring the concentration of VOC before and after the membrane system. VOCs can be measured as total carbon, using a flame ionisation detector. The performance is improved by controlling the VOC concentration on both membrane sides. For safety reasons the VOC / oxygen ratio has to be carefully controlled (explosion risk).

Economics

Type of costs	Costs	Remarks
Capital costs [per 1000 Nm^3/h]	EUR 300000 [1]	a 200 Nm^3/h treatment system
Operating costs labour utilities	EUR 1500/yr [1] EUR 60000/yr per 1000 Nm^3/h [1]	4 days per year
[1] [cww/tm/70]		

Cost-relevant parameters are the waste gas flow rate and the technical service life of the membrane. Revenue is the recovered VOC.

System costs vary in relation to the desired recovery target, capacity and design. Payback periods in connection with high-value products are reported to be between four months and one year under favourable conditions [cww/tm/74]. On the other hand there might be no payback at all. Combination with another process (e.g. adsorption or absorption) might prove to be more profitable compared with a one-step membrane separation.

3.5.1.2 Condensation

Description

Condensation is a technique that eliminates solvent vapours from a waste gas stream by reducing its temperature below its dew point.

There are different methods of condensation, depending on the operating temperature range:

- coolant condensation, down to condensation temperature of about 25 °C
- refrigerant condensation, condensation temperature down to about 2 °C
- brine condensation, condensation temperature down to about -10 °C
- ammonia brine condensation, condensation temperature down to about -40 °C (one-stage) or -60 °C (two-stage)
- cryogenic condensation, condensation temperature down to about -120 °C, in practice often operated between -40 and -80 °C in the condensation device
- closed-cycle inert gas condensation.

Condensation is carried out by means of direct (i.e. contact between gas and cooling liquid) or indirect cooling (i.e. cooling via heat exchanger). Indirect condensation is preferred because direct condensation needs an additional separation stage. Recovery systems vary from simple, single condensers to more complex, multi-condenser systems designed to maximise energy and vapour recovery [cww/tm/71].

Closed-cycle inert gas condensation is designed for closed-cycle systems together with high vapour concentrations. A fixed volume of inert gas – generally nitrogen – is continuously recycled around the oven and the condensation unit. A proportion of the nitrogen/vapour mixture is continuously drawn into the recovery module, where a series of heat exchangers cools and condenses the vapours [cww/tm/71].

The design and operation of condensers are highly dependent on the cooling medium used in the process. Some examples are:

- Devices for liquid-cooled (i.e. not cryogenic) condensation are operated with two types of heat exchangers:

  Conventional shell-and-tube heat exchanger [cww/tm/71], which is either water-cooled or air-cooled. The condensation efficiency can be improved by two-stage operation, using water in the first stage and refrigerated liquid (water, brine etc.) as cooling medium in the second stage. Such a two-stage system consists of (see Figure 3.49 [cww/tm/71]):

  - the recuperator, using the cold purified gas stream as chilling agent
  - the pre-cooler for further cooling, using chilled water or the cold purified gas stream
  - the main refrigerator condenser
  - vents and ducts.

  Another option involves partial condensation at a slightly higher temperature followed by removal of the remaining VOC from the gas stream by a different technique, such as adsorption (see Section 3.5.1.3).

  To minimise fog formation, a series of condensers can be used, as well as a demister supported by gas velocity reduction in the condenser.
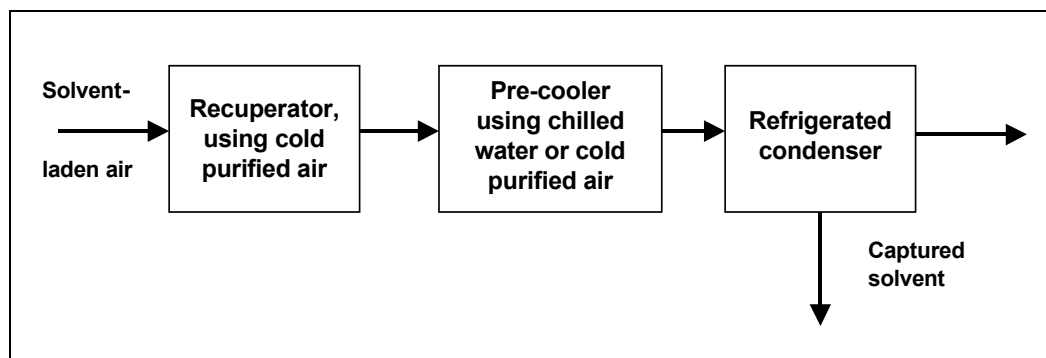
Figure 3.49: Two-Stage Condensation System

Spiral heat exchanger [cww/tm/71], basically consisting of two long strips of plate wrapped to form a pair of concentric spiral passages. The cooling medium enters through a peripheral nozzle, spirals to the centre and exits, via a pipe, to a nozzle on the periphery. Process vapours enter through the bottom of the condenser and flow upwards in cross-flow.

If cooling towers are included and/or surface water is used, the heat exchangers can tend to fouling, which requires flushing programmes and/or cooling water treatment.

In the presence of acidic or alkaline components, a recirculation system containing acid or alkali dosage might be considered.

- Cryogenic condensation is operated, using the vaporisation of liquid nitrogen as coolant medium, to condense VOC vapour at the condenser surface. The evaporated nitrogen is used to provide inert blanketing. A variant is condensation under inert atmosphere, i.e. nitrogen, to enable the gas stream to contain higher concentrations of VOC. Examples of cryogenic condensation are given in Figure 3.50 and Figure 3.51 [cww/tm/71].
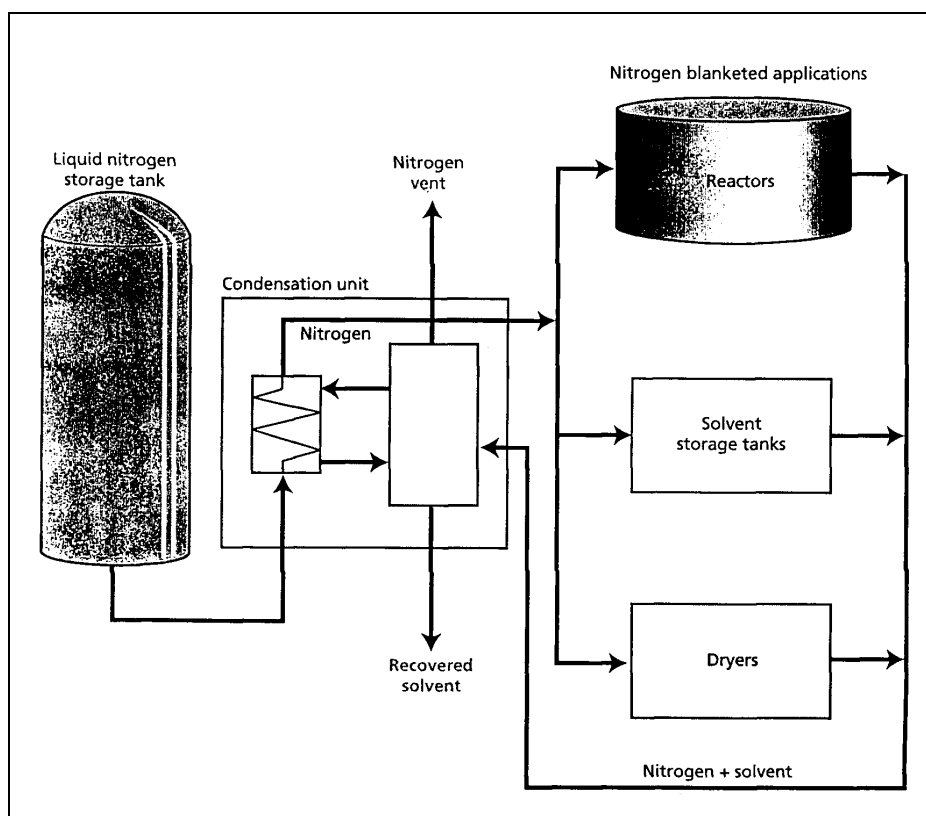
Figure 3.50: Cryogenic Condensation Recovery System Integral with a Typical Nitrogen Blanketing Operation
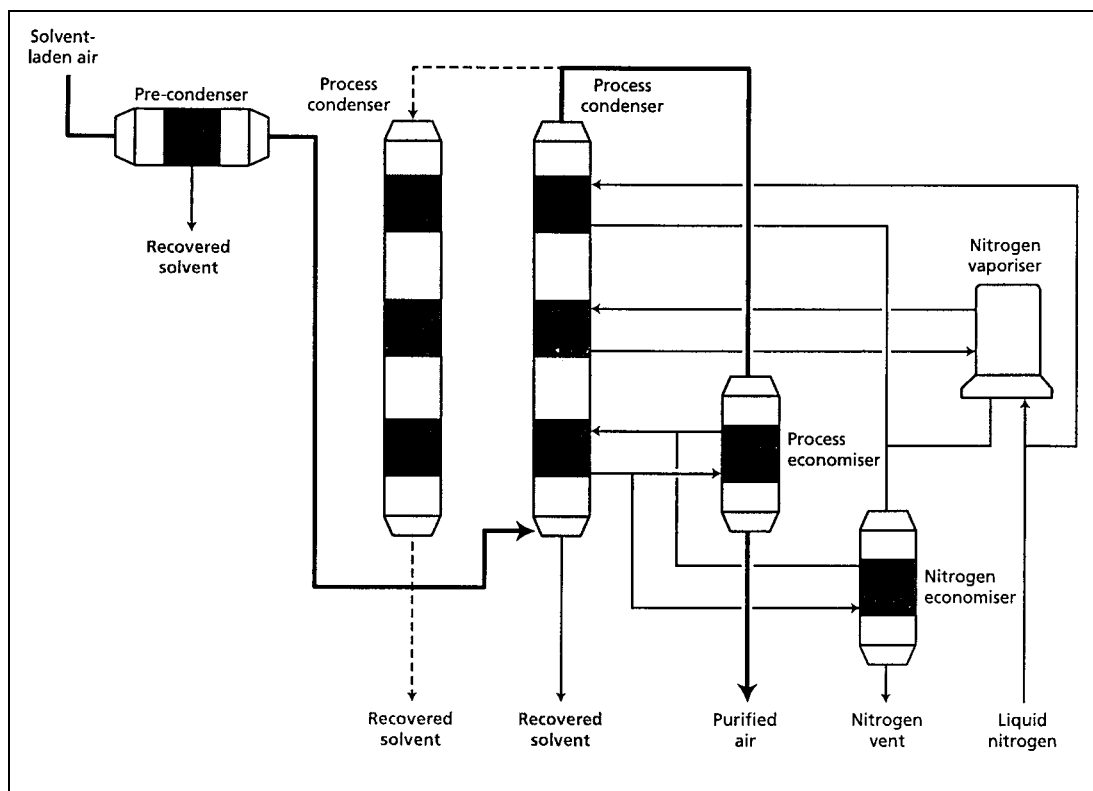
Figure 3.51: Cryogenic Recovery System under Inert Atmosphere

The cryogenic condensation system consists of:

- the pre-condenser, using chilled water or glycol
- the main process condenser(s)
- the process economiser
- the nitrogen economiser
- the nitrogen vaporiser
- the necessary vents and ducts.

- A typical closed-cycle inert gas condensation system consists of (see Figure 3.52 [cww/tm/71]):

- the heat exchanger, pre-cooling the gas stream
- the main condenser, mechanically refrigerated to as low as -40 ºC
- the solvent separator, the nitrogen supply.

Application

Coolant condensation

Coolant condensation is applied to more or less saturated gas streams (i.e. high dew point) of volatile compounds (organic and inorganic) and odorous substances, the latter being removed from a water-saturated gas stream where the condensed water acts as absorbant (provided they are soluble in water).

An essential application of coolant condensation is pretreatment or post-treatment for upstream or downstream waste gas treatment facilities. The removal of the main VOC load relieves treatment facilities such as adsorbers (see Section 3.5.1.3), scrubbers (see Section 3.5.1.4), incinerators (see Section 3.5.2.4). On the other hand, condensation is a suitable post-treatment for enriched gas streams from, e.g. membrane separation (see Section 3.5.1.1) or waste water stripping (see Section 3.3.4.2.14) and distillation (see Section 3.3.4.2.12).
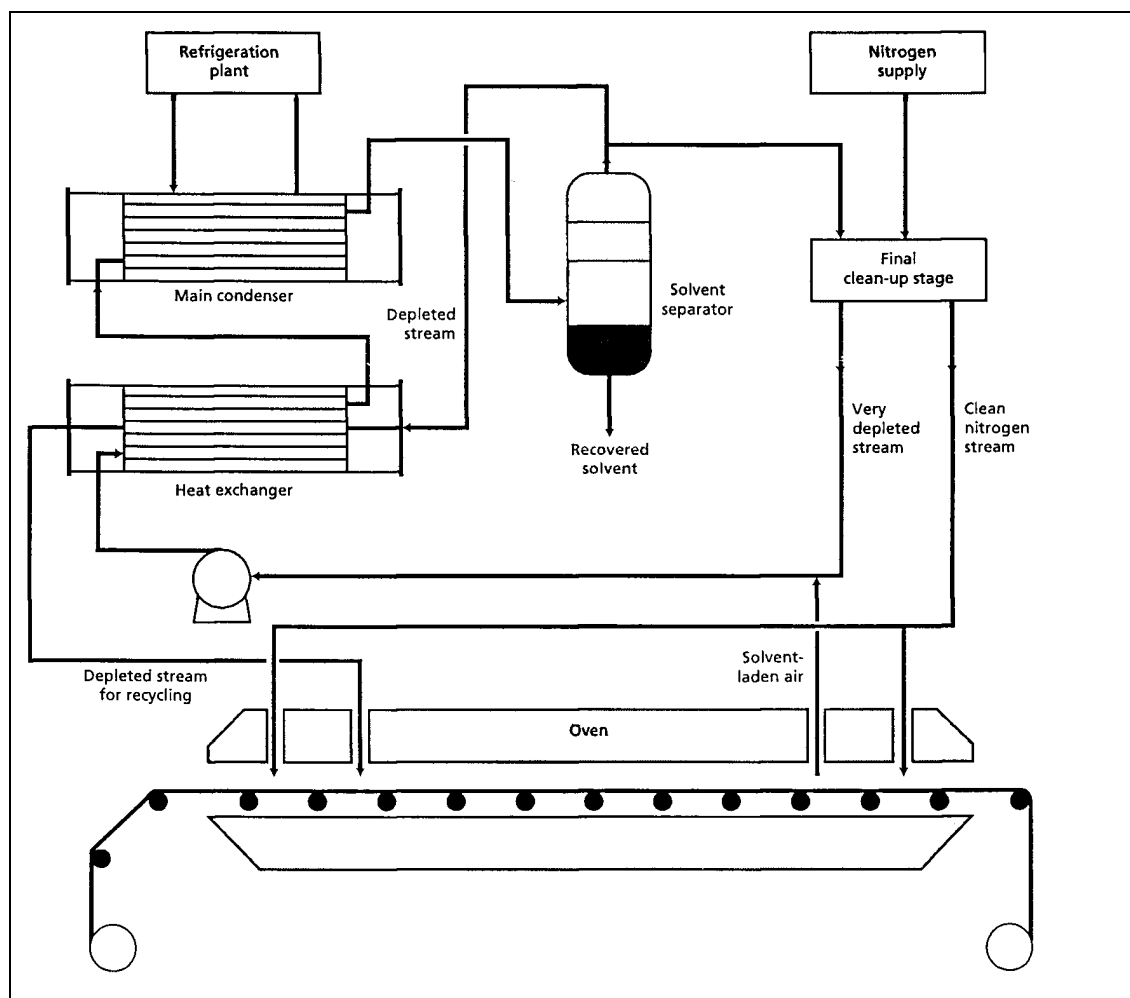
Figure 3.52: Typical Closed-cycle Inert Gas Condensation System

Application limits and restrictions are [cww/tm/70]:

	Limits / restrictions
Gas flow	100–100000 Nm^3/h
Incoming gas temperature	50–80 °C
Water content	gas needs to be essentially water-free when condensation below 0 °C
Pressure	atmospheric
Dust	<50 mg/Nm^3 (non sticky)
Odour	>100000 ou/Nm^3
Ammonia	200–1000 mg/Nm^3

Cryogenic condensation

Cryogenic condensation can cope with all VOC and volatile inorganic pollutants, irrespective of their individual vapour pressures. The applied low temperatures allow very high condensation efficiencies in such a way that it is well suited as final VOC emission control. On the other hand, temperatures below the freezing point of water require an essentially water-free gas feed. It is able to respond instantly to changes in VOC flow rate and solvent loading and can recover virtually any VOC species even under varying conditions. This flexibility makes it particularly suitable for VOC control in multi-product, multi-purpose plants where batch or continuous processes are employed [cww/tm/150].

Application limits and restrictions are:

	Limits / restrictions
Gas flow	up to 5000 Nm^3/h
Incoming gas temperature	up to 80 °C
Pressure	2–600 kPa [1]

[1] [cww/tm/70]

Advantages/Disadvantages

Advantages	Disadvantages
Coolant condensation • Compact technology. • Good process handling, emissions can at least be calculated approximately. • Downstream treatment facilities are relieved of high loads and can therefore be operated more economically. • Solvent recovery, provided the gas stream does not contain a VOC mixture difficult to separate. • Heat recovery is possible.	Coolant condensation • The amount of cooling water is an issue in regions with water deficiency. • Efficiency considerably dependent on gas flow rate and composition. • Subsequent work-up and/or treatment step necessary.
Cryogenic condensation • Compact technology. • Recovery of organic solvents, provided they can be separated from the condensed mixture. • High VOC removal efficiency. • Nitrogen gas is recycled. • Good process handling possible, emissions can at least be calculated approximately.	Cryogenic condensation • Not suitable for wet gas streams because of ice formation that impedes heat transfer. • Need for nitrogen generation facility, or instead external delivery of nitrogen • Coolants below 0 °C can cause ice formation on heat exchanger.

Achievable Emission Levels / Performance Rates

Coolant condensation

Parameter	Performance rate [%]	Emission level [mg/Nm^3]	Remarks
Odour	60–90 [1]		initially > 100000 ou/Nm^3
Ammonia	20–60 [1]		initially 200-1000 mg/Nm^3

[1] [cww/tm/70]

Cryogenic condensation

Parameter	Performance rate [%]	Emission level [mg/Nm^3]	Remarks
Dichloromethane		<20-<40 [1]	at –95 °C, initially 20-1000 g/Nm^3
Toluene		<100 [1]	at –65 °C, initially 20-1000 g/Nm^3
Methyl ethyl ketone (MEK)		<150 [1]	at –75 °C, initially 20-1000 g/Nm^3
Acetone		<150 [1]	at –86 °C, initially 20-1000g/Nm^3
Methanol		<150 [1]	at –60 °C, initially 20-1000 g/Nm^3
VOC		1000–5000 [1]	initially 200–1000 g/Nm^3

[1] [cww/tm/70]

Cross-media Effects

Coolant condensation

Consumable	Amount	Remarks
Cooling medium (air, water, brine, ammonia-brine)		highly dependent on individual application
Energy [kWh/1000 Nm^3]		vents, pumps, cooling facilities
Pressure drop [kPa]	0.1–0.2 [1]	
[1] [cww/tm/70]		

The quantity of waste water generated by the condensation facility is directly proportional to the amount of condensate, which in turn is directly proportional to the moisture content and the chosen cooling temperature. Typical ranges of condensate contents are:

- condensation of VOC: 200–1000 mg/l COD
- condensation of ammonia / amines: 400–2000 mg/l Kjeldahl-N.

Cryogenic condensation

Consumable	Amount	Remarks
Nitrogen as cooling medium	10–15 kg/kW cooling [1]	depends on plant design, solvent type, etc.
Energy [kWh/1000 Nm^3]	70	input at 80 °C, output at –70 °C
Pressure drop [kPa]	2–5 [2]	
[1] [cww/tm/71] [2] [cww/tm/70]		

Further consumables are:

- steam as thawing agent, when a condenser is frozen because of moisture in the waste gas stream
- moisture-free compressed air for pneumatic operations.

The condensate can be re-used, reprocessed or disposed of.

The consumption of liquid nitrogen is divided into:

- stand-by processing (to keep the temperature)
- cooling of the incoming gas stream to condensation.

There are still moderately high VOC concentrations after condensation processes, which may require further treatment (e.g. adsorption, or incineration).

Inert gas cycle condensation

Consumable	Amount	Remarks
Nitrogen as inert gas, for emergency purges and/or refrigeration	1–2 tonnes/day [1]	
Energy [kWh/1000 Nm^3]		vents, pumping, cooling facilities
Pressure drop [kPa]		
[1] [cww/tm/71]		

Monitoring

The efficiency of the condensation system as an air cleaning system may be determined by monitoring the concentration of the solvent vapours before and after. VOCs can be measured as total carbon, excluding particulate matter, using a flame ionisation detector. Abatement efficiencies for odorous emissions are determined by taking grab samples at appropriate sampling points and subsequently analysing them by olfactometry. Cryogenic systems require pressure drop monitoring.

Cryogenic systems use standard programmable logic controllers to control nitrogen requirements for cooling. Automatic operation of the plant should be possible, provided alarms are set as required and routine checks are carried out by operators during each shift.

Additionally, in inert gas cycle systems, oxygen analysis is carried out to ensure that an inert atmosphere of less than 5 % oxygen is maintained – for safety reasons – in the oven vent stream. If the oxygen content is too high, nitrogen is injected to restore the inert atmosphere [cww/tm/71].

Economics

Type of cost	Costs		
	Coolant condensation	Cryogenic condensation	Closed-cycle inert gas condensation
Capital costs [a]	EUR 5000 [b] [1]	EUR 500000 [c] [1]	
Operating costs: labour costs	2 hours per week + 1 staff-day per year [1]	1 staff-day per week [1]	
[a] per 1000 Nm^3/h [b] excluding pumps, pipes, cooling tower [c] excluding secondary techniques and nitrogen storage [1] [cww/tm/70]			

Revenue is the recovered VOC.

Cost factors [cww/tm/71]:

Factors	Influence / results
Emission flow rate	overall size of the system, utility requirement
Required temperature reduction, i.e. cooling load	equipment costs (directly proportional), supply of cooling agent (directly proportional)
Solvent mixtures	complexity of downstream separation techniques (directly proportional), energy intensity of separation techniques (directly proportional)
Solvent solubility	complexity of downstream separation techniques (directly proportional), energy intensity of separation techniques (directly proportional)

Retrofittability [cww/tm/71]:

Coolant condensation	Cryogenic condensation	Closed-cycle inert gas condensation
readily retrofittable when cooling water is available, with the heat exchangers being positioned nearby or on top of the relevant piece of equipment	can be skid-mounted, may replace any existing nitrogen vaporisers, should be installed near a liquid nitrogen source to minimise the length of cryogenic pipeline, systems can either be retro-fitted to existing plants or integrated into new plants	are difficult to retrofit onto existing production plants; they are more suited to new plants

3.5.1.3 Adsorption

<u>Description</u>

Adsorption is a heterogeneous reaction in which gas molecules are retained on a solid surface (adsorbent) that prefers specific compounds to others and thus removes them from effluent streams. When the surface has adsorbed nearly as much as it can, the adsorbed content is desorbed as part of regenerating the adsorbent. When desorbed, the contaminants are usually at a higher concentration and can either be recovered or abated (destroyed) [cww/tm/135].

Major types of adsorption systems are:

- fixed-bed adsorption
- fluidised-bed adsorption
- continuous moving-bed adsorption
- pressure-swing adsorption (PSA).

Fixed-bed adsorption processes (see Figure 3.53 [cww/tm/71]) are widely used. Waste gas, exhausted air, etc. are conditioned upstream by cooling, partial condensation of water vapour and heating to reduce the relative humidity to minimise the co-adsorption of water. The gas is fed at about 40 °C to the adsorber, passes upwards and leaves purified. To allow regeneration, adsorbers are normally operated as multiple (2 or 3) bed facilities, i.e. one bed is loaded, the other regenerated and, optionally, a third bed is in stand-by mode. A twin bed adsorption process is illustrated in Figure 3.53.
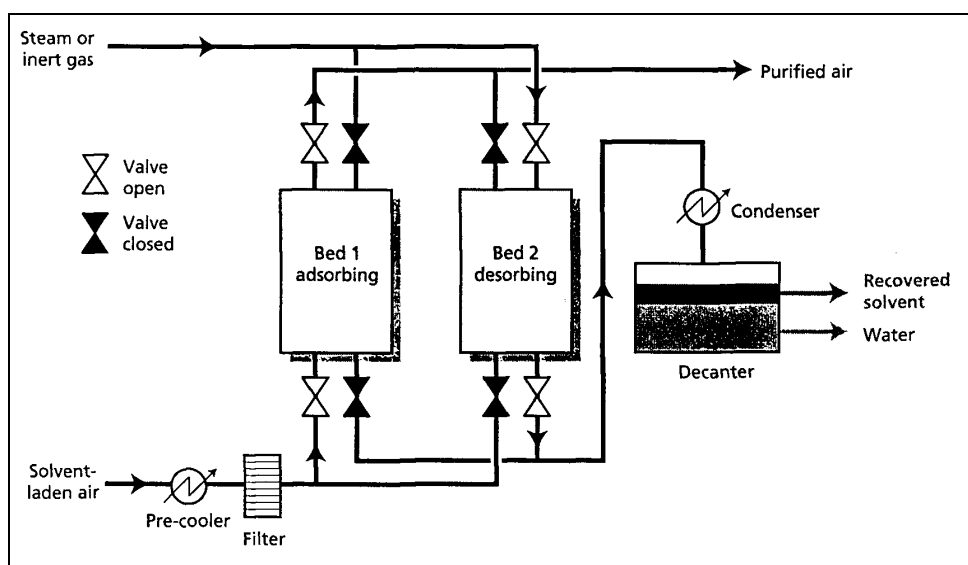
Figure 3.53: Typical Twin Bed Adsorption Process

Fluidised-bed processes (see Figure 3.54 [cww/tm/132]) use the gas velocity (mainly in the range of 0.8–1.2 m/s) to maintain the adsorbent in a fluidised state. These systems require attrition-resistant adsorbent beads. They are operated with continuous adsorption / desorption, the adsorbent regenerated in a heat exchanger underneath the adsorber and subsequently returned pneumatically to the fluidised bed.

With **Continuous moving-bed** processes (see Figure 3.55 [cww/tm/71]) the adsorbent is continuously fed on top of the adsorber, passing the gas stream in counter-current. The saturated adsorbent at the bottom of the vessel is continuously transferred to a moving-bed regenerator.

Pressure-swing adsorption (PSA) can separate gases or vapours in a waste gas mixture and simultaneously regenerate the adsorbent. It consists of four steps:

Step 1: pressure is built up by the gas streaming into the adsorber
Step 2: adsorption at high pressure and hence production of pure components
Step 3: depressurisation
Step 4: purging at low pressure or under vacuum.

This four-step process causes a separation of components according to their bond strength to the adsorbent. With downstream treatment facilities this technique improves the ability of waste gas mixtures to be recovered and re-used.
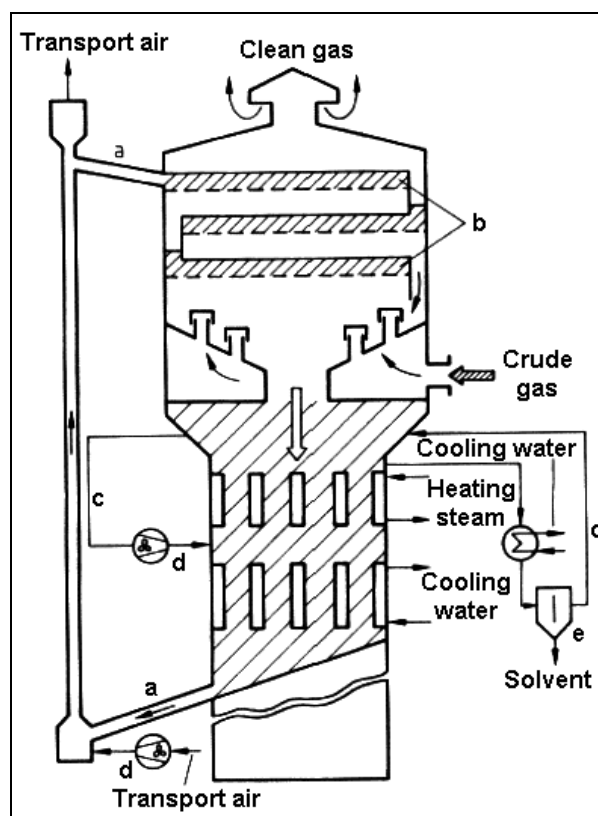
Figure 3.54: Fluidised-Bed Adsorption
a) regenerated adsorbent, b) fluidised bed, c) inert gas, d) fan, e) separator

Typical adsorbents are, e.g. [cww/tm/71]:

- granular activated carbon (GAC), the most common adsorbent with a wide efficiency range and not restricted to polar or non-polar compounds; GAC can be impregnated with, e.g. oxidants such as potassium permanganate or with sulphur compounds (improving retention of heavy metals) [cww/tm/70]

- zeolites, properties depending on its manufacture, working either as mere molecular sieves, selective ion exchanger or hydrophobic VOC adsorber
- macroporous polymer particles, which are used as granules or beads, not being highly selective with respect to VOC
- silica gel
- sodium-aluminium silicates.

Besides the continuous and simultaneous regeneration methods described above, there are several methods to regenerate the adsorbent of fixed-bed adsorbers:

- thermal-swing regeneration
- vacuum regeneration
- PSA, described above.
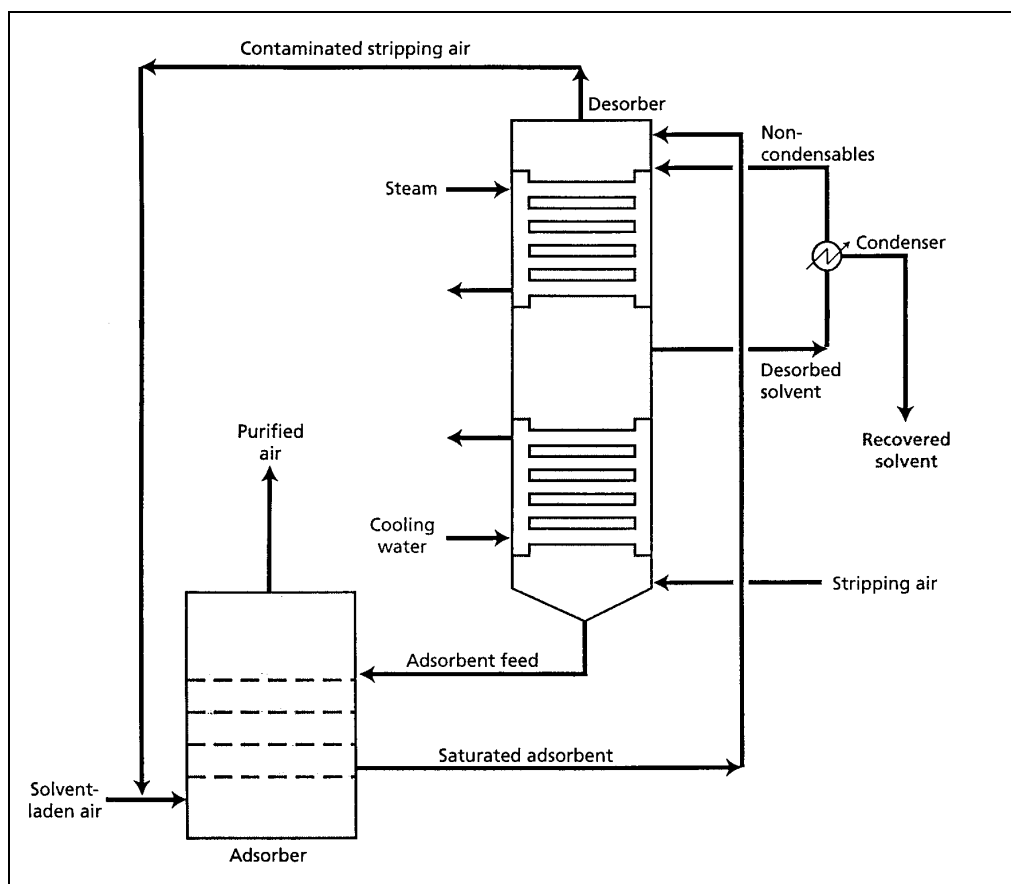
Figure 3.55: Continuous Moving Bed Adsorption and Desorption

Thermal-swing regeneration uses several heat sources:

- steam, as the most common
- microwaves
- embedded heaters
- heated gas, the use of an inert hot gas for safety reasons with GAC as adsorbent.

Superheated steam is passed downward through the adsorbent and thus carries the loaded compounds down to a condensation and separation unit, such as gravity separators or distillation facilities. Superheated steam is the main regeneration method for GAC, but heated inert gases are also applied. Zeolites can be regenerated by hot air streams. Polymer adsorbers allow much lower regeneration temperatures for steam or hot gas (about 80 °C).

Vacuum regeneration enables desorption at ambient adsorbent temperature, which is suitable to recover and re-use vulnerable substances. This method is applied to GAC, zeolite and polymer adsorbents.

Application

The application of adsorption encompasses:

- recovery of VOC (raw material, product, solvent, fuel from filling operations, etc.) for re-use or recirculation, probably as a concentration step to improve the viability of further recovery operations such as membrane separation (see Section 3.5.1.1)
- abatement of pollutants (hazardous substances from production or treatment facilities [e.g. WWTP] such as VOC, odours, trace gases etc.) that cannot be recirculated or otherwise used, possibly with GAC as adsorbent, not regenerated but incinerated
- as guard filter after final treatment facilities.

The application as abatement technology is not recommended for waste gases with very high VOC concentrations, because the consequent regeneration requirements would adversely affect profitability. There are normally more suitable techniques.

Adsorption technology is applicable to control, recover, recycle or prepare (for downstream treatment) VOC and organic hazardous air pollutant emissions, e.g. emissions from:

- degreasing
- paint spraying
- solvent extraction
- metal foil coating
- plastic film coating
- paper coating
- pharmaceuticals
- fuel gas, gasoline, etc.

Application limits and restrictions:

	Limits / restrictions		
	GAC	**Zeolites**	**Polymers**
Gas flow [Nm³/h]	100–100000 [1]	<100000 [1]	
Temperature [°C]	15–80 [1]	<250 [1]	
Pressure [MPa]	0.1–2 [1]	atmospheric [1]	
VOC content	maximum 25 % of LEL	maximum 25 % LEL	maximum 25 % LEL
Dioxins [ng/Nm³ TEQ]	10–100 [1]		
Relative humidity	maximum <70 % as low as possible		
[1] [cww/tm/70]			

Advantages/Disadvantages

Advantages	Disadvantages
- High efficiency for VOC removal and recovery. - Simple and robust technology. - High saturation grade of the adsorbent. - Simple installation. - Simple maintenance.	- Particulates in the waste gas stream can cause problems. - Mixtures can cause early breakthrough. - Not suitable with wet waste gas streams. - Risk of bed fires (GAC and zeolites, whereas polymers are operated at lower temperatures). - Potential for polymerisation of unsaturated organic compounds on GAC.

Achievable Emission Levels / Performance Rates

Parameter	Performance rate [%]	Emission level [mg/Nm^3]	Remarks
VOC	80–95 [1]		GAC
Toluene	90 [1]		GAC
Odour	80–95 [1]		GAC, Zeolite
Mercury		<0.01-0.05 [1]	GAC
Hydrogen sulphide	80–95 [1]		GAC
Dioxins		<0.1 ng/Nm^3 TEQ [1]	GAC
[1] [cww/tm/70]			

Cross-media Effects

Consumables are:

Consumable	Amount			Remarks
	GAC	Zeolite	Polymer	
Steam (desorption) [kg/kg solvent regained]	1.5-6 [1]			
Nitrogen gas (hot gas desorption) [Nm^3/tonne solvent]	35 [1]			
Cooling water (condensation) [m^3/tonne solvent]	35–60 [2] 100–150			for all 3 adsorption techniques
Loss of adsorbent [kg/tonne solvent]	0.5–1 [2]			
Pressure drop [kPa]	2–5 [2]			
Energy [kWh/tonne solvent]	35–100 [2] 130–260			
[1] [cww/tm/71] [2] [cww/tm/64]				

Steam regeneration produces waste water with relatively high loads of contaminants which has to be discharged to a waste water treatment. When there is no regeneration, the adsorbent has to be disposed of, i.e. normally transferred to incineration, a route that is not suitable for mercury-loaded adsorbent. Regeneration and/or disposal of adsorbent can also be done by external companies.

Further downstream gas treatment can be necessary, depending on legal requirements.

Since all adsorption processes are exothermic, they cause a temperature rise, which is not desirable for the adsorption of organic compounds. Carbon or metals on GAC as well as zeolites can catalyse the oxidation of some components when the adsorbent is hot, resulting in bed fires which also consume part or all of GAC, but not of zeolite. This is a hazard when adsorbing certain hydrocarbons (such as ketones or comparable active compounds) at ambient temperatures that are close to those that cause the organic compound to oxidise. Such a GAC bed fire can either alter the pore size of the remainder of the bed, or oxidise the bed to ash, which means a serious incident that may burn down the whole facility. These fires may be suppressed by humidification of the air and by intentional cooling of the GAC.

Monitoring [cww/tm/79]

The abatement efficiency of the system is determined by monitoring the concentration of VOC/odour before and afterwards. VOCs can be measured as total carbon (excluding particulate matter), using a flame ionisation detector. A qualitative analysis of the emissions can be carried out if grab samples of gas are taken at selected sampling points and are subsequently analysed by GC/MS or GC/FID. Abatement efficiencies for odorous emissions are determined by taking grab samples at appropriate sampling points and subsequently analysing them by olfactometry.

The most important measurement is the pressure drop across the dust filters and across the adsorbent bed. Across the filters the pressure should rise steadily after renewal or cleaning. Too rapid a rise gives warning of too high a pressure drop later on due to an abnormal dust load.

Across the bed the pressure should remain roughly constant. Any increase indicates either dust bypassing the dust filter or adsorbent dust from granule breakdown. There should also be an alarm for high pressure.

Temperature monitoring of the gas outlet of the GAC adsorber is required to prevent fire risk.

Adsorption systems are typically controlled by a programmable logic controller, with new systems based on breakthrough sequencing of the beds. When the emission level from an operating bed reaches a pre-set level, the beds are switched over and regeneration starts. This is energy efficient as desorption is always performed on a saturated bed.

Subject to consideration of flammable hazards, control systems can be designed to allow a solvent concentration of up to 25 % of the LEL. This minimises both fan power and steam consumption. If flow rates and solvent loading are variable, power requirements can be optimised by fitting control dampers or variable speed drives for the fan. [cww/tm/71]

Economics

Type of cost	GAC	Zeolite	Polymer	Remarks
Capital [per 1000 Nm^3/h]	EUR 5000-10000 [1]			excluding regeneration
	EUR 240000 [1]			including regeneration [a]
Operating costs				
Utilities				
Consumables	EUR 600–1300 per tonne GAC			including disposal
[a] facility for 1000 Nm^3/h [1] [cww/tm/70]				

Cost factors [cww/tm/71]:

Factors	Influence / results
Emission flow rate	Overall size of the system, utility requirement
Solvent adsorption efficiency, solvent concentration	Quantity of adsorbent required
Solvent type	Choice of adsorbent
Solvent solubility	Complexity of downstream separation techniques (directly proportional to solubility), energy intensity of separation techniques (directly proportional)
Solvent mixtures	Complexity of downstream separation techniques (directly proportional), energy intensity of separation techniques (directly proportional)
Solvent solubility	Complexity of downstream separation techniques (directly proportional), energy intensity of separation techniques (directly proportional)
Solvent loading	Use of utilities (steam) in adsorption / desorption cycle and rate of adsorbent degradation
Presence of impurities	Reducing lifetime of adsorbent
Ease of solvent desorption	Desorption temperature

Retrofittability [cww/tm/71]:

GAC	Zeolite	Polymer
Provided sufficient space is available, retrofitting an adsorption system to an existing manufacturing process is generally straightforward. The space requirement of a continuous adsorption/desorption unit is approximately 25 % that of a two-bed adsorber system.		

3.5.1.4 Wet Scrubbers for Gas Removal

Description

Wet scrubbing (or absorption) is a mass transfer between a soluble gas and a solvent – often water – in contact with each other. Physical scrubbing is preferred for chemicals recovery, whereas chemical scrubbing is restricted to removing and abating gaseous compounds. Physico-chemical scrubbing takes an intermediate position. The component is dissolved in the absorbing liquid and involved in a reversible chemical reaction, which enables the recovery of the gaseous component [cww/tm/132].

The major waste gas treatment applications of scrubbing processes are:

- removal of gaseous pollutants, such as hydrogen halides, SO_2, ammonia, hydrogen sulphide or volatile organic solvents
- removal of SO_2 or hydrogen halides
- but also removal of dust with certain types of scrubbers (see Section 3.5.3.4)

Depending on the pollutants to be removed, several aqueous scrubbing liquids are used:

- water, to remove solvents and gases such as hydrogen halides or ammonia, with the main aim to recover and re-use these contaminants
- alkaline solutions, to remove acid components such as hydrogen halides, sulphur dioxide, phenols, chlorine; also used for second-stage scrubbing to remove residual hydrogen halides after first-stage aqueous absorption; biogas desulphurisation
- alkaline-oxidation solutions, i.e. alkaline solutions with sodium hypochlorite, chlorine dioxide, ozone or hydrogen peroxide
- sodium hydrogensulphite solutions, to remove odour (e.g. aldehydes)
- Na_2S_4 solutions to remove mercury from waste gas
- acidic solutions, to remove ammonia and amines
- monoethanolamine and diethanolamine solutions, suitable for the absorption and recovery of hydrogen sulphide.

Various types of scrubbers are operated, e.g.:

- fibrous packing scrubber
- moving bed scrubber
- packed bed scrubber
- impingement plate scrubber
- spray tower.

Their choice depends on the

- requirement for performance efficiency
- energy need
- reagents
- properties of the waste gas stream.

An optimum design of scrubbing systems to achieve low exit concentrations includes high reliability, automatic operation and counter-current flow of liquid and gas. Scrubbers are normally operated with pre-coolers (e.g. spray chambers and quenchers) to lower the inlet gas temperature and simultaneously saturate the gas stream, thus avoiding reduced absorption rates and solvent evaporation. Such additional devices exert low pressure drops.

- **Fibrous Packing Scrubber**
  The fibrous packing scrubber (fibre-bed scrubber) consists of a chamber with gas inlet and outlet, containing mats of fibrous packing material which are sprayed with liquid. The units may be designed for horizontal or vertical gas flow. Typical fibre materials are glass, plastic and steel. They are used to remove acidic components (hydrogen fluoride, hydrogen chloride, sulphuric acid and chromic acid) and organic/inorganic compounds from effluent gas streams.

  The blockage of nozzles, plugging of fibre beds and insufficient irrigation of fibrous mats might cause problems.

  Waste gas streams are often cooled before entering fibrous packing scrubbers to condense as much of the liquid in the flow as possible and to increase the size of the existing aerosol particles through condensation. A pre-filter is generally used to remove larger particles from the gas stream prior to its entering the scrubber [cww/tm/110].

- **Moving-bed Scrubbers**
  Moving-bed scrubbers consist of zones of mobile packing, usually plastic spheres. The vessel shell contains support grids, on which the packing material is placed, inlets and outlets for gas scrubbing liquor and a mist eliminator. Moving-bed scrubbers are applied to remove sulphur dioxide, hydrogen fluoride and odours. They are also used to treat waste gases that contain dust and when scale might be formed. A typical device is shown in Figure 3.56 [cww/tm/79].
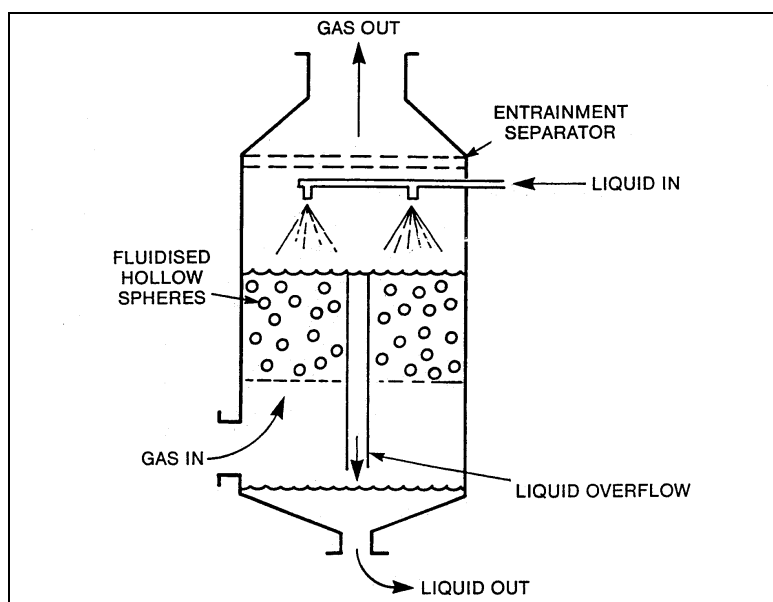
Figure 3.56: Moving-bed Scrubber

Moving-bed scrubbers are packed with low-density plastic spheres that are free to move within the support grids. These scrubbers are less susceptible to plugging because the spherical, hollow plastic balls are kept in a constant state of agitation and fluidisation. The column mobile packing resists clogging. This constant movement and the smooth surface of the balls prevent scale from adhering to the packing.

- **Packed-bed Scrubbers**

    Packed-bed scrubbers consist of an outer shell containing a bed of variously shaped packing material on support grids, liquid distributors, gas and liquid inlets and outlets and a mist eliminator. In vertical designs (packed towers), the gas stream flows up the chamber (counter-current to the liquid). They are the most commonly used gas absorbers for pollution control. Packed-bed scrubbers, with appropriate reagents, are used to absorb sulphur dioxide, chromic acid, hydrogen sulphide, ammonia, chlorides, fluorides and VOC. A typical example is shown in Figure 3.57 [cww/tm/79].

    Packed-bed scrubbers are not suitable for particle collection because of plugging. They are generally limited to applications in which the particle content is less than 0.5 g/Nm^3. Plugging and scaling are serious problems for packed-bed scrubbers because the packing is more difficult to access and clean than other scrubber designs. Consequently a separate, very efficient, particulate abatement device may be necessary to precede a packed-bed absorber.
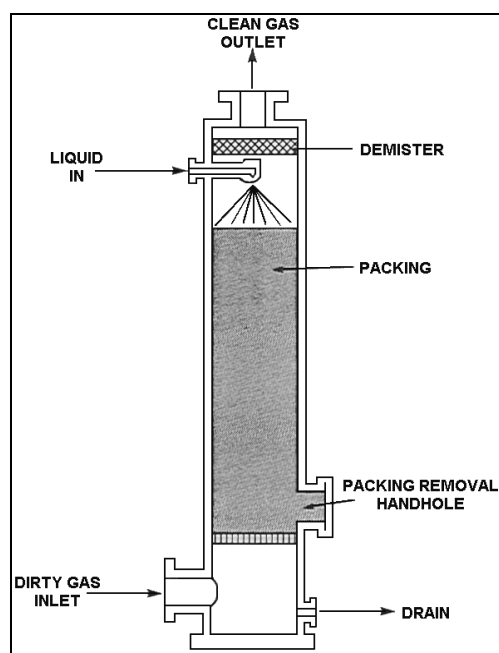
Figure 3.57: Packed-bed Scrubber

- **Impingement Plate Scrubbers**

    Impingement plate scrubbers consist of a vertical tower with several horizontal perforated (bubble cap or sieve) trays stacked in it. Baffles are situated a short distance above the apertures in the plates. The typical application for plate scrubbers is the absorption of acids, sulphur dioxide and odours. An example is given in Figure 3.58 [cww/tm/79].

    Plate scrubbers are not suitable for foaming liquids. When absorption is used to abate VOC, packed scrubbers are usually more cost effective than plate scrubbers. However, the impingement plate design is preferred over packed scrubbers when either internal cooling is desired, or where low liquid flow rates would not adequately wet the packing.

    Plate scrubbers are typically used because of their high efficiency and easy maintenance. They are usually designed to provide operator access to each tray, making them relatively easy to clean and maintain. The height of the column and the amount of packing material and/or the number of metal trays, along with the pressure drop in the column, generally determine the waste gas flow. Pressure drop is a determining factor in the choice of scrubber and, in this respect, plate scrubbers compare most favourably with other gas cleaning methods on the basis of efficiency-to-cost ratio. At high gas flow rates, plate towers exhibit larger pressure drops and have larger liquid hold-ups.
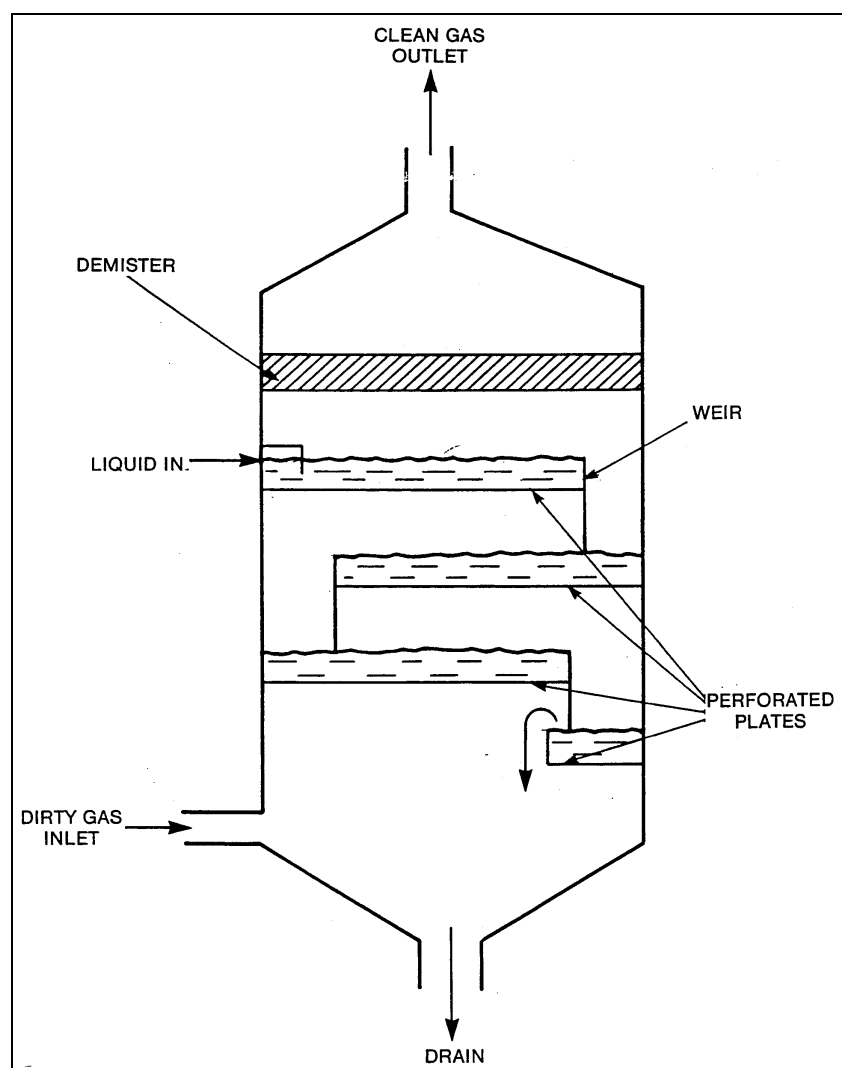
Figure 3.58: Impingement Plate Scrubber

The chemical absorption of noxious gaseous contaminants such as sulphur dioxide, chlorine and hydrogen sulphide can be achieved by contacting the air stream with suitable chemicals on the plates. Packed columns, however, are preferred to plate towers when acids and other corrosive materials are involved because tower construction can then be of fibreglass, PVC, or other less costly corrosive-resistant materials.

- **Spray Towers**
  Spray towers (or spray scrubbers) consist of spray nozzles at the top of the tower, through which the scrubbing liquid enters, and a gas inlet near the bottom. Generally the waste gas stream passes up the tower counter-current to the liquid flow. The typical application for spray towers is to remove acid gases and odours. An example is shown in Figure 3.59 [cww/tm/79].
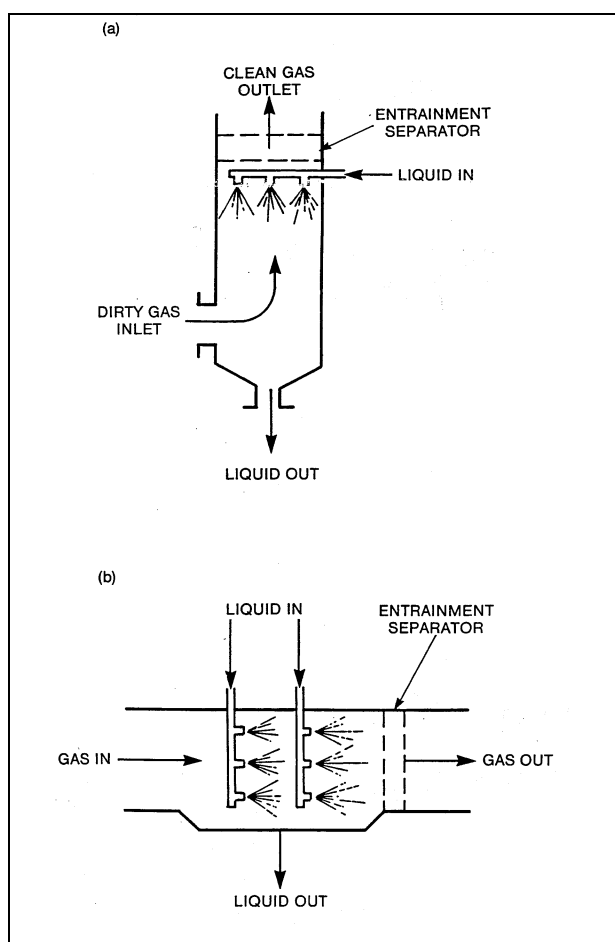
Figure 3.59: Spray Tower, (a) Counter-Current, (b) Co-Current

Plugging of spray nozzles might cause problems.

Spray towers are the traditional wet scrubber configurations used to bring waste gases into contact with a sorbent. They exert, however, the least effective mass transfer capability and so are generally limited to the removal of highly soluble gases.

Typical pollutant concentrations range from 100 to 10000 mg/Nm^3. Spray tower wet scrubbers are not as prone to fouling as packed scrubbers, but very high liquid-to-gas ratios (>3 l/m^3) are required to capture fine particulate.

When absorbed gases are to be recovered, an additional desorption step is necessary. The usual method of desorption / regeneration of the organic content is distillation or steam stripping, transferring the gaseous content back to the gaseous phase. With stripping as regeneration, the stripped gas is subsequently condensed and collected. The condensate is either re-used directly in the process or segregated into its components by, e.g. distillation. Stripping and distillation are carried out at reduced pressure in order to reduce the temperature and minimise the degradation risk of the organic compounds [cww/tm/71].

A typical absorption / desorption system is shown in Figure 3.60 [cww/tm/71]. The vacuum desorption, as described in Figure 3.60, is not the general case, but an option. It makes it easier to boil the scrubbing liquid (solvent), but makes its condensation more difficult.
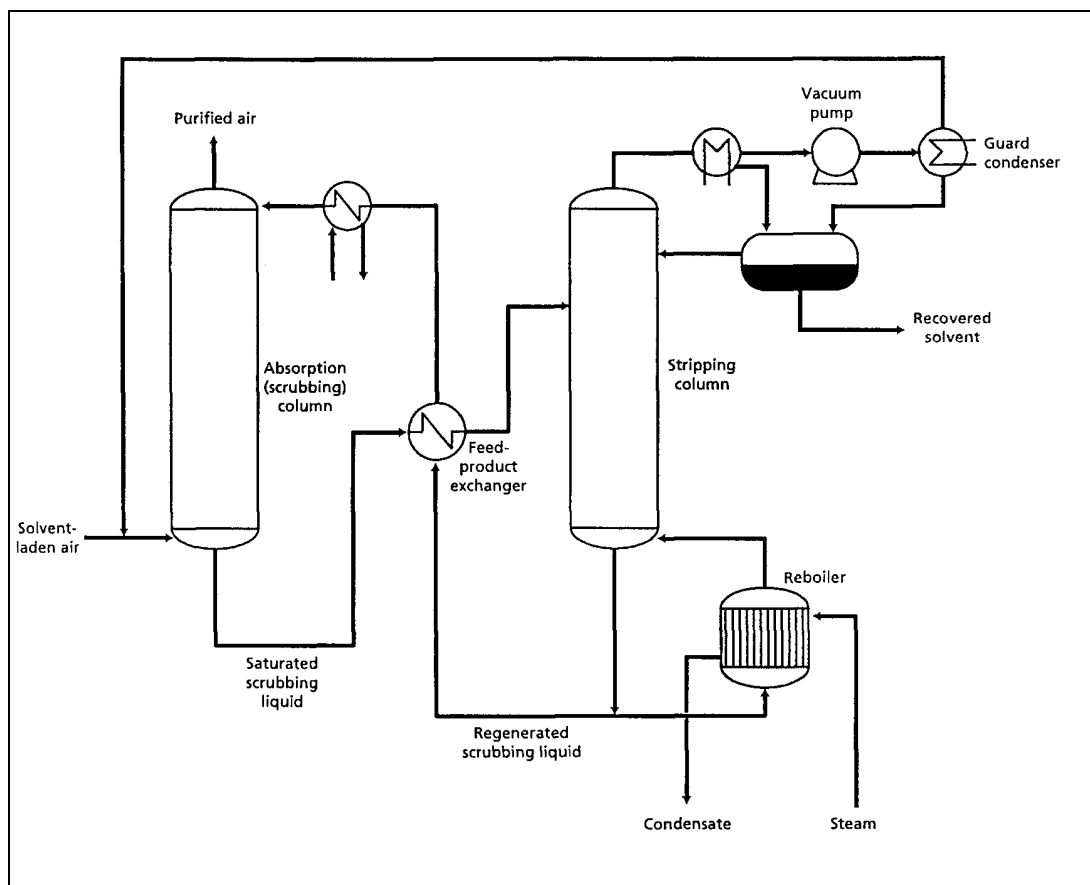
Figure 3.60: Typical Absorption / Desorption System

Application

Absorption is widely used as a raw material and/or product recovery technique for separation and purification of gaseous streams containing high concentrations of VOC, especially compounds soluble in water – such as alcohols, acetone or formaldehyde. The use of absorption as the primary control technique for organic vapours is subject to the availability of a suitable solvent, with a high solubility for the gas, low vapour pressure and low viscosity.

As a final control technique for emissions, gas scrubbing is commonly employed for inorganic compounds rather than for VOC. Its suitability as a pollution control method depends on:

- recovery value of the pollutant
- the waste water disposal cost
- the required removal efficiency
- the pollutant concentration in the inlet waste gas
- the availability of suitable solvent / chemical reagent.

Absorption is enhanced by:

- larger contacting surface
- higher liquid-gas ratios
- higher concentrations in the gas stream
- lower temperature.

Low outlet gas concentrations will typically be required for hazardous VOC, leading to impractically tall absorption towers, long contact times and high liquid-gas ratios that may not be cost-effective. Therefore, wet scrubbers are more effective with hazardous VOC control when used in combination with other control devices, such as GAC adsorbers (see Section 3.5.1.3) or waste gas incinerators (see Sections 3.5.2.4 and 3.5.2.5).

Application limits and restrictions are:

	Limits / restrictions
Gas flow [Nm³/h]	50–500000 [1]
	1800–170000 (fibrous packing scrubber) [2]
	900–130000 (packed-bed scrubber) [3]
	1700–130000 (impingement plate scrubber) [4]
	2500–170000 (spray tower) [5]
Temperature [°C]	5–80 (generally) [1]
	<60 (fibrous packing scrubber) [2]
	4–38 (packed-bed scrubber, for gaseous pollutant control) [3]
	4–38 (impingement plate scrubber, for gaseous pollutant control) [4]
	4–38 (spray tower, for gaseous pollutant control) [5]
	10–40 (alkaline-oxidation scrubbing) [1]
	30 (biogas desulphurisation) [1]
	(high gas temperature can lead to significant scrubbing liquid evaporation losses)
Pressure	atmospheric
Pollutant loading [g/Nm³]	0.2–11 (fibrous packing scrubber) [2]
Particulates [mg/Nm³]	450 (packed-bed scrubber) [3]
[1] [cww/tm/70] [2] [cww/tm/110] [3] [cww/tm/113] [4] [cww/tm/111] [5] [cww/tm/114]	

Advantages/Disadvantages

Advantages	Disadvantages
General • Wide range of uses. • Very high efficiency. • Compact installation thanks to favourable ratio between capacity and device volume. • Simple and robust technology. • Simple maintenance. • Only few wear-sensitive components. • Can handle flammable and explosive gas/dusts with little risk. • Can also cool hot gas streams. • Can handle mists. • Corrosive gases and dusts can be neutralised.	General • Water or diluted chemicals are required for replacement of the purged water and the evaporation losses. • Waste water due to replacement of scrubbing liquid needs treatment. • Conditioning agents (e.g. acids, bases, oxidants, softeners) are required for many applications. • Dust, separated as sludge, needs to be treated either for re-use or for disposal operations. • For roof fitting, support structures needed. • For outdoor fitting, frost protection needed (according to climate). • Packing material sensitive to clogging because of dust or grease. • Potential for corrosion. • Collected particulates may be contaminated and may not be recyclable. • Off-gas may require reheating to avoid visible (steam) plume.
Packed-bed Scrubbers • Low to medium pressure drop. • Plastic and fibreglass-reinforced plastic (FRP) scrubbers can operate in highly corrosive atmospheres. • High mass-transfer efficiency. • Ability to collect gases as well as particulates. • Low capital cost. • Small space requirements.	Packed-bed Scrubbers • Tendency to bed plugging. • Relatively high maintenance costs, compared to other scrubber techniques. • When FRP construction is used, it is sensitive to temperature. • Relatively high maintenance costs.

Advantages	Disadvantages
Impingement Plate Scrubbers • Flexibility in operating conditions (variation of flow rate). • High versatility in case of low gas flow-rate, as they can also operate with low liquid flow. • Provides gas absorption and dust collection in a single unit. • Improves gas-slurry contact for SO_2 removal. • Easy maintenance and operating.	Impingement Plate Scrubbers • Dust build-up around valves and/or on plates. • Higher costs than other wet scrubbers.
Spray Towers • Low pressure drop. • FRP constructions can operate in highly corrosive atmospheres. • Low energy consumption. • Low capital costs. • Relatively free from plugging. • Relatively small space requirements. • Capable to collect gases as well as particulates.	Spray Towers • Low mass-transfer efficiency. • Low efficiency in removing fine particulates. • When FRP construction is used, sensitive to temperature. • High operational costs.

Achievable Emission Levels / Performance Rates

Parameter	Performance rate [a] [%]	Emission level [mg/Nm³] [b]	Remarks
Alcohols	up to 95 [1]	down to 100 [1]	water
Hydrogen fluoride	>99 [1]	<50 [1]	water
		<1 [1]	alkaline
Hydrogen chloride	>99 [1]	<50 [1]	water
		<10 [1]	alkaline
Chromic acid		<0.1–1 [1]	water
Ammonia	>99.9 [c]	<1 [1]	acid
Amines	>99 [1]	<1 [1]	acid
Sulphur dioxide	80–99 [d 2]	<40 [1]	alkaline
Phenols	>90		alkaline
Hydrogen sulphide	90–95 [1]		alkaline
	80->99 [h 5]		
Inorganic compounds	95–99 [d,f,h 2,3,5]		
VOC	50–95 [d,e 2]		
	70->99 [f,g 3,4]		

[a] high feed concentration
[b] low feed concentration
[c] feed concentration 25 g/Nm³ ammonia, effluent concentration <10 mg/Nm³
[d] spray tower, several reagents
[e] may achieve > 99 %
[f] packed-bed scrubber
[g] fibrous packing scrubber
[h] impingement plate scrubber
[1] [cww/tm/70]
[2] [cww/tm/114]
[3] [cww/tm/113]
[4] [cww/tm/110]
[5] [cww/tm/111]

Cross-media Effects

The main utilities and consumables required for absorption systems are [cww/tm/71]:

Consumable	Amount	Remarks
Scrubbing water		
Chemicals (acidic, alkaline, oxidants)		
Desorption facilities: cooling water for condenser, steam for steam stripper	30-40 kg/1000 Nm^3 waste gas (steam 120 °C) [1]	
Energy [kWh/1000 Nm^3]	0.2-1 [2]	dependent on application, desorption not included
Pressure drop [kPa]	0.4-0.8 [1]	dependent on application
[1] [cww/tm/71] [2] [cww/tm/70]		

An additional work-up of the recirculating liquid is normally required, depending on its degradation (e.g. insoluble solid contents) and evaporation losses.

Scrubbing generates waste water which needs treatment, if the scrubbing liquid with its content is not used otherwise. Adequate treatment is desorption of the waste gas content, which is operated in any case when recovery of the gas is the aim of scrubbing. Desorption can cause emissions to air. Its energy need should be borne in mind.

Monitoring [cww/tm/79]

The abatement efficiency of the scrubbing system is determined by monitoring the gaseous pollutant concentration before and afterwards. Sulphur dioxide is usually monitored with infra-red analysers; wet chemical methods are used for hydrogen halides. VOC are measured as total carbon, excluding particulate matter, using a flame ionisation detector. A qualitative analysis of the emissions can be done if grab samples of gas are taken at selected sampling points and are subsequently analysed by GC/MS. Abatement efficiencies of odorous emissions are determined by taking grab samples at appropriate sampling points and subsequently analysing them by olfactometry.

Further routine measurement is necessary for:

- the pressure drop across the scrubber, as a means to discover operational anomalies that might require maintenance
- the scrubber make-up water flow rate
- the recycle water flow rate
- the reagent flow rate
- in some cases pH, temperature, electrical conductivity and ORP.

Wet scrubbers need regular inspection to identify any deterioration in the plant, such as corrosion or blockages. Access to the scrubber should be readily available. It is essential that operating failures are detected quickly, and adequate instrumentation with alarms should be applied at the outlet vent of the absorption plant to ensure that warning is given if equipment fails.

A programmable logic controller (PLC) system or a digital computer system (DCS) is typically used to manage the operation of the plant automatically (e.g. operating at set pH and ORP values, optimised for high gas absorption). A program is available which can predict the optimum operating parameters, i.e. circulation and steam requirement, for a given waste gas composition. This is particularly useful where changes in the gas flow and/or solvent concentration are likely to be significant.

Action by plant operators is minimal, provided that automatic shutdown is fitted and alarms set up on the control system, e.g. for low liquid flow or loss of vacuum.

Maintenance requirements are likely to be low. They are mainly limited to routine checks on the desorber system, because the quality of desorption is a key factor in the performance of the absorption, and equipment with moving parts. [cww/tm/71]

Economics

Type of costs	Costs				
	Fibrous packing	**Moving bed**	**Packed-bed**	**Impingement plate**	**Spray towers**
Capital costs [per 1000 Nm^3/h]	USD 600-1800 [1]		USD 6200-33500 [2]	USD 1300-7000 [3]	USD 500-2200 [4]
Annual operating costs [per 1000 Nm^3/h]	USD 1000-21100 [1]		USD 9300-42300 [2]	USD 1500-42000 [3]	USD 800-28100 [4]
Cost effectiveness [per tonne per year of pollutant controlled]	USD 40-710 [1]		USD 0.24-1.09 [2]	USD 51-1300 [3]	USD 28-940 [4]
[1] [cww/tm/110] [2] [cww/tm/113] [3] [cww/tm/111] [4] [cww/tm/114]					

Cost factors [cww/tm/71]:

Factors	Influence / results
Emission flow rate	Overall size of the system, utility requirement
Recovery efficiency required	Height of the scrubbing column
Solvent absorption efficiency	Scrubbing liquid recirculation rate and hence pumping requirements
Solvent type	Choice of scrubbing liquid
Solvent solubility	Complexity of downstream separation techniques (directly proportional to solubility), energy intensity of separation techniques (directly proportional)
Solvent mixtures	Complexity of downstream separation techniques (directly proportional), energy intensity of separation techniques (directly proportional)
Solvent loading	Rate of desorption and subsequent utility requirements such as steam
Scrubbing liquid degradation	High purge rate of spent liquid and hence high treatment and/or disposal costs
Ease of solvent desorption	Desorption temperature

Retrofittability [cww/tm/71]:

Fibrous packing	Moving bed	Packed-bed	Plate	Spray towers
Provided sufficient space is available, absorption systems can be relatively easily retrofitted to existing plants. Retro-fits of existing absorption systems with improved structured packings and/or liquids can also be carried out to improve the operation of recovery equipment.				

3.5.2 Abatement Operations and Processes for VOCs and Inorganic Compounds

3.5.2.1 Biofiltration

<u>Description</u>

The waste gas stream is passed through a bed of organic material, such as peat, heather, compost, or some inert material such as clay, charcoal or polyurethane, where it is biologically oxidised by naturally occurring micro-organisms into carbon dioxide, water and biomass.

A biofilter is shown in Figure 3.61 [cww/tm/79].
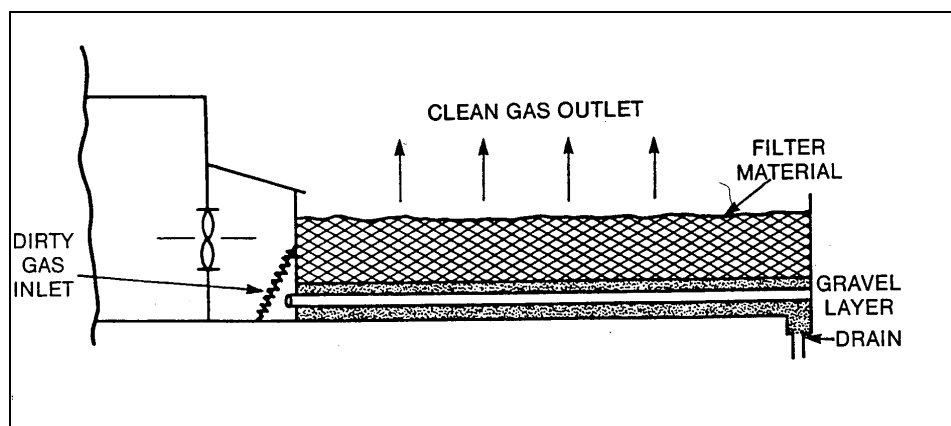
Figure 3.61: Biofilter Construction

Biofilters can be divided into:

- open biofilters
- enclosed biofilters.

An open biofilter consists of a layer of porous biofiltering material underlain by a network of pipes through which the contaminated air is blown to the filter. These filters require a long residence time and therefore tend to be large. They might be used for low gas rates. An alternative are multi-level biofilters, where several layers set above each other obviate the need for a large area. In areas with cold climate (frost), the suitability of open biofilters is restricted.

An enclosed biofilter consists of a layer of material supporting a suitable microbial population and placed under a distribution system which supplies the contaminated waste gas stream to the filter uniformly. The gas stream is drawn to the filter by electric fans. Gas flow is from top to bottom or vice versa. The blower, ventilation system and biofilter construction materials should minimise the effects of corrosive waste gas, excess condensate and dust / sludge.

The majority of operating biofilters are open bed filters, which are less costly than enclosed biofilters but are less efficient. Hence enclosed filter systems with controlled feed and outflow of off-gas might be preferred. It can be assumed that in many cases open filter systems do not allow a sufficient removal of emissions and often lack the technological features to achieve a comprehensive VOC reduction. Enclosed high-tech biofilters can be upgraded to achieve a reduction of a wide range of xenobiotic compounds.

The micro-organisms are enclosed in a fixed bed. The height of the filter material is between 0.5 and 1.5 m, with a maximum of two to three layers. The specific load of the filter bed is between 100 and 500 Nm^3/h per m^2 of filter surface. The moisture balance is usually very critical

(relative gas moisture of about 95 % and more is required). It is regulated by a pre-connected humidifier or gas scrubber, at times in combination with moistening the filter material. The relative humidity of the filter material should be below 60 % to avoid clogging. The moistening device needs protection against freezing in regions where temperatures considerably below 0 °C are an issue.

For application to warm waste gas streams (>35 ºC) cooling is necessary, either by mixing with air or introducing a gas scrubber or heat exchanger. Wet scrubbing can be applied as pretreatment with the aim of decreasing excessive particulate content, pollutant load and amount of pollutants not suitable for biofiltration.

The residence time to allow an effective abatement of, e.g., odour depends on the pollutant concentration. As a rough guide, a minimum residence time of 30 to 45 seconds should be aimed for.

The material quality and process operation of biofilter machinery need to offer protection against corrosion. The removal of condensed water from ducts needs to be ensured [cww/tm/46].

A typical biofilter process is shown in Figure 3.62 [cww/tm/64]. It includes a wet scrubber as pretreatment facility.

Application

Biofiltration is used in the chemical and petrochemical industry as well as in sewage treatment plants. It is an abatement technique that removes readily biodegradable components, such as amines, hydrocarbons, hydrogen sulphide, toluene, styrene and odorous contaminants. Biofiltration is well suited to low concentrations of pollutants easily soluble in water. It is normally not suited, however, for waste water containing many different and/or changing pollutants. Furthermore, methane is not abated, because the residence time needed would be too long for normal filter dimensions.
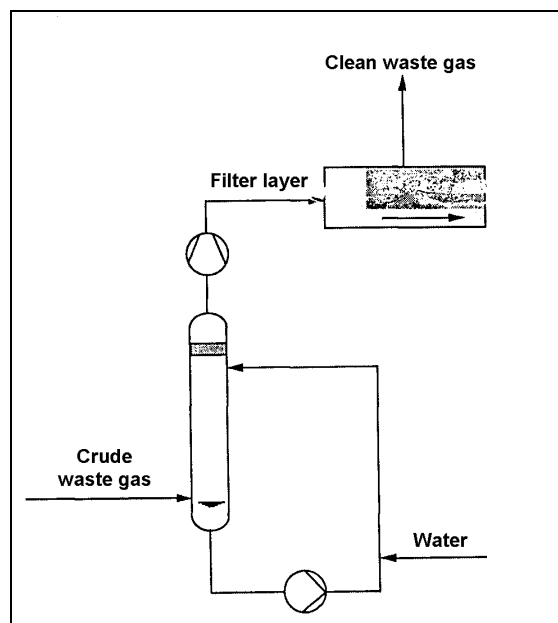
Figure 3.62: Typical Biofilter Process

Application limits and restrictions:

	Limits / restrictions
Gas flow [Nm^3/h]	100–400 per m^2 of filter surface [1], up to 200000
Temperature [°C]	15–40 [2] 55, with thermophilic bacteria
Pressure	atmospheric [2]
Oxygen concentration	near ambient level [1]
Relative humidity [%]	>95, nearly saturated with water [1]
Content of dust, grease, fat	cause clogging, hence pretreatment necessary [3]
Hydrocarbon concentration [mg/Nm^3]	200–2000 [2,4]
Ammonia	• can decrease efficiency of degradation for hydrocarbons • can be degraded to N_2O
Odour concentration [ou/Nm^3]	20000–200000 [2]
Toluene concentration [mg/Nm^3]	20–500 [2]
Styrene concentration [mg/Nm^3]	50–500 [2]
Compounds containing N, S or Cl	can acidify and deactivate the biofilter without buffer capacity, which brings about an increase of replacement frequency
Climatic conditions	frost, rain and high ambient temperature affect the filter material and decrease efficiency
[1] [cww/tm/64] [2] [cww/tm/70] [3] [cww/tm/132] [4] comment	

Advantages/Disadvantages

Advantages	Disadvantages
• Simple construction. • In combination with adsorption and absorption also suitable for barely soluble components. • High efficiency for biodegradable compounds, e.g. odorous substances.	• Dried-out peat and compost filter beds are difficult to re-wet. • Relatively bulky design. • Poisoning and acidification of the biomass must be avoided. • Fluctuations in the gas stream have a great impact on performance. • Packing is sensitive to clogging because of dust.

Achievable Emissions Levels / Performance Rates

Parameter	Performance rates [%]	Emission level [mg/Nm^3]	Remarks
Hydrocarbons	75–95 [1]	>5 [1]	
Toluene	80–95 [1]	>5 [1]	
Styrene	80–90 [1]	>10 [1]	
Odour	75–95 [1]	>5000 ou/Nm^3 [1]	Odour of biofilter 200-500 ou/Nm^3
[1] [cww/tm/70]			

The efficiency of biofiltration depends strongly on the composition of the waste gas stream.

Cross Media

The main utilities and consumables are:

Consumable	Amount	Remarks
Filter material [a]		
Chemicals (nutrients, alkali and acidic compounds for pH correction)		
Water	5 l/1000 Nm^3 [1]	
Energy [$kWh/1000\ Nm^3$]	<1 [1]	
Pressure drop [kPa]	0.5–2 [1]	
[a] service life of filter material depends on its stress by acidification, poisoning, depletion, typically not more than 1 year [1] [cww/tm/70]		

With open biofilters the filter material has to be regularly worked-up and disposed of from time to time. Waste gas channelisation can occur through the filter bed, thereby decreasing the biofilter efficiency. Since not all VOC sent through the biofilter are biodegradable, there might be loaded filter material containing hazardous contaminants that has to be disposed of as waste (incineration). The percolate water that is released from the filter material may contain organic residues and has to be disposed of. Enclosed biofilters usually recirculate the leachate.

Monitoring

The moisture balance has to be carefully examined because it is a critical item for the accurate operation of biofilters.

The efficiency may be determined by assessing the inlet and outlet gases, the appropriate method depending on the pollutants to abate. Regular pH examination of the percolate water released from the filter bed is required.

Economics

Type of costs	Costs	Remarks
Capital costs	EUR 5000–20000 [1] [per 1000 Nm^3/h]	
	ATS 4000–180000 [2] [per m^3 filter]	
Operating costs [a]	ATS 10000–20000 [2]	
labour		1 h per week per filter + 2 days per year [1]
utilities		
consumables	EUR 200 per m^3 filter material [1]	
Maintenance [b]	ATS 5000–300000 [2] <ATS 1000 [c] [2]	
[a] per year per 1000 Nm^3/h capacity [b] per year [c] per year per 1000 Nm^3/h capacity [1] [cww/tm/70] [2] [cww/tm/46]		

Operation and maintenance costs are low, because no fuel or chemicals are needed.

Cost-relevant parameters are:

- the waste gas flow rate
- the pollutant concentration in the gas stream
- the type of component in the gas stream
- the required efficiency
- the character of the filter material.

3.5.2.2 Bioscrubbing

Description

Bioscrubbing combines wet gas scrubbing (absorption) (see Section 3.5.1.4) and biodegradation, the scrubbing water containing a population of microbes suitable to oxidise the noxious gas components. The microbes are suspended in water. Hence, the conditions to use bioscrubbers are:

- it ought to be possible to wash out the waste gas constituents
- the washed-out constituents must be biodegradable under aerobic conditions.

A bioscrubber is shown in Figure 3.63 [cww/tm/132].
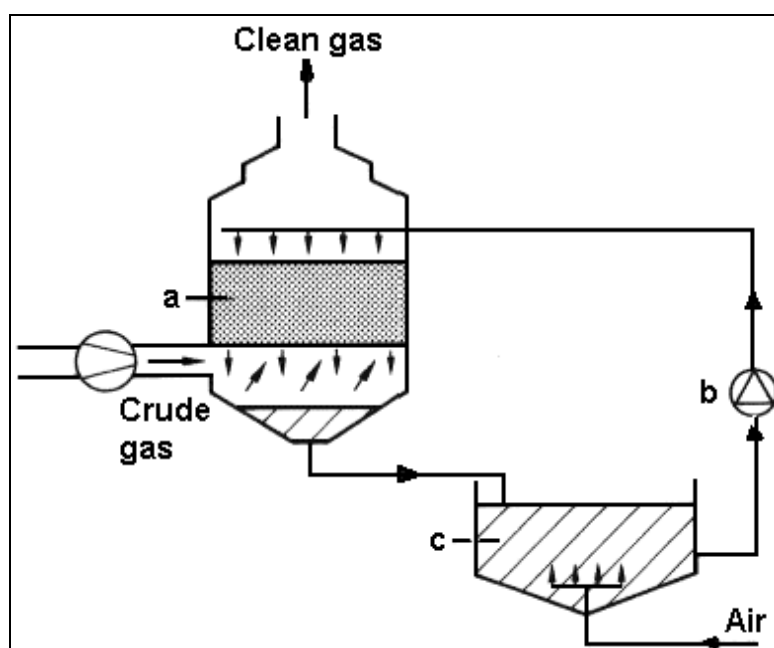
Figure 3.63: Typical Bioscrubber
(a) Absorber, (b) Activated Sludge Circulation, (c) Activating Tank

The bioreactor design is founded on an activated sludge or a sludge-on-carrier system (details in Section 3.3.4.3.1). The water sludge mixture is recirculated into the reactor. The absorbed pollutants are degraded in aerated sludge tanks. The scrubbing tower should be designed in such a way that a contact time of about one second, depending on the contaminants, is provided.

Bioscrubbers are frequently inoculated with activated sludge from, e.g. a biological waste water treatment plant. Depending on the composition of the waste gas, the performance of the bioscrubber will only attain the desired level after some weeks of adaptation. Inoculation with cultures prepared in fermenters is particularly applied to contaminants that contain sulphur (mercaptans, hydrogen sulphide, dimethyl sulphide, etc.) or chlorine (chlorinated methanes or ethanes) [cww/tm/70].

A typical bioscrubber process is shown in Figure 3.64 [cww/tm/64].
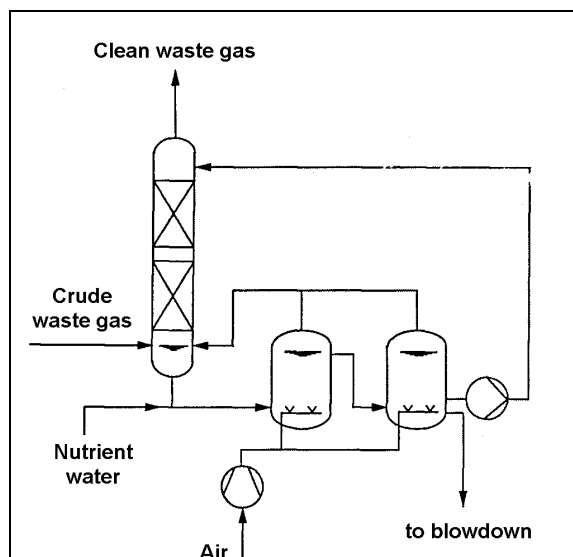
Figure 3.64: Typical Bioscrubbing Process

Evaporation accompanied by mineralisation and dosage of nutrients and/or neutralisation agents normally causes an increase of salt content in the absorbent. This effect might inhibit the biological process, though it has been found that stable biodegradation rates can be maintained, even with salt concentrations corresponding to a conductivity of up to 5000 μS/cm [cww/tm/53].

Measures to prevent excessive salt formation are, e.g.:

- adequate removal of absorbent and simultaneous addition of fresh water
- operation with softened water
- vapour saturation of the upstream waste gas.

Compounds containing sulphur, chlorine and/or nitrogen lead to acidification (formation of sulphuric, hydrochloric or nitric acid), which is corrected by pH control.

A residence time of the absorbent of 20–40 (maximum) days has proved to be appropriate.

Application

Bioscrubbing is used in chemical and petrochemical industry as well as in sewage treatment plants. It is an abatement technique that removes readily biodegradable components, such as ammonia, amines, hydrocarbons, hydrogen sulphide, toluene, styrene and odorous contaminants. Bioscrubbing is well suited to low concentrations of pollutants easily soluble in water.

Typical and proven applications of bioscrubbers are illustrated in Table 3.14 [cww/tm/53].

	Elimina-tion of odours	Aliphatic hydro-carbons	Aromatic hydro-carbons	Oxygen-based com-pounds	Sulphur-based com-pounds	Nitrogen-based com-pounds	Haloge-nated hydro-carbons	H_2S	NH_3	Ethe-real oils
Activated sludge tanks of biological sewage plants	X	X	X	X	X	X		X	X	
Enzyme production	X			X						
Odorant production	X		X	X						X
Rubber industry	X				X			X		
Conditioning of paint wastes	X	X	X	X		X				
Methionine production	X				X					
Polymerisation production	X			X						
Gases from hazardous waste dumps	X	X	X	X		X		X	X	

Table 3.14: Typical Bioscrubber Applications

The applicability of bioscrubbing to compound groups is [cww/tm/53]:

Well suited	Basically suited	Not suited
Alcohols (methanol, ethanol, butanol, glycol, diglycol, butyl glycol) Aldehydes and ketones (form-aldehyde, acetaldehyde, ace-tone, MIBK) Carboxylic acids and their esters (acetic acid, propionic acid, butyric acid, n-butyl acetate, ethyl acetate, methyl methacrylate, glycolic acid ester) Phenols (phenol, cresol) Heterocyclic sulphur compounds Mercaptans Amines Heterocyclic nitrogen com-pounds Chlorophenols Hydrogen sulphide	Naphthalene Thioethers (sulphides) Ammonia	Aliphatic hydrocarbons (methane, pentane, hexane, longer chain hydrocarbons, acetylene etc., cyclohexane) Aromatic hydrocarbons (benzene, toluene, xylene, styrene), except naphthalene Ethers (tetrahydrofuran, di-ethyl ether, dioxan) Carbon disulphide Nitro compounds Halogenated hydrocarbons (dichloromethane, trichloro-ethene, perchloroethene, 1,1,1-trichloroethane, 1,2-dichloroethane, VCM), except chlorophenols

Application limits and restrictions:

	Limits / restrictions
Gas flow [Nm^3/h]	1000–3000 Nm^3/h per m^2 of column surface [1]
Temperature [°C]	15–40 [2] 30–35 (optimum) [3]
Pressure	atmospheric [2]
Concentration of micro-organisms	>15 g/l dry matter [3]
VOC-concentration in waste gas	100–2000 mg/Nm^3 [2,3]
Concentration of ammonia	50–200 mg/Nm^3 [2]
Odour concentration [ou/Nm^3]	>20000 [2]
[1] [cww/tm/64] [2] [cww/tm/70] [3] [cww/tm/53]	

Advantages/Disadvantages

Advantages	Disadvantages
• High concentrations can be abated owing to high microbial conversion. • Also suitable for high concentrations of compounds containing sulphur, chlorine, and/or nitrogen.	• Biomass builds up, needs to be disposed of as waste and can result in blockage of the circulating water. • Poorly soluble components are more difficult to abate. • Fluctuations, e.g. changing concentrations, in the gas stream have a great impact on performance. • Percolate water needs treatment.

Achievable Emission Levels / Performance Rates

Parameter	Performance rates [%]	Emission level [mg/Nm^3]	Remarks
VOC	80-90 [1]		
Ammonia	80–95 [1]		
Odour	70–80 [1]		
[1] [cww/tm/70]			

Cross-media Effects

The main utilities and consumables are:

Consumable	Amount	Remarks
Chemicals (nutrients, alkali compounds for pH correction)		
Water		
Activated sludge		
Energy [kWh/1000 Nm^3]	0.2–0.5 [1]	
Pressure drop [kPa]	0.2–0.5 [1]	
[1] [cww/tm/70]		

Because of biological activities in the bioscrubber, the salt concentration in the circulation water increases and thus has to be discharged from time to time. This waste water effluent has to be treated or disposed of in some other way.

Surplus activated sludge has to be disposed of, dependent on the contaminants or degradation products, e.g. by incineration.

Odour might occasionally arise from the tanks storing the circulation water, so collection of exhaust air and its subsequent ducting to a treatment facility might be obligatory.

Monitoring

Efficiency is determined by chemical analysis or assessing the odour of inlet and outlet gases. pH control of the process is required.

Economics

Type of costs	Costs	Remarks
Capital costs [per 1000 Nm^3/h]	EUR 5000–15000 [1]	
Operating costs labour utilities consumables		½ day per week [1]
[1] [cww/tm/70]		

3.5.2.3 Biotrickling

Description

Biotrickling works with similar conditions to bioscrubbing. In contrast to bioscrubbing, the microbes are fixed on supporting elements. The process principle is shown in Figure 3.65.
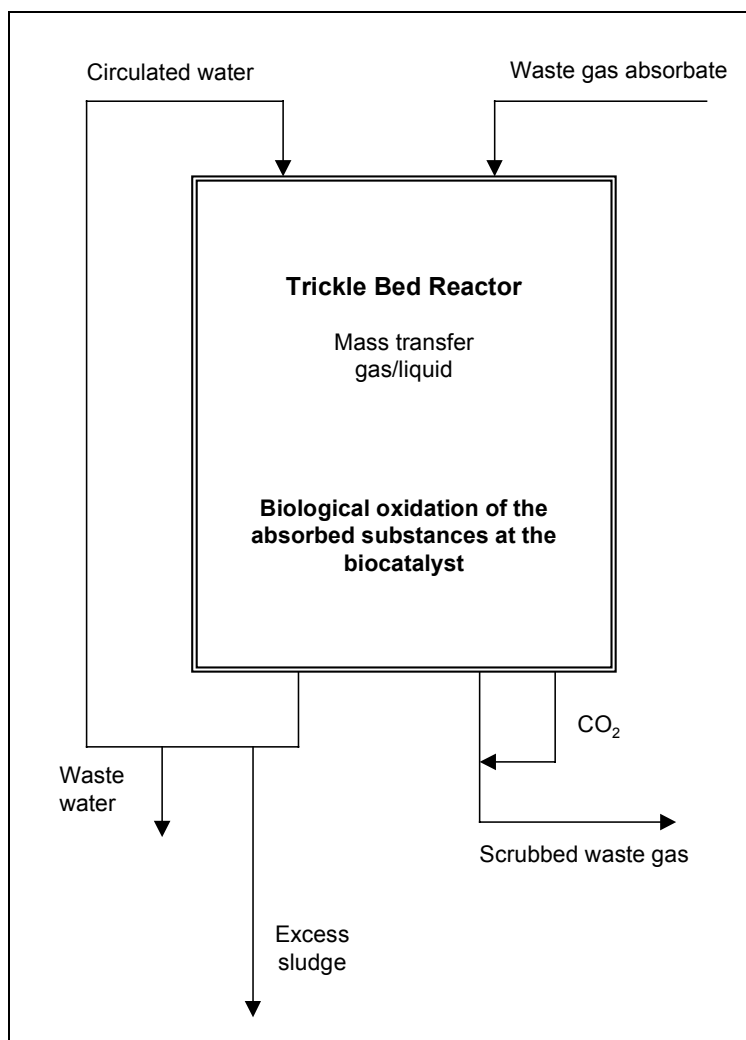
Figure 3.65: Flow Sheet of Biotrickling Process

In a biological trickle bed reactor, an aqueous phase is continuously circulated through a bed of inert material. This packing can consist of irregular bulk material, such as rings, saddles, etc. or of structured packings. When selecting the packing material, it is necessary in every individual case to ensure that even in the event of an anticipated excess sludge formation, the reactor will not become choked in the long term. The surface properties should be such that the biofilm adheres firmly. The pollutants in the waste gas and the oxygen are absorbed by the water phase and transported to the biofilm, where the biological transformation takes place. The quality of the mass transfer from the gas to the liquid phase and the elimination performance of the reactor depend essentially on the wetted surface area of the packing. In order to achieve optimum elimination results, i.e. to maximise the wetted surface area, the liquid phase should be distributed uniformly over the surface of the biofilm [cww/tm/53].

The immobilisation of the biomass and the formation of the biofilm are generally a naturally controlled process which starts after inoculation of the water phase. The continuously circulating liquid phase takes on the function of supplying the microbe population with the

necessary nutrients. At the same time, excess activated sludge and reaction products which can also be inhibitors, such as e.g. hydrogen chloride during the degradation of dichloromethane, are washed out of the reactor. In the liquid phase, the essential conditions such as pH, nutrients and salt accumulation need to be controlled [cww/tm/53].

As with bioscrubbing, an increase of salt content in the absorbent takes place. Measures to prevent exceeding salt formation are, e.g.:

- adequate removal of absorbent and simultaneous addition of fresh water
- operation with softened water
- vapour saturation of the upstream waste gas.

A biotrickling facility is illustrated in Figure 3.66.
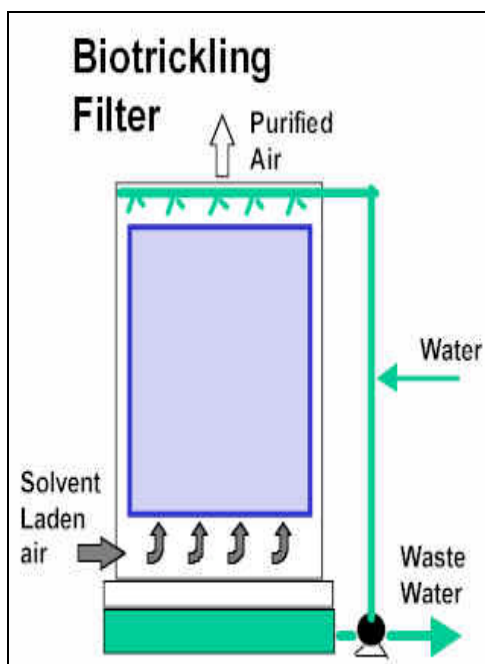
Figure 3.66: Typical Biotrickling Facility

Application

The application of biotrickling is comparable to that of bioscrubbing. Slight differences are found in the pollutant compounds for which both treatment techniques are suitable.

The applicability of biotrickling to compound groups is [cww/tm/53] (compare with the corresponding table in Section 3.5.2.2):

Well suited	Basically suited	Not suited
Alcohols (methanol, ethanol, butanol, glycol, diglycol, butyl glycol) Aldehydes and ketones (formaldehyde, acetaldehyde, acetone, MIBK) Carboxylic acids and their esters (acetic acid, propionic acid, butyric acid, n-butyl acetate, ethyl acetate, methyl methacrylate, glycolic acid ester) Phenols (phenol, cresol) Mercaptans Amines Ammonia Heterocyclic nitrogen compounds Dichloromethane, 1,2-dichloroethane, chlorophenols Hydrogen sulphide	Styrene, naphthalene Heterocyclic sulphur compounds Carbon disulphide Trichloroethene, VCM	Aliphatic hydrocarbons (methane, pentane) Perchloroethene, 1,1,1-trichloroethane,

Application limits and restrictions [cww/tm/70]:

	Limits / restrictions
Temperature [°C]	15–40 [1] 30–35 (optimum) [2]
Pressure	atmospheric [2]
Concentration of micro-organisms	>15 g/l dry matter [3]
VOC-concentration in waste gas [mg/Nm^3]	400–2000 [1,2]
Ammonia concentration [mg/Nm^3]	100–400 [1]
Odour concentration [ou/Nm^3]	>20000 [1]
Hydrogen sulphide concentration [mg/Nm^3]	50–200 [1]
Mercaptan concentration [mg/Nm^3]	5–100 [1]
[1] [cww/tm/70] [3] [cww/tm/53]	

Advantages/Disadvantages

Advantages	Disadvantages
• Biodegradation of absorbed components. • Suitable for medium concentrations of acidifying components containing sulphur, chlorine and nitrogen. • Small pH corrections are possible.	• Fluctuations of intake air stream conditions have great impact on effectiveness. • Poorly soluble components are more difficult to abate. • Toxic and high concentrations of acidifying substances should be avoided.

Achievable Emission Levels / Performance Rates

Parameter	Performance rates [%]	Emission level [mg/Nm^3]	Remarks
VOC	80-95 [1]		
Ammonia	80–95 [1]		
Odour	70–90 [1]		
Hydrogen sulphide	80–95 [1]		
Mercaptans	70–90 [1]		
Carbon disulphide	98–99 [2]		Feed concentration 100 mg/Nm^3
Styrene	80 [2]		Feed concentration about 160 mg/Nm^3
VCM	99 [2]		Feed concentration up to 100 mg/Nm^3
[1] [cww/tm/70] [2] [cww/tm/53]			

Cross-media Effects

The main utilities and consumables are:

Consumable	Amount	Remarks
Chemicals (nutrients, alkali compounds for pH correction)		
Water		
Activated sludge		
Energy [kWh/1000 Nm^3]	<1 [1]	
Pressure drop [kPa]	0.1-1 [1]	
[1] [cww/tm/70]		

Because of biological activities in the biotrickler, the salt concentration in the circulation water increases and thus has to be discharged from time to time. This waste water effluent has to be treated or disposed of in some other way.

Surplus activated sludge has to be disposed of, depending on the contaminants or degradation products, e.g. by incineration.

Odour might occasionally arise from the tanks storing the circulation water, so collection of exhaust air and its subsequent ducting to a treatment facility might be obligatory.

Monitoring

The effectiveness of the biotrickling system is determined by the gas feed and outlet concentrations. The composition of the absorbing water should be monitored by continuous measuring of the parameters [cww/tm/53]:

- pH
- temperature
- oxygen concentration
- conductivity.

Economics

Type of costs	Costs	Remarks
Capital costs [per 1000 Nm³/h]	EUR 5000–20000 [1]	
Operating costs labour utilities consumables		½ day per week [1]
[1] [cww/tm/70]		

3.5.2.4 Thermal Oxidation

Description

Thermal oxidation is the oxidation process of combustible gases and odorants in a waste gas stream, by heating a mixture of contaminants with air or oxygen above its auto-ignition point in a furnace and maintaining it at high temperature for sufficient time to complete combustion to carbon dioxide and water. Time, temperature (about 200–400 °C above auto-ignition), turbulence (for mixing) and the availability of oxygen all affect the rate and efficiency of the combustion process. These factors provide the basic design parameters for VOC oxidation systems. When halogenated VOC are present, special conditions might be needed to suppress the generation (or de-novo synthesis) of dioxins, though normally there is only a negligible dioxin formation with the combustion of gaseous waste streams:

- residence time ≥1 s [cww/tm/118 and 120]
- temperature ≥1100 ºC [cww/tm/118 and 120]
- oxygen content >3 %
- quenching of flue gas after incinerator to rush through the 'recombination window' of dioxins.

Additional facilities, e.g. alkaline scrubbers, need to be installed to remove hydrogen halides.

Several types of thermal oxidisers are operated:

- the straight thermal oxidiser, comprised of a combustion chamber and not including any heat recovery of exhaust air

- the regenerative thermal oxidiser, following the steps [cww/tm/132]:
  - exhaust gas stream entering the oxidiser through the common inlet and passing into a regenerative chamber through a butterfly valve
  - then passing through a ceramic heat exchange matrix, which raises the gas temperature near to oxidation temperature
  - then entering the combustion chamber, which is maintained at about 800 °C by burners, the released heat decreasing the fuel consumption of the burners
  - then leaving the combustion chamber through a second ceramic heat exchanger matrix, transferring its thermal energy to be re-used for preheating the next cycle
  - the clean gas stream released through an outlet valve to discharge.

Due to the relatively high combustion space temperature, the large excess of air and small influence of flame, only small amounts of carbon monoxide and NO_x are formed.

This system is particularly suitable for waste gas streams of comparatively high flow rates (up to 200 Nm³/s). 90–97 % heat recovery (waste gas preheating) is generally achieved [cww/tm/132].

Examples of regenerative thermal oxidation systems are schematically given in Figure 3.67 [cww/tm/132]:
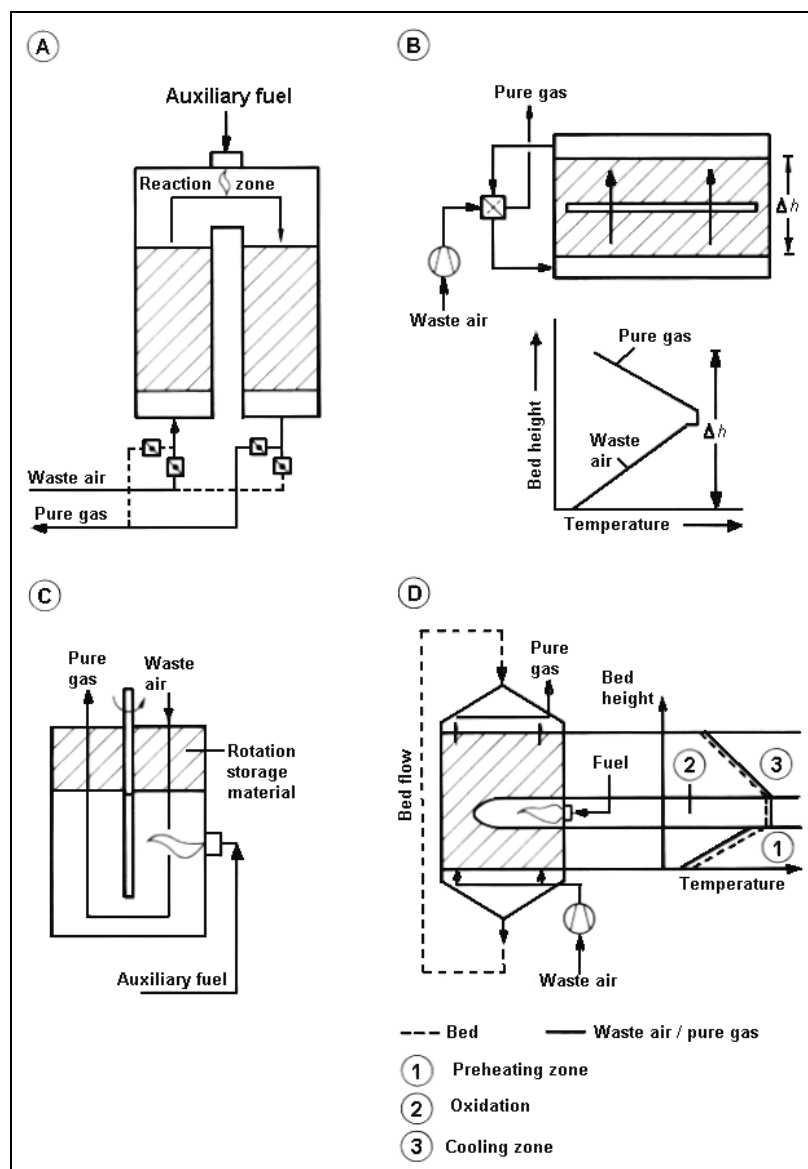
Figure 3.67: Schemes of Various Regenerative Combustion Systems
A) Fixed-bed regenerator, B) Combu-Changer, C) Ljungstrom regenerator, D) Moving-bed regenerator

- the recuperative thermal oxidiser, comprised of a combustion chamber, the waste gas preheater and, if appropriate, a secondary energy recovery heat exchanger, the heat continuously transferred to the preheater. This system is particularly suitable for waste gas streams of comparatively low flow rates (<14 Nm^3/s). 50–80 % heat recovery is generally achieved [cww/tm/132]

- gas engines and/or steam boilers [cww/tm/133], with 57–67 % energy recovery. The waste gas is burned in the engine, if necessary natural gas is added as support fuel. Downstream generators produce electricity. The engine contains a catalytic converter, especially to oxidise the carbon monoxide in the gas stream. The engine is coupled with a steam boiler to use the waste heat of the exhaust gas for the production of steam. The boiler feed water is preheated by the engine cooling water. With low combustion temperatures the formation of NO_x is low. The exhaust gas leaving the gas engine is led over oxidation catalysts to reduce the carbon monoxide content.

The design criteria for a thermal oxidiser system depend mainly on the nature of the waste gas stream, which determines the combustion conditions. Some of the most important items are:

- The burners
  Some types of burners are described in Table 3.15 [cww/tm/79].

Burner	Characteristics
Distributed Burner	gives much better mixing of the fuel and combustion air and of hot gases with the bypass air. This produces short flames and thus allows a greater residence time. However, only clean gases and gaseous fuels can be used. There is limited turndown (ratio between full and minimum output) and combustion air with a high oxygen content may be required.
Single Source Burner	is less expensive than distributed burners.
Pre-mix Burner	provides efficient combustion, but can only take gaseous fuel and clean air.
Diffusion Burner	can take liquid or gaseous fuel and clean or dirty air.
Vortex Burner	provides efficient combustion and a short flame, but a fan capable of delivering 500 mm water gauge is needed, there is low turndown and liability to fouling.
Oil Burner	gives longer flames, is more expensive, requires more maintenance, has more limited turndown and is generally not as clean as a gas burner.

Table 3.15: Types of Burner

- The mixing section [cww/tm/79]
  Good mixing can be achieved by:
  - natural diffusion between turbulent streams
  - impingement of gas streams at an angle
  - changes in direction of flow, round corners or past baffles.

- The combustion chamber [cww/tm/79]
  Conditions for dimensioning the combustion chamber are:
  - its diameter must allow turbulent flow
  - it has to be large enough to take the flame without quenching
  - its length is determined by the length of the flame plus the length needed to achieve mixing
  - it must be resistant to temperature and corrosion
  - it must withstand frequent expansion and contraction.

- Waste gas pretreatment [cww/tm/79]
  When pretreatment is necessary before entering the thermal oxidiser:
  - condensing out water vapour from a wet waste gas
  - removal of solid and liquid contaminants
  - concentration (e.g. by GAC or zeolite adsorption and subsequent desorption) to reduce the total gas volume to be treated by the oxidiser
  - preheating, which reduces fuel requirements.

- Safety equipment [cww/tm/79]
  Necessary safety devices are:
  - protection against flame flashback by devices, e.g. parallel plate flame arrestors, multiple screen flame arrestors, and/or water seals
  - burner purge period on start up of the thermal oxidiser
  - shut off flows in the event of flame failure
  - limiting of peak temperatures.

Application

Thermal oxidisers are used to reduce emissions from almost all VOC sources, including reactor vents, distillation vents, solvent operations and operations performed in ovens, dryers and kilns. They can handle minor fluctuations in flow, but excess fluctuations require the use of a flare. Their fuel consumption can be high, when low-loaded waste gases are fed, so thermal units are best suited for smaller process applications with moderate-to-high VOC loadings. Thermal oxidisers are used to control VOC from a wide variety of industrial processes, e.g.:

- storing and loading / unloading of petroleum products and other volatile organic liquids
- vessel cleaning (rail tank cars, road tankers, barges)
- process vents in the synthetic organic chemicals manufacturing industry
- paint manufacturing
- rubber products and polymer manufacturing
- flexible vinyl and urethane coating
- hazardous waste treatment storage and disposal facilities.

Application limits and restrictions [cww/tm/70]:

	Limits / Restrictions
Typical gas flows [Nm^3/h]	900–86000 (straight and regenerative thermal oxidiser) [1,2] 90–86000 (recuperative thermal oxidiser) [3]
Temperature [°C]	750–1000 [4] 980–1200 with hazardous components [1,2,3]
VOC-concentration in waste gas	<25 % LEL [1,2,3]
Residence time [s]	0.5–2 [5] (dependent on temperature)
Substances	no substances that can generate corrosive compounds when gas engines or steam boilers are used
[1] [cww/tm/120] [2] [cww/tm/119] [3] [cww/tm/118] [4] [cww/tm/132] [5] [cww/tm/64]	

Advantages/Disadvantages

Advantages	**Disadvantages**
- High and constant performance. - Simple principle. - Reliable in operation. - Recuperative and regenerative oxidation have a high thermal efficiency, with the effect of lower extra fuel consumption and hence lower carbon dioxide emission. - Process integration of waste heat or steam generation is possible.	- Emission of carbon monoxide and nitrogen oxides. - Risk of dioxin formation, when chlorinated compounds are incinerated. - Flue gas treatment necessary for VOCs containing sulphur and/or halides. - Additional fuel needed, at least for start-up operation and VOC concentration below auto-ignition point.

Achievable Emission Level / Performance Rates

Parameter	Performance rate [%]			Remarks
	straight	regenerative	recuperative	
VOC	98->99.9 [1]	95-99 [2]	98-100 [a][3]	
PM$_{10}$	25-99.9 [1]		25-99.9 [3]	Petroleum and coal products
	50-99.9 [1]		50-99.9 [3]	Chemical and allied products
Parameter	Emission level [mg/Nm^3]			Remarks
	straight	regenerative	recuperative	
VOC	<1-20 [b]			Oxygen content 3 v-%

[a] >99.9999 %
[b] low levels for hazardous substances, high levels for less hazardous
[1] [cww/tm/120]
[2] [cww/tm/119]
[3] [cww/tm/118]

The efficiency of thermal oxidation to abate VOC is higher than that of catalytic oxidation.

Cross-media Effects

The main utilities and consumables are:

Consumable	Amount	Remarks
Fuel during start-up and non-autothermal conditions [a]		
Energy [kWh/1000 Nm^3]	3–8 [1,2]	
Pressure drop [kPa]	1–5 [1]	

[a] autothermal range for VOC 1–10 g/Nm^3 [1]
[1] [cww/tm/70]
[2] [cww/tm/96]

Besides the emissions of carbon dioxide there are traces of carbon monoxide and NO$_x$ in the effluent gas, depending on the raw waste gas content and the operation of the thermal oxidiser. The content of carbon monoxide is abated, e.g. by application of an appropriate catalyst; relevant NO$_x$ amounts can undergo further treatment (see Section 3.5.4.2). The presence of sulphur and halogens require further flue gas treatment, e.g. water or alkaline scrubbing (see Section 3.5.1.4) to absorb hydrogen halides, lime injection (see Section 3.5.4.1) to absorb sulphur dioxide or GAC adsorption (see Section 0) to abate dioxins, if dioxin combination/recombination is not prevented during the incineration process. The presence of organosilicon compounds can cause highly dispersed amorphous silicon dioxide which needs abatement by suitable filter techniques. Additional gas treatment can cause waste water which has to be treated as well, e.g. by sedimentation (see Section 3.3.4.1.2) or neutralisation.

Monitoring [cww/tm/79]

Monitored parameters causing an alarm when set values are exceeded are:

- combustion temperature
- concentration of VOC
- concentration of carbon monoxide
- pressure
- feed of liquefied gas
- feed of compressed air.

A further important parameter to monitor is the oxygen content of the effluent gas, which provides information about the combustion conditions. This is crucial when halogen compounds are thermally oxidised.

The abatement efficiency of the system may be determined by monitoring the concentration of VOC and/or odour before and after the thermal oxidiser. VOCs can be measured as total carbon, using a flame ionisation detector. A qualitative analysis of the emissions can be done by taking grab samples at selected sampling points and by subsequently analysing them by GC/MS. Abatement efficiencies for odorous emissions are determined by taking grab samples at an appropriate sampling point and subsequently analysing them by olfactometry.

Burners have to be inspected regularly and, if necessary, cleaned. If deposits build up rapidly, preventive action needs to be taken. Effective pretreatment may be necessary to clean the contaminated waste gas before it enters the burner. If the deposits are due to carbon this may indicate the use of the wrong waste gas/fuel ratio and the need to check the control settings.

Economics

Type of costs	Costs			Remarks
	Straight	Regenerative	Recuperative	
Capital costs [per 1000 Nm^3/h]	USD 2800-59000 [1]	USD 24000-89000 [3]	USD 8900-77000 [4]	
	EUR 10000-40000 [2]	EUR 20000-30000 [2]	EUR 10000-50000 [2]	
		FIM 131000-174000 [5]		
Annual operating costs [per 1000 Nm^3/h]	USD 24000-45000 [1]	USD 2400-5900 [3]	USD 2800-14800 [4]	
		FIM 6500 [5]		
labour utilities consumables	0.5 days per week	2 days per year		
Cost effectiveness [per tonne pollutant per year]	USD 440-3600 [1]	USD 110-21000 [3]	USD 110-2200 [4]	
[1] [cww/tm/120] [2] [cww/tm/70] [3] [cww/tm/119] [4] [cww/tm/118] [5] [cww/tm/96]				

Cost factors [cww/tm/80]:

Factors	Influence / results
Volume of waste gases to be treated	Dimensions of combustion chamber
Heat content of waste gas	Design of combustion equipment, support fuel requirement
Combustion temperature	Construction materials
Instrumentation	
Heat recovery options	
Installation requirements (indoor, outdoor, ground level, rooftop, etc.)	

Kilns and boilers can be used for the thermal oxidation of VOC, if temperature and residence time are in the correct range. This can be an attractive option where the kiln or boiler is already on site.

3.5.2.5 Catalytic Oxidation

Description

Catalytic oxidisers operate in a very similar way to thermal oxidisers, with the main difference that the gas, after passing through the flame area, passes through a catalyst bed. The catalyst has the effect of increasing the oxidation reaction rate, enabling conversion at lower reaction temperatures than in thermal oxidation units. Catalysts, therefore, also allow smaller oxidisers to be used. The principle is illustrated in Figure 3.68 [cww/tm/79].
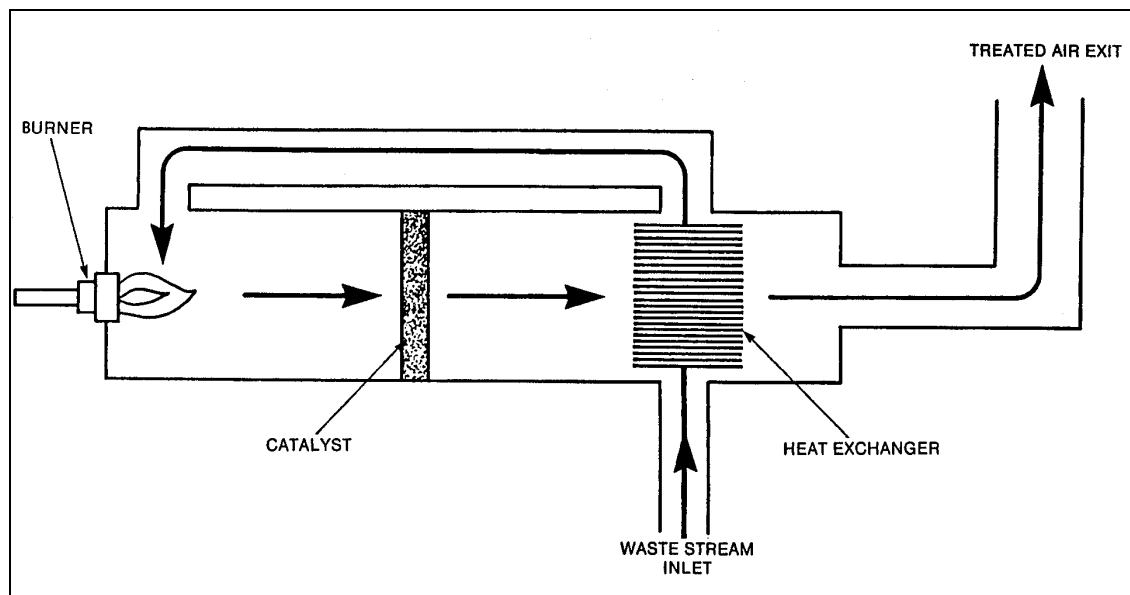
Figure 3.68: Principle of Catalytic Oxidation

The waste gas is heated by auxiliary burners to approximately 300–500 °C before entering the catalyst bed. The maximum design exhaust temperature of the catalyst is typically 500–700 °C [cww/tm/116].

The method of contacting the gas stream with the catalyst serves to distinguish catalytic oxidation systems. Both fixed-bed and fluidised-bed systems are used.

The fixed-bed catalytic oxidiser may use a monolith catalyst or a packed-bed catalyst. The monolith catalyst is a porous solid block containing parallel, non-intersecting channels aligned in the direction of the gas flow. Its advantage is minimal attrition due to thermal expansion / contraction during start-up / shutdown and low overall pressure drop. The packed-bed catalyst consists of particles which are supported either in a tube or in shallow trays through which the gas passes. Compared to the monolith catalyst its pressure drop is inherently high and the catalyst particles tend to break due to thermal expansion when the confined catalyst bed is heated / cooled during start-up / shutdown.

Fluidised-bed catalytic oxidisers have the advantage of very high mass transfer rates, although the overall pressure drop is somewhat higher than for a monolith. An additional advantage of fluidised beds is a high bed-side heat transfer as compared to a normal gas heat transfer coefficient. A further advantage is their higher tolerance of particulate matter in the gas stream than either fixed-bed or monolithic catalysts. This is due to the constant abrasion of the fluidised catalyst pellets, which helps remove particulates from the exterior of the catalysts in a continuous manner. A disadvantage is the gradual loss of catalyst by attrition.

Catalysts for VOC oxidation are typically either precious metals, such as platinum, palladium and rhodium, supported on ceramic or metal, or base metals supported on ceramic pellets, single or mixed metal oxides, often supported by a mechanically strong carrier, such as oxides of copper, chromium, manganese, nickel, cobalt etc.

Catalysts such as chromia/alumina, cobalt oxide and copper oxide / manganese oxide are used for the oxidation of gases containing chlorinated compounds. Platinum-based catalysts are active for the oxidation of sulphur-containing VOC, whereas they are rapidly deactivated by the presence of chlorine.

The presence of catalyst poisons or masking (blinding) agents in the waste gas stream, such as particulates or reactive chemicals, can have a significant impact on the working life of the catalyst. Poisoning by blinding can be reversible, e.g. coating of the catalyst surface by oils or fats reduces its efficiency but the coating can be burnt off by raising the temperature. However, if certain chemicals are present, the poisoning of the catalyst becomes irreversible. Such catalyst poisons are, e.g.:

- fast acting inhibitors, such as phosphorous, bismuth, arsenic, antimony, lead, mercury, causing an irreversible loss of catalytic activity at a rate dependent on concentration and temperature
- slow acting inhibitors, such as iron, tin, silicon, causing an irreversible loss of activity, but higher concentrations than those of fast acting inhibitors may be tolerated
- reversible inhibitors, such as sulphur, halogens, zinc, causing – depending on the catalyst – a reversible surface coating of catalyst active area at a rate dependent on temperature and concentration
- surface maskers, such as organic solids, causing a reversible coating of active surfaces
- surface eroders and maskers, such as inert particles, causing the coating of active surfaces, plus erosion of catalyst at a rate dependent on particle size, grain loading and gas velocity [cww/tm/80].

As with thermal oxidation, several types of oxidisers are operated:

- the straight catalytic oxidiser
- the regenerative catalytic oxidiser
- the recuperative catalytic oxidiser.

Normal operating conditions for catalytic oxidisers are, e.g.:

- natural gas as the preferred fuel (when additional fuel is needed)
- distributed burner as suitable burner
- chambers constructed of stainless steel or carbon steel
- burner section constructed of sufficient length to provide even flow and temperature distribution across the catalyst surface
- flat flow profile across the catalyst surface
- waste gas moving through the catalyst bed in 'plug flow' with minimum backmixing
- typical residence time 0.3–0.5 seconds.

As with thermal oxidation, some waste gas pretreatment can be necessary, such as condensing the water vapour from a wet waste gas, removal of solids and liquids and – typical for the catalytic system – removal of catalyst poisons. The safety requirement are almost the same as with thermal oxidation (see Section 3.5.2.4).

The catalytic oxidation should be designed in such a way as to facilitate the removal of the catalyst for cleaning or replacement purposes.

An example of a regenerative catalytic oxidiser is given in Figure 3.69 [cww/tm/132].
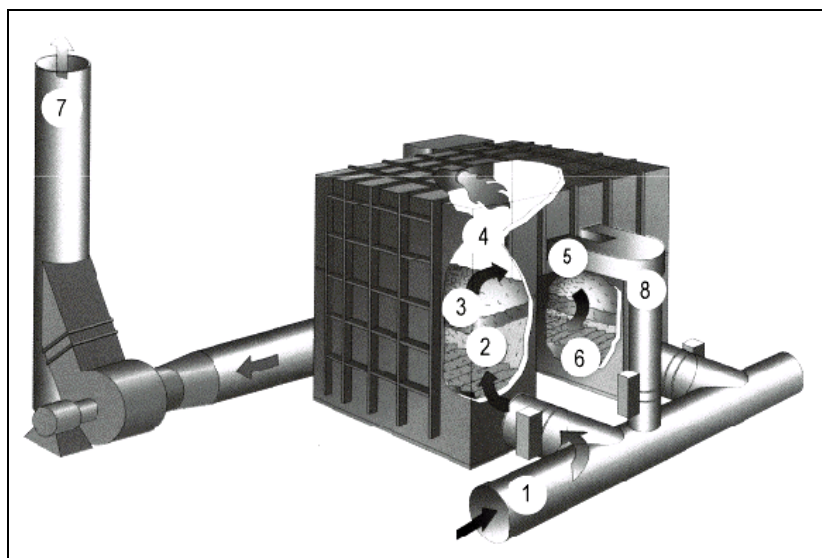
Figure 3.69: Regenerative Catalytic Oxidiser
1) Exhaust inlet, 2) Bed of ceramic heat-sink material, 3) Catalyst layer, 4) Combustion chamber, 5) Exit layer of catalyst, 6) Regenerative chamber, 7) Outlet manifold, 8) Transition duct

Application

Catalytic oxidation is used to reduce emissions from a variety of stationary sources. The main emission source is VOC from solvent evaporation, and catalytic oxidation is widely used by many industry sectors in this category. Examples from the chemical and related sectors are:

- petrol bulk loading stations
- process vents in the synthetic organic chemical manufacturing industry
- rubber products and polymer manufacturing
- polythene, polystyrene and polyester resin manufacturing.

Catalytic oxidation is most suited to systems with lower exhaust volumes, when there is little variation in the type and concentration of VOC, and where catalyst poisons or other fouling contaminants are not present. Other components to abate are carbon monoxide and – to a certain degree – particulates, though the latter require special operational devices.

Application limits and restrictions:

	Limits / restrictions
Typical gas flows [Nm^3/h]	1200–86000 (straight and regenerative catalytic oxidiser) [1,2]
	90–86000 (recuperative catalytic oxidiser) [3]
Temperature [°C]	300–500 before the catalyst
	500–700 after the catalyst
VOC concentration in waste gas	<25 % LEL [1]
Residence time [s]	0.3–0.5 (dependent on catalyst bed volume)
[1] [cww/tm/116] [2] [cww/tm/119] [3] [cww/tm/118]	

Advantages/Disadvantages

Advantages	Disadvantages
• More compact than thermal oxidisers. • Requiring lower temperatures and less additional fuel than thermal oxidisers. • Little or no NO_x produced from atmospheric fixation (about 20–30 % of the amount formed by thermal oxidation). • CO in the waste gas stream is simultaneously abated by the catalyst. • High, constant and reliable performance possible. • Recuperative and regenerative oxidation have a high thermal efficiency, with the effect of lower extra fuel consumption and lower carbon dioxide emission. • Process integration of residual heat or steam generation is possible. • Little or no insulation requirements. • Reduced fire hazards compared with thermal oxidiser.	• Lower efficiency in VOC destruction than thermal oxidation. • System sensitive to changes of gas heating value. • Risk of dioxin formation, when chlorinated compounds are incinerated. • All catalysts susceptible to poisoning agents, fouling agents and activity suppressants. • Particulates must often be removed first. • Spent catalyst that cannot be regenerated may need to be disposed of.

Achievable Emission Levels / Performance Rates

Parameter	Performance rate [%]			Remarks
	straight	regenerative	recuperative	
VOC	95 [1]	90-99 [2]		
	98-99 [a][1]			
PM10	25-99.9 [1]			Petroleum and coal products
	50-99.9 [1]			Chemical and allied products
CO		>98 [b][2]		
Odour	80-95 [3]			
Parameter	Emission level [mg/Nm³]			Remarks
VOC	<1-20 [c]			
[a] require larger catalyst volumes and/or higher temperatures [b] precious metal-based catalyst [c] low levels for hazardous substances, high levels for less hazardous substances [1] [cww/tm/116] [2] [cww/tm/119] [3] [cww/tm/70]				

Cross-media Effects

The main utilities and consumables are:

Consumable	Amount	Remarks
Fuel during start-up and non-autothermal conditions [a] [Nm³ methane per 1000 Nm³]	0–100	
Energy [kWh/1000 Nm³]	1–2 [1]	
Pressure drop [kPa]	1–5 [1]	
[a] autothermal range for VOC 1–2 g/Nm³ [1] (regenerative system) and 3–5 g/Nm³ (recuperative system) [1] [cww/tm/70]		

Emissions to the environment include traces of carbon monoxide and, because of the relatively low temperature compared to thermal oxidation, a low NO_x content. Emission levels of 15 mg/Nm³ are achievable.

The catalyst has a working life of two years and probably more. It then has to be regenerated or disposed of as chemical or even hazardous waste.

When the oxidised VOCs contain sulphur and/or halogens, further emissions of sulphur dioxide and/or hydrogen halides might be be expected. These have to be abated with suitable techniques.

Monitoring [cww/tm/79]

The bed temperature, pressure drop across the bed, combustion temperature and the carbon monoxide and oxygen content of the effluent gas stream should be monitored to control the combustion conditions.

The abatement efficiency of the system may be determined by monitoring the concentration of VOC and/or odour before and behind the oxidiser. VOCs can be measured as total carbon, using a flame ionisation detector. A qualitative analysis of the emissions can be done by taking grab samples at selected sampling points and by subsequently analysing them by GC/MS. Abatement efficiencies for odorous emissions are determined by taking grab samples at an appropriate sampling point and subsequently analysing them by olfactometry.

Burners have to be inspected regularly and, if necessary, cleaned. If deposits build up rapidly, preventive action needs to be taken. Effective pretreatment may be necessary to clean the contaminated waste gas before it enters the burner. If the deposits are due to carbon this may indicate the use of the wrong waste gas/fuel ratio and the need to check the control setting.

Economics

Type of costs	Costs			Remarks
	Straight	Regenerative	Recuperative	
Capital costs [per 1000 Nm^3/h]	USD 14000-58000 [1] EUR 10000-80000 [2]	USD 24000-89000 [3] EUR 30000-40000 [2]		
Annual operating costs [per 1000 Nm^3/h]	USD 2800-21000 [1]	USD 3600-12000 [3]		
labour utilities consumables	0.5 days per week	2 days per year		
Cost effectiveness [per tonne pollutant per year]	USD 440-3600 [1]	USD 150-26000 [3]		
[1] [cww/tm/116] [2] [cww/tm/70] [3] [cww/tm/119]				

Cost factors [cww/tm/80]:

Factors	Influence / results
Waste gas flow rate	Dimensions of combustion chamber
Heat content of waste gas	Design of combustion equipment, support fuel requirement
Solvent destruction efficiency required	Space velocity and consequently the amount of catalyst required
Catalyst type	
Instrumentation	
Type of heat exchanger	
Installation requirements (indoor, outdoor, ground level, rooftop, etc.)	

3.5.2.6 Flaring

<u>Description</u>

Flaring is a high-temperature oxidation process used to burn combustible components of waste gases from industrial operations. There are two types of flares:

- elevated flares
- ground flares.

Elevated flares, the more common type, have larger capacities than ground flares. In elevated flares, a waste gas stream is fed through a stack anywhere from 10 to over 100 metres tall and is combusted at the tip of the stack. The flame is exposed to atmospheric disturbances (wind, precipitation). Elevated flares are generally designed for large capacities (hundreds of tonnes per hour) and are more suitable to large variations of gas flow.

The typical elevated flare system (see Figure 3.70 [cww/tm/143]) consists of [cww/tm/143]:
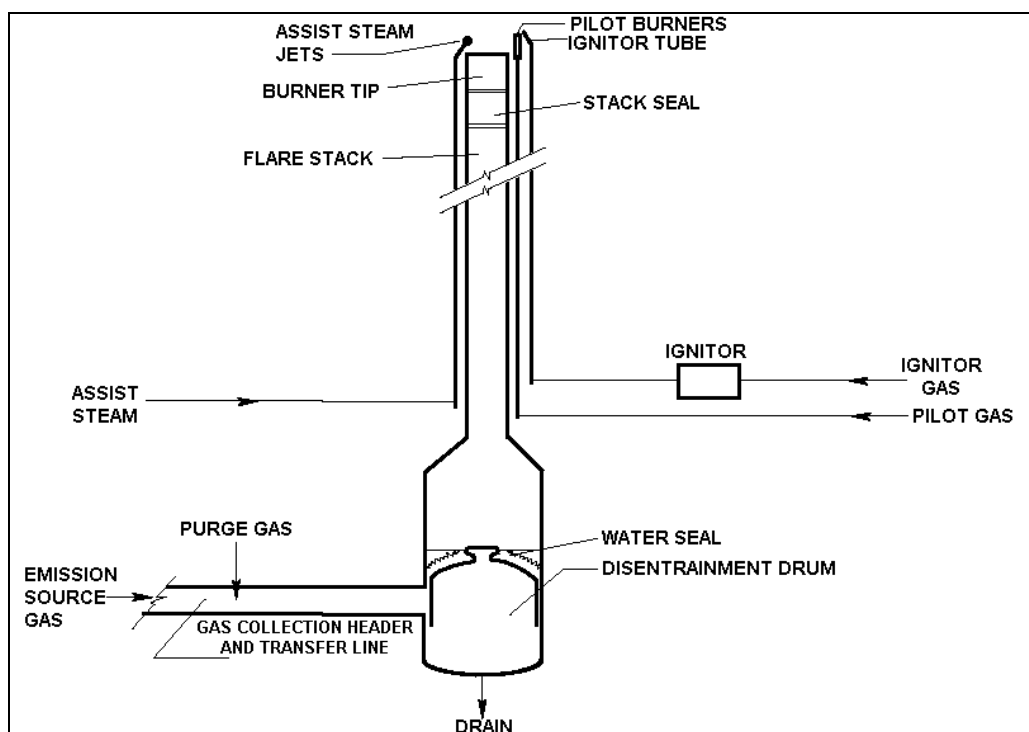
Figure 3.70: Typical Elevated Flare System [cww/tm/143]

- gas collection header and piping for collecting gases from processing units
- knockout drum (disentrainment drum) to remove and store condensables and entrained liquids
- proprietary seal, water seal or purge gas supply to prevent flash-back
- single- or multiple-burner unit and a flare stack
- gas pilots and an ignitor to ignite the mixture of waste gas and air
- if required, provision for external momentum force (steam injection or forced air) for smokeless flaring.

Natural gas, fuel gas, inert gas or nitrogen can be used as purge gas.

In **ground flares**, combustion takes place at ground level. They vary in complexity and may consist either of conventional flare burners discharging horizontally with no enclosures or of

multiple burners in refractory-lined steel enclosures. They are designed for smaller capacities (tens of tonnes per hour) and handle the base load of combustible gases generated by all the point sources connected to the flare system during normal operation. This includes mainly leaking safety valves and any start-up and shutdown processes.

The large diameter of the ground flare provides the possibility of more burners. Thus the ground flare can be adjusted to varying amounts of flare gas by adjusting the number of burners that are operating. This improves the combustion conditions and results in higher combustion efficiency.

A new type of ground flare works as a **premixed surface combustion system** (enclosed burner), where premixed gas and air burns on a permeable medium. The permeable medium consists of several layers of metal fibres and withstands temperatures up to 1300 °C. The gas is fed to a venturi injector at the bottom end of the burner system, the injector drawing in the air needed for stoichiometric combustion. Air ratios between 1 : 12 and 1 : 19 can be achieved. In the diffusor directly on top of the venturi injector, the velocity of the mixture is decreased and hence the pressure increased, which increases the efficiency of the venturi injector and causes static pressure to let the gas mixture flow through the permeable medium. From the diffusor the gas mixture enters the premix chamber and flows through the permeable medium, where it is ignited by a pilot burner. The combustion takes place just above the permeable medium. Heat is released in a convective way, making energy recovery with heat exchanger an option. The enclosed combustion zone prevents discharge of heat and light. The technique is described in Figure 3.71 [cww/tm/153].
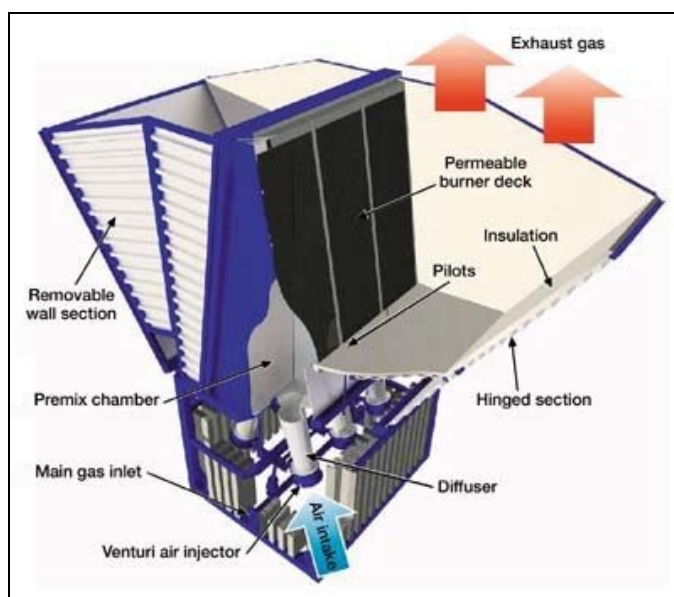
Figure 3.71: Principal Components of the Enclosed Burner

The fibre mat is constantly cooled by the flow of gas and air. Because the metal fibres have a large surface area relative to their volume, they cool rapidly. This also makes the unit resistant to flash back. Even at the lowest flow rate the premix stream is sufficient to cool the mat so that the premix side of the mat will not exceed 150 °C [cww/tm/153].

A single module comprises six burner units in two back to back banks with a total capacity of 90 MW for natural gas (Wobbe index 47.8 MJ/Nm^3). The flame is shielded and then directed upward by insulated walls. Heat radiation to the surrounding area is minimised and local ambient temperature rises are limited to less than 5 K [cww/tm/153].

Complete combustion with flare systems requires sufficient combustion air and proper mixing of air and waste gas. Smoking may result from combustion, depending upon waste gas

components and the quantity and distribution of combustion air. Waste gases containing methane, hydrogen, carbon monoxide and ammonia usually burn without smoke. Waste gases containing heavy hydrocarbons such as paraffins above methane, olefins and aromatics cause smoke. Industry usually requires a smokeless capacity of 10–15 % for elevated flares and 100 % for ground flares. An external momentum force is used as smoke suppressant, such as :

- steam, supplied at up to 0.7 MPa gauge pressure, normally used on large sites where steam is easily available
- air, suited to applications requiring a small and relatively inexpensive installation
- high-pressure gas, which is very costly
- water, supplied at a water pressure of about 2 MPa gauge, suitable where water is freely available in large quantities.

External momentum is rarely required in ground flares.

Waste gases to be flared must have a heat content of at least 11 MJ/Nm^3 for complete combustion, otherwise auxiliary fuel must be added. In some cases, even flaring waste gases having the necessary heat content will also require supplemental heat. If fuel-bound nitrogen is present, flaring ammonia with a heating value of 13.6 MJ/Nm^3 will require higher heat to minimise NO_x formation.

Industrial sites often operate an integrated flare system, i.e. a combination of a ground flare with an optimal burner design for waste gas flows during regular operation and an elevated flare for high flow rates during emergencies and process upsets.

Different kinds of flares are shown in Figure 3.72 – Figure 3.74 [cww/tm/64].
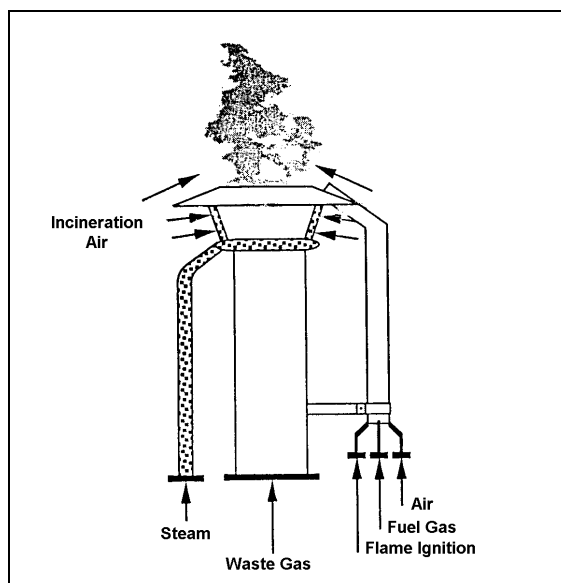
Figure 3.72: Injector Rod Flare
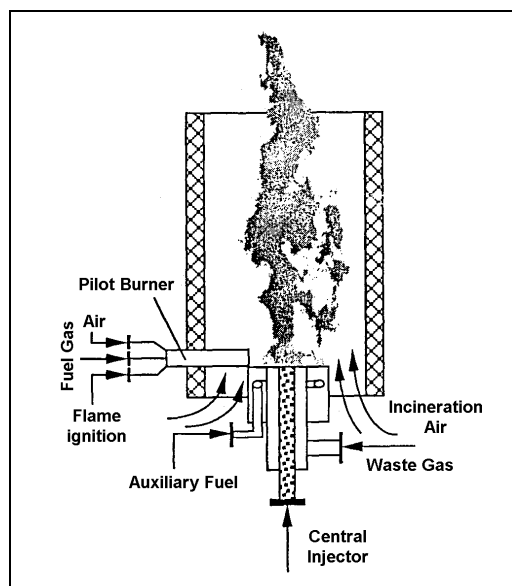
Figure 3.73: Shielded Flare
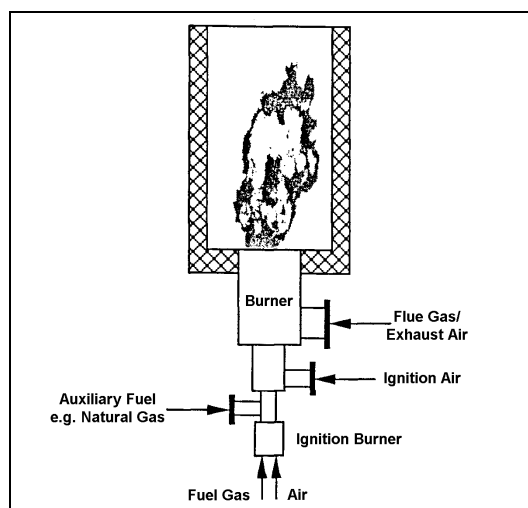
Figure 3.74: Muffle Flare

<u>Application</u>

Flares are widely used in the oil, gas and petrochemical industry to safely dispose of surplus combustible gases and vapours when there is no opportunity to use or recycle them. VOC from vents, pumps and compressors are collected and routed to a flare system. A significant function of flares is to prevent the unwanted occurrence of larger amounts of inflammable gases as a safety measure or under emergency conditions. Technically, all points in a chemical plant with a potential safety release of combustible gases are connected to a flare system. Flares are normally not, however, regularly used as a continuous measure. They can also be used to burn waste gases generated by sewage / sludge digesters.

Whereas elevated flares are normally used as emergency and relief gas flaring, ground flares are more often employed as routine flaring, provided that the waste gas does not contain toxic constituents. Ground flares cannot - in contrast to elevated flares – handle large fluctuations in gas flow. When these fluctuations can occur, combination with an elevated flare is required.

As reported [cww/tm/153], the premix surface combustion type is also applicable to toxic and hazardous gases, e.g. gas mixtures with hydrogen sulphide content.

Application limits and restrictions:

	Limits / restrictions
Typical gas flows	0–1800000 Nm^3/h [1] (upper limit for elevated flares) 600-210000 Nm^3/d (Wobbe Index range 15-52 MJ/Nm^3) for ground flares of the premixed surface combustion type
Combustion temperature [°C]	>800 [2] 900-1260 °C (ground flares of the premixed surface combustion type)
Residence time in combustion chamber [s]	1–2 [2]
Pressure range [kPa gauge]	0-0.73 (ground flares of the premixed surface combustion type)
VOC concentration in waste gas	0–100 % LEL with safety engineering [2] 0–50 % LEL without safety engineering [2]
Oxygen content after incineration	>5 % [3] (muffle flare)
Flare velocity [m/s]	0–20 [3] (to prevent backflash)
[1] [cww/tm/117] [2] [cww/tm/132] [3] [cww/tm/64]	

Advantages/Disadvantages

Advantages	**Disadvantages**
General • Efficient abatement system concerned with surplus combustible and non-recyclable gases or sudden releases of large amounts of gas. • Can be used to control intermittent or fluctuating waste gas streams.	General • No pollutant abatement (SO$_x$, NO$_x$, carbon monoxide, hydrogen halides) beyond the flare. • Smoke suppressants needed. • Heat of combustion not recoverable. • High costs in case of retrofitting
Elevated flares • Quick and safe release of large amounts of waste gas amounts. • Stand-by equipment for emergency use.	Elevated Flares • Light nuisance. • Noise nuisance. • Difficulties in handling low flows. • Coke formation may cause tip blockage.
Ground flares • Reliable flare ignition (less affected by wind). • Flexible; can handle gas flow variations in the low range.	Ground flares • Limited capacity. • Cannot handle large variations of gas flow, requiring a combination with elevated flares. • Increased health and safety risks at malfunction. • Potentially reduced efficiency due to poor fuel quality. • Odour nuisance.
Ground flare premixed surface combustion • Complete combustion. • Modular system for rapid rig-up and easy transportation. • Very broad turn-down ratio (1 : 30 with Wobbe-Index 15-52 MJ/Nm^3) • Direct start-up at full capacity without needing a period of start-up time. • Low NO$_x$ emissions. • Energy recovery is an option. • Low emissions of light and heat.	Ground flare premixed surface combustion • New technology, therefore not yet recognised worldwide. • High costs when compared with conventional flares.

Achievable Emission Levels / Performance Rates

Parameter	Elevated flare		Ground flare	
	Performance rate [%]	Emission level [mg/Nm³]	Performance rate [%]	Emission level [mg/Nm³]
VOC	>98 [a][1]		>99 [a][2]	
	80-86 [3]		99.9 [c][3]	
NOx		400 (200 ppm)		400 (200 ppm)
				11.6 (3.9 ppmv) [b,c]
NO				8.6 (2.9 ppmv) [b,c]
Hydrocarbons (included BTEX)				<2.8 (<1 ppmv) [b,c]
CO				-
Noise				73 dB(A) [b,d]
[a] at optimum condition: heat content of waste gas >11 MJ/Nm³ [1], low flows and low heat content achieve lower combustion efficiencies [b] premixed surface combustion system [c] corrected to 3 % O_2 [d] at 50 m at free field conditions [1] [cww/tm/117] [2] [cww/tm/84] [3] [cww/tm/153]				

The achievable emission levels mentioned in the table report the destruction of air pollutants (VOC and Hydrocarbons) by flaring. The other parameters (NO and NOx) refer to emissions caused by flaring. Flaring has no exhaust gas treatment installed, hence pollutants caused by the incineration process of sulphur and/or halogens containing waste gases, NOx, carbon monoxide, soot etc. normally are not controlled. For these reasons, ground flares are not suited for toxic and hazardous gases. The combination / recombination reaction to dioxins, however, is not favoured because of the lack of a 'recombination window' and metal surfaces acting as catalyst.

The abatement performance of flaring, as described in the table above, is only valid under the optimum conditions. The performance range under non-optimum conditions covers 0-98 % [cww/tm/84], what means that flaring is very sensitive to changes of these conditions. That makes flaring a very unreliable abatement technique when used in everyday operation.

Cross-media Effects

The main utilities and consumables are:

Consumable	Amount	Remarks
Smoke suppressants (steam, air, water, natural gas)		
Ignition gas for ignition pilot (propane or butane)		
Purge gas (nitrogen or fuel) to keep the system on over-pressure		
Pilot gas		
Energy [kWh/1000 Nm³]		
Pressure drop [kPa]	1 [1]	
[1] [cww/tm/64]		

Flaring can cause the emission of noise. The most significant noise sources are [cww/tm/94]:

- smoke suppressant injection
- combustion process
- vents.

Any steam-assisted flare generates noise, due to the high-pressure steam jets and injectors and the combustion noise associated with hydrocarbons. High-pressure steam generates high-frequency noise, which is most serious to humans, and also improves combustion efficiency, thereby increasing energy release and burning rate, which again results in higher combustion

noise. Combustion noise is typically low-frequency noise, comparable to the vent noise from turbulent mixing of waste gases and air.

The suppression of noise is a crucial environmental issue and thus an important design aspect that needs addressing at an early stage. Noise avoidance aspects are, e.g.:

- reduction or attenuation of the high frequency steamjet noise by using multiport steam injectors, which, on the other hand, can lead to increased coke formation under low-flow conditions; orifice design to cope with the latter drawback is essential
- siting of the injectors in a way that the jet streams can interact and reduce the mixing noise
- increasing the efficiency of suppressant with better and more responsive forms of control
- restricting steam pressure to <0.7 MPa gauge
- using a silencer around the steam injector as an acoustic shield for the injectors
- using air-blown flares or enclosed ground flares.

Further impacts are:

- light nuisance from elevated flares
- odour nuisance because of insufficient combustion (mostly with ground flares).

It should be mentioned that flaring is involved in a significant number of fire and explosion events in the chemical and petrochemical industries, as is reported by the French Ministry of the Environment (through its Bureau of Risk Analysis and Industrial Pollution). The results can be found in the AIDA database, managed by that organisation.

Monitoring [cww/tm/94]

The flow rate of the smoke suppressant to the flare tip has to be checked to ensure that sufficient suppressant is introduced, but not more than is required to prevent smoking. This can be achieved in three different ways:

- by an array of thermo-couples rated for at least 1000 ºC
- by a ground-based infra-red detector
- by metering flare gas flow to the ratio of suppressant flow to flare gas flow. Flow control usually takes place with control valves or, in the case of air-blown flares, with varying fan pitch, inlet vane pitch or blower speed.

A more stringent monitoring policy is required for ground flares because of health and safety risks.

Rapid response of the control system is essential, preferably by means of electronic transmission of control signals between the, usually remote, flare stack and the relevant control room. Installation of TV to monitor the flare in the control room should be considered to allow a manual intervention of suppressant control if this should be necessary.

For the pilot, the operational monitoring equipment to apply includes:

- thermo-couples (but beware of erroneous signals)
- direct surveillance of the pilot flame (e.g. TV-surveillance)
- infra-red monitoring (caution: water absorbs IR), sometimes modified with optical monitoring to surmount the IR-absorption of water
- luminosity measurement
- UV-monitoring
- ionisation probes
- low-pressure alarm
- flow control of the purge gas.

A device is required for continuous detection of the presence of the pilot flame.

Economics

Type of costs	Elevated flare	Ground flare	Remarks
Capital costs [per 1000 Nm^3/h]	USD 8300-560000 [1]		
Operating costs [per 1000 Nm^3/h]	USD 420-36500 [1]		
Cost effectiveness [per tonne pollutant controlled per year]	USD 14-6400 [1]		
[1] [cww/tm/117]			

Flares considered are those with tips between 2.5 cm and 2.3 m in diameter, burning 100 % combustible waste gas with a heat content of approximately 17 MJ/Nm^3 and operated between 1 and 100 hours per year. Flares at the lower end of the capital and operating costs have a higher flow capacity (approximately 300000 Nm^3/h) with a flare tip diameter of up to 2.3 m and are operated 100 hours per year or more. The flares at the higher end of the cost ranges have lower flow capacity (approximately 36 Nm^3/h), flare tip diameters as small as 2.5 cm and are operated for fewer than 10 hours per year.

Because flares are primarily safety devices which deal with flows of short duration (generally an upset condition or an accidental release from a process) rather than a control device which treats a continuous waste stream, it is not entirely appropriate to compare the cost effectiveness of flares to other control devices. Cost per tonne of pollutant controlled largely depends upon the annual hours of operation. Infrequent use of the flare will result in greater cost per tonne of pollutant controlled, while more frequent use means the lower costs per tonne of pollutant controlled.

3.5.3 Recovery and Abatement Techniques for Particulates

Particulate pollutants are dust, heavy metals and their compounds, aerosols, mist and soot, which can frequently be found in waste gas streams, flue gas streams and exhaust air streams in the chemical industry. Dust particles and heavy metals (and/or compounds) are found in production waste gas streams, when solids and powdery compounds are handled, formed and/or stored, as well as in the flue gas or exhaust air streams of combustion sites, e.g. power plants or waste incineration. Aerosols and mist appear, e.g., during reaction and work-up of production mixtures. The common treatment systems are described below.

3.5.3.1 Separator

Description

The waste gas stream is passed into a chamber where the dust, aerosols and/or droplets are separated from the gas under the influence of gravity / mass inertia, the effect increased by reducing the gas velocity by design means, e.g. baffles, lamellae or metal gauze.

The design should ensure a good uniform speed distribution inside the vessel. Preferential flows have an adverse effect on efficiency. The employment of internal obstructions in the inertia separator enables operation at higher speeds, which represents a reduction in volume of the separator compared with the settling chamber. The drawback is the increasing pressure drop.

Application

A separator is usually installed as a preliminary step to various dust filter systems, scrubbers, cooling towers etc. It is used, e.g., to prevent entrainment of the washing liquid with the purified waste gas and/or to remove abrasive particles. It is not applicable to treat particulates in flue gas.

Application limits and restrictions are [cww/tm/70]:

	Limits / restrictions
Waste gas flow [Nm^3/h]	100–100000 [1]
Dust content	No restriction
Particulate size	>PM$_{10}$, better >PM$_{50}$ [2]
Temperature	Normally about 540 °C, but dependent on vessel material [2]
[1] [cww/tm/70] [2] [cww/tm/108]	

Advantages/Disadvantages

Advantages	Disadvantages
• No moving parts, hence low maintenance. • Very low pressure drop. • Suitable for higher temperatures.	• Low removal efficiency, especially for small particles. • Not suitable when the density difference between gas and particulates is small.

Achievable Emission Levels / Performance Rates

Parameter	Performance rate [%]	Emission level [mg/Nm^3]	Remarks
PM	10–90 [1]		Dependent on PM size
Droplets		100 [1]	In demisters
[1] [cww/tm/70]			

Cross-media Effects

Consumable	Amount	Remarks
Water (optional cleaning system for baffles or lamellae)	100–200 l/m^2 [1]	
Energy [kWh/1000 Nm^3]		Only for fan
Pressure drop [kPa]	<0.5 [1]	
[1] [cww/tm/70]		

Residues are the separated dust and/or the separated droplets which have to be disposed of when re-use / recirculation is not possible. Depending on its source, the separated dust might be contaminated with toxic and hazardous content which needs to be considered for further treatment or disposal.

Economics

The capital costs are low but since the separator is usually integrated in other systems, a useful figure cannot be given.

3.5.3.2 Cyclone

Description

Cyclones use inertia to remove particles from the gas stream, imparting centrifugal forces, usually within a conical chamber. They operate by creating a double vortex inside the cyclone body. The incoming gas is forced into circular motion down the cyclone near the inner surface of the cyclone tube. At the bottom the gas turns and spirals up through the centre of the tube and out of the top of the cyclone. Particles in the gas stream are forced toward the cyclone walls by the centrifugal force of the spinning gas but are opposed by the fluid drag force of the gas travelling through and out of the cyclone. Large particles reach the cyclone wall and are collected in a bottom hopper, whereas small particles leave the cyclone with the exiting gas.

Wet cyclones are high-efficiency units, spraying water into the waste gas stream to increase the weight of the particulate material and hence also removing fine material and increasing the separation efficiency.

There are two types of cyclones, the reverse flow and the straight through cyclone [cww/tm/79]:

- **the Reverse Flow Cyclone** (see Figure 3.75 [cww/tm/79]), which is the most common, consists of:
  - a cylindrical shell with conical base
  - a dust collection hopper
  - an air inlet, either tangential or axial
  - outlets.
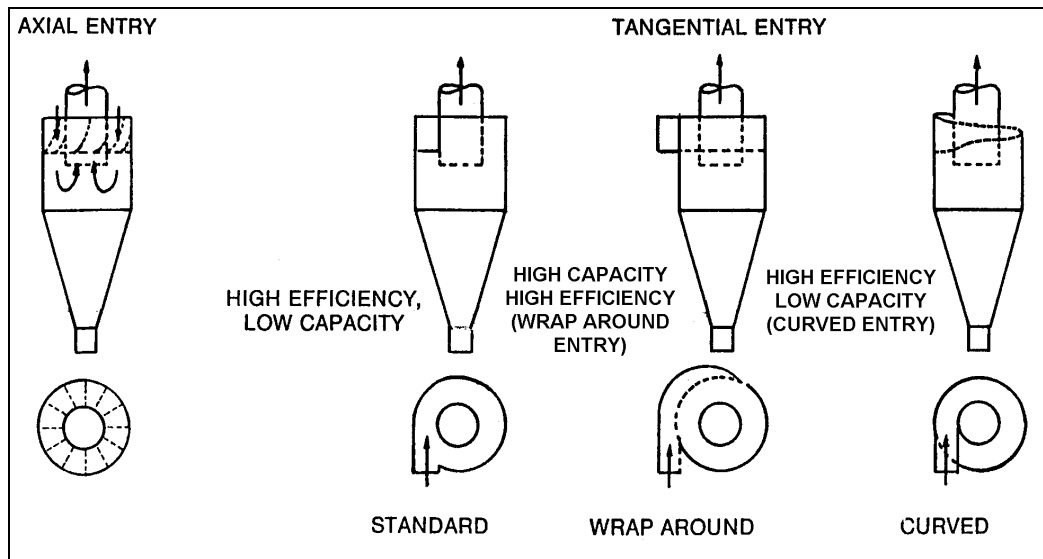
Figure 3.75: Reverse Flow Cyclone

- **the Straight Through Cyclone** (see Figure 3.76 [cww/tm/79]) is equipped with fixed or moving impellers, the inlet gas channelling into a spiral, the clean gas concentrating along the centre axis and particulates concentrating near the wall.
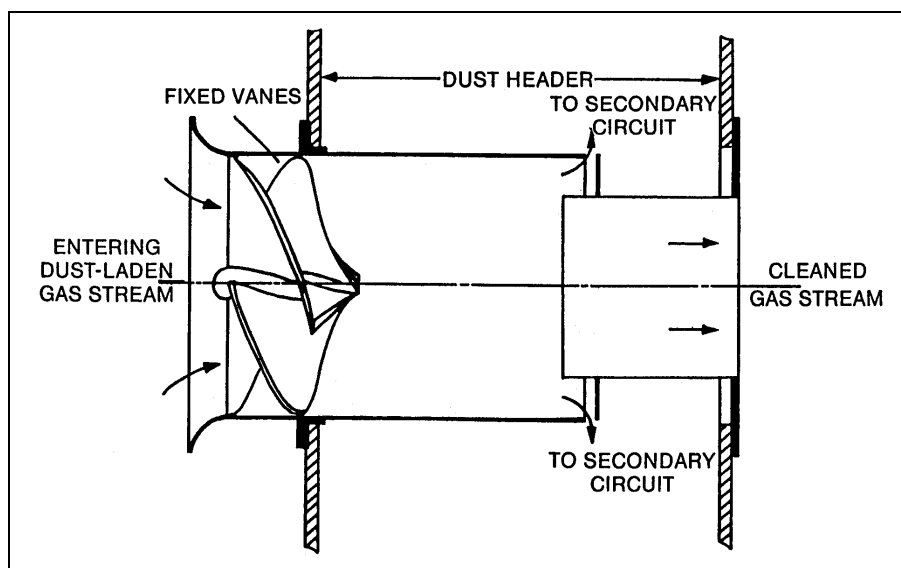
Figure 3.76: Straight Through Cyclone

Application

Cyclones are used to control particulate material, and primarily PM >10 μm. There are, however, high efficiency cyclones designed to be effective even for PM$_{2.5}$ [cww/tm/107].

Cyclones themselves are generally not adequate to meet air pollution regulations, but they serve a purpose as precleaners for more expensive final control devices such as fabric filters (see Section 3.5.3.5) or electrostatic precipitators (see Section 3.5.3.3). They are extensively used after spray drying operations and after crushing, grinding and calcining operations. Fossil fuel-fired industrial fuel combustion units commonly use multiple cyclones which operate with greater efficiency than a single cyclone and can separate PM <2.5 μm.

Application limits and restrictions are:

	Limits / restrictions
Waste gas flow [Nm^3/h]	1–100000 [1,2], (single cyclone unit)
	up to 180000 [2] (multiple cyclones in parallel)
Dust content [g/Nm^3]	1–16000 [2]
Particulate size	<PM$_{2.5}$ -<PM$_{200}$ [2]
Temperature	dependent on vessel material, can be >1200 °C [1]
[1] [cww/tm/132] [2] [cww/tm/107]	

Advantages/Disadvantages

Advantages	Disadvantages
• Simplicity of the installation. • Recovery of raw material. • No moving parts, hence few maintenance requirements and low operating costs. • Dry collection and disposal, except wet cyclones. • Relatively small space requirements.	• Relatively low particulate collection, particularly for PM <10 μm. • Axial entry cyclones cannot be used with particles likely to cause excessive erosion or clogging of the vanes in the inlet. • Unable to handle sticky or tacky materials. • Emission to waste water with wet cyclone. • Noise.

Achievable Emission Levels / Performance Rates

Cyclones perform more efficiently with higher pollutant loadings, provided that the device does not become choked. Higher pollutant loadings are generally associated with higher flow designs [cww/tm/107].

The collection efficiency of cyclones varies as a function of particle size and cyclone design. It increases with [cww/tm/107]:

• particle size and/or density
• inlet duct velocity
• cyclone body length
• number of gas revolutions in the cyclone
• ratio of cyclone body diameter/gas exit diameter
• dust loading
• smoothness of the cyclone inner wall.

The collection efficiency decreases with [cww/tm/107]:

- increasing gas viscosity
- increasing gas density
- increasing gas inlet duct area
- leakage of air into the dust outlet.

Parameter	Performance rate [%]				Remarks
	Conventional	High-efficiency	High-through-put	Multi-cyclone	
PM	70–90 [1]	80-99 [1]	80-99 [1]		
PM$_{10}$	30-90 [1]	60-95 [1]	10-40 [1]		
PM$_5$		90 [1]		80-95 [1]	
PM$_{2.5}$	0-40 [1]	20-70 [1]	0-10 [1]		
[1] [cww/tm/107]					

Cross-media Effects

Consumables are:

Consumable	Amount	Remarks
Water (wet cyclones)		
Energy [kWh/1000 Nm^3]	0.25–1.5 [1]	
Pressure drop [kPa]	0.5–1 [2]	Low-efficiency units (high throughput)
	1–1.5 [2]	Conventional
	2–2.5 [2]	High-efficiency units
[1] [cww/tm/64] [2] [cww/tm/107]		

Dust is emitted as residue and has to be disposed of. The amount depends on the dust load of the waste gas. Depending on its source, the separated dust can be contaminated with toxic and/or hazardous substances.

The operation of cyclones is a significant noise source which has to be abated, e.g. by enclosing the equipment.

Monitoring [cww/tm/79]

A mass emission to assess the performance of a cyclone can be determined by monitoring the particulate concentration in the effluent gas stream, using an isokinetic sampling probe or a meter based on, e.g., UV/visible opacity, beta rays or particle impingement.

Maintenance requirements for cyclones are low – there should be easy access to enable periodic inspection of the cyclone for erosion or corrosion. The pressure drop across the cyclone is routinely monitored and the dust handling system is checked for blockages.

<u>**Economics**</u>

Type of costs	Costs		Remarks
	Single conventional cyclone	Multiple cyclones	
Capital costs [per 1000 Nm^3/h]	USD 1200-1500 [1]	USD 1100-1400 [1]	
	EUR 900 [2]		
Annual operating costs [per 1000 Nm^3/h]	USD 700-7800 [1]	USD 450-750 [1]	
	EUR 200 [2]		
Cost effectiveness [per tonne pollutant controlled per year]	USD 0.45-460 [1]	USD 0.32-50 [1]	
[1] [cww/tm/107] [2] [cww/tm/70]			

For the conventional single cyclone, flow rates are assumed to be between 1800 and 43000 Nm^3/h, PM loading between 2.3 and 230 g/Nm^3 and control efficiency to be 90 %. For the multiple cyclone these are assumed to be between 36000 and 180000 Nm^3/h and the same range of pollutant loading and control efficiency.

As a rule, smaller units controlling a waste gas stream with a low PM concentration will be more expensive (per unit flow rate and per quantity of pollutant controlled) than a large unit controlling a waste gas stream with a high PM concentration.

3.5.3.3 Electrostatic Precipitator (ESP)

<u>**Description**</u>

An ESP is a particulate control device that uses electrical forces to move particles entrained within a waste gas stream onto collector plates. The entrained particles are given an electrical charge when they pass through a corona where gaseous ions flow. Electrodes in the centre of the flow lane are maintained at high voltage and generate the electrical field that forces the particles to the collector walls. The pulsating DC voltage required is in the range of 20–100 kV.

There are several types of ESP:

- the dry wire-plate ESP
- the dry wire-pipe ESP
- the wet wire-plate ESP
- the wet wire-pipe ESP.

In the **wire-plate ESP** (see Figure 3.77 [cww/tm/79]), the waste gas flows horizontally and parallel to vertical plates of sheet material. The high voltage electrodes are long wires that are weighted and hang between the plates. Within each flow path, gas flow must pass each wire in sequence as it flows through the unit.

In the **wire-pipe ESP** (or tubular ESP) (see Figure 3.78 [cww/tm/79]), the exhaust gas flows vertically through conductive tubes, generally with many tubes operating in parallel. The high voltage electrodes are long wires suspended from a frame in the upper part of the ESP that run through the axis of each tube.
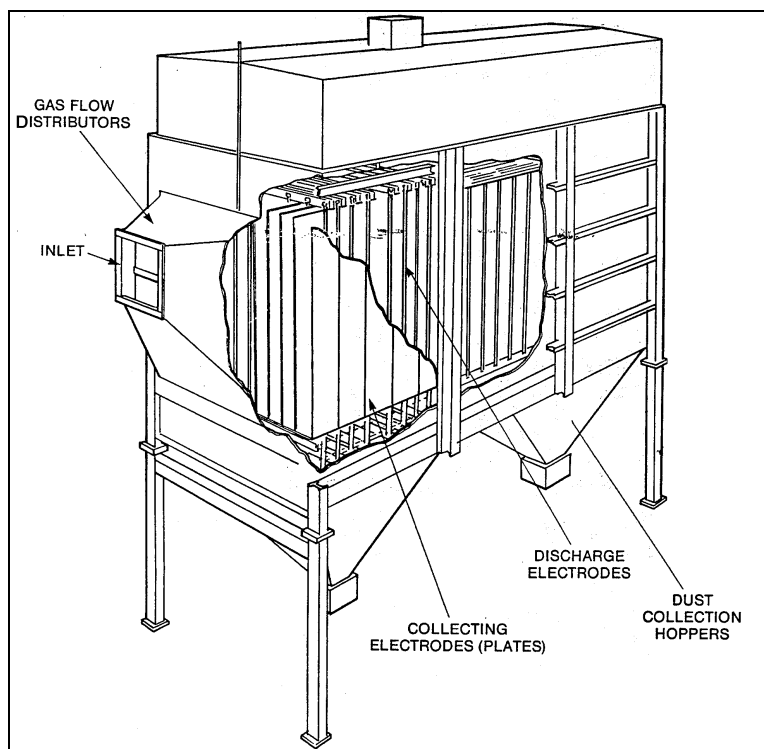
Figure 3.77: Wire-Plate ESP
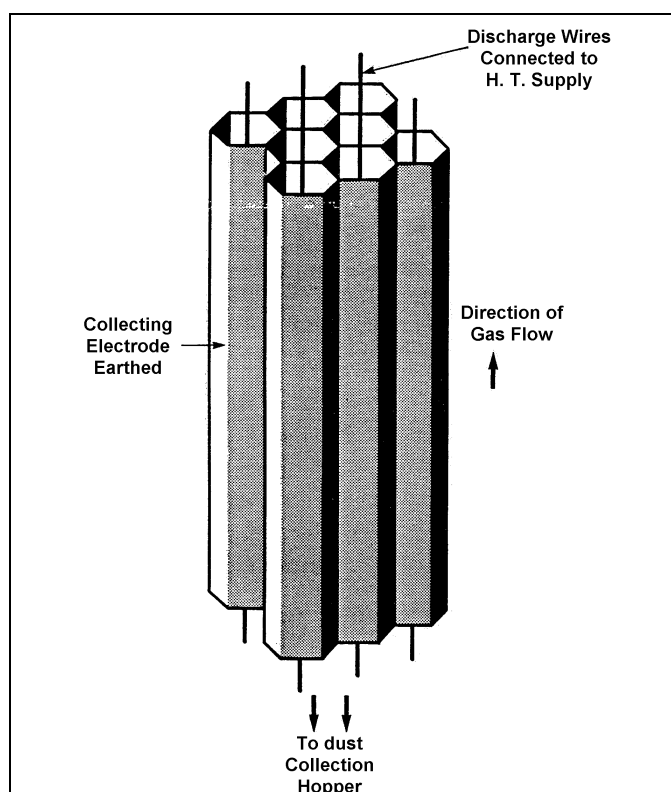
Figure 3.78: Wire-Pipe ESP

In dry ESP the collectors are knocked or rapped by various mechanical means to dislodge the particulate matter, which slides downward into a hopper. The rapping procedure can project some of the particles back into the gas stream. The particles re-entrained in the last section of the ESP cannot be recaptured and so escape the unit. A part of the waste gas might also flow

around the charging zones. For this reason anti-sneakage baffles are placed to force the sneakage flow to mix with the main gas stream.

Dry wire-pipe ESP can be cleaned acoustically with sonic horns. In contrast to wire-plate ESP, wire-pipe ESP provide no sneakage paths around the collecting region, but field non-uniformities may allow some particles to avoid charging.

In wet ESP, the collectors are either intermittently or continuously washed by a spray of water, the collection hoppers replaced with a drainage system. The wet effluent is collected and treated. Wet ESP require a source of wash water to be injected or sprayed near the top of the collector pipes either continuously or at timed intervals. This wash system replaces the rapping or acoustic mechanism usually used by dry ESP. The water flows with the collected particles into a sump from which the fluid is pumped or drained. A portion of the fluid may be recycled to reduce the total amount of water required.

ESPs work as Single- or Two-Stage ESPs. In single-stage ESP, the electric field that generates the corona discharge is also employed to attract and hence remove the charged particles, with charging and discharging taking place in one appliance. In a two-stage ESP, charging and removal of the particles occur in separate electric fields, the second one being purely electrostatic.

The principal difference between single- and two-stage ESP is illustrated in Figure 3.79 [cww/tm/79].
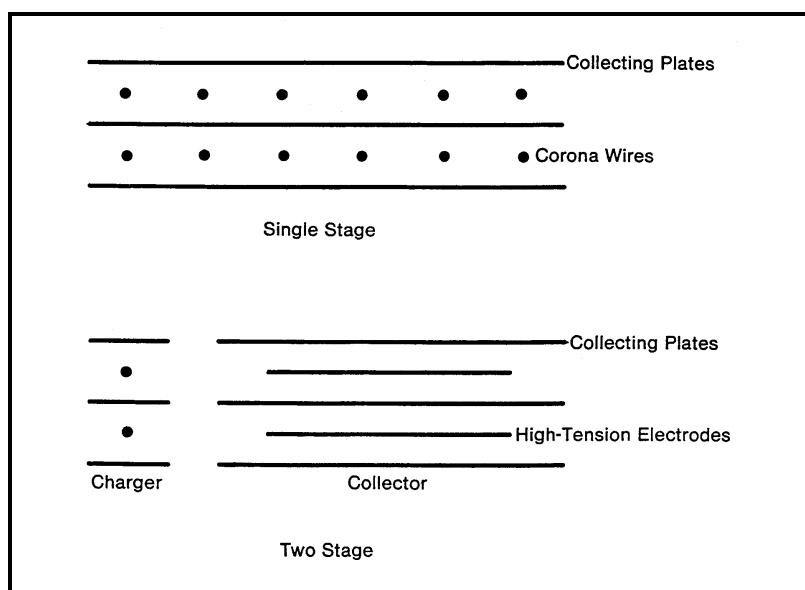
Figure 3.79: Schematic Diagram of Single-Stage and Two-Stage ESP

One of the main operation parameters is the specific collection area (SCA) – the ratio of the surface area of the collection electrodes to the gas flow. Higher SCA equates to better removal efficiencies but also requires larger collectors. SCA normally are in the range of 40–160 s/m.

Systems with elevated risks, such as explosion and fire, must be equipped with safety devices, such as explosion hatch or sprinkler system.

Application

ESP are applied to remove particulate matter down to $PM_{2.5}$ and smaller and hazardous air pollutants, such as most metals (with the notable exception of mercury).

Application areas in the chemical industry and related sectors are:

Sector	ESP Type
Boilers	Dry wire-plate
Chemical manufacture (e.g. sulphuric acid)	Dry and wet wire-plate, dry and wet wire-pipe
Refineries	Dry wire-plate
Incineration	Dry wire-plate, dry and wet wire-pipe

Wet ESP are used in situations for which the dry variant is not suited, e.g.:

- wet and sticky material
- flammable / explosive mixtures
- material with high resistivity
- when higher collection efficiencies are desired
- to control acid mists.

The single-stage ESP is used in large complex flue gas treatment systems, e.g. in power stations and waste incinerations as a dust and fly ash abatement. As part of the dust, heavy metals and their compounds are eliminated as well and disposed of together with the other particulates. It is also suitable for separating aerosols and mists.

The two-stage ESP is applied to remove dust and oil mists. It is an alternative to surface filtration (HEPA-filter). The two-stage ESP is common where small waste gas streams (<25 Nm^3/s) and a high proportion of submicron particles, e.g. smoke or oil mist, are involved.

Application limits and restrictions are:

	Limits / restrictions
Typical waste gas flow [Nm^3/h]	360000–1800000 (dry wire-plate) [1]
	1800–180000 (dry wire-pipe) [2]
	180000–900000 (wet wire-plate) [3]
	1800–180000 (wet wire-pipe) [4]
Temperature [°C]	up to 700 (dry ESP) [1,2]
	<80 – 90 (wet ESP) [3,4]
Typical dust content [g/Nm^3]	2–110 (wire-plate) [1,3]
	1–10 (wire-pipe) [2,4]
Resistivity [Ω cm]	5×10^3–2×10^{10} [1,3] (dry ESP)
Particulate size	>$PM_{1.0}$ (dry ESP)
[1] [cww/tm/125] [2] [cww/tm/124] [3] [cww/tm/127] [4] [cww/tm/126]	

Advantages/Disadvantages

Advantages	Disadvantages
• High efficiency even for small particles. • Suitable for wide temperature, pressure and gas flow ranges. • Low pressure drop, hence energy requirement tends to be low. • Wet ESP can also handle sticky particles, mists and highly resistive or explosive dusts.	• Explosion risk with dry ESP. • The separation capacity depends on the resistivity of dust particles (with dry ESP). • Re-entrainment can be a problem due to high gas velocities, poor rapping or poor gas flow. • Corrosion near the top of the wires because of air leakage and acid condensation, which is also an issue with wet ESP. • Sensitive to maintenance of the correct geometrical alignment, e.g. wire discharge electrodes. • Sensitive to fluctuations in gas stream conditions (flow rates, temperatures, PM and gas composition, particulate loading). • Relatively large space required. • High quality personnel required. • Special precautions to protect personnel from the high voltage. • Dry ESP not recommended to remove sticky or moist particles.

Achievable Emission Levels / Performance Rates

The size of the ESP is the main factor in determining the collection efficiency. Other parameters that affect the collection efficiency are:

• dust resistivity
• composition of dust and gas
• temperature
• particulate size distribution.

Parameter	Performance rate [%]		Remarks
	Dry ESP	Wet ESP	
total PM	99.0–99.2 [1]	99.0–99.2 [2]	
PM_{10}	97.1–99.4 [1]	97.1–99.2 [2]	
$PM_{2.5}$	96.0–99.2 [1]	97.4–99.2 [2]	

Parameter	Emission level [mg/Nm³]		Remarks
	Dry ESP	Wet ESP	
Dust	5–15		For well designed and properly sized ESP

[1] [cww/tm/125]
[2] [cww/tm/127]

Cross-media Effects

Consumables are:

Consumable	Amount	Remarks
Water (for wet ESP)		
Energy [kWh/1000 Nm³]	0.5–2 [1]	
Pressure drop [kPa]	0.05–0.3 [1,2]	Single-stage ESP
	0.5	Two-stage ESP

[1] [cww/tm/64]
[2] [cww/tm/70]

With dry ESPs, the separated dust is emitted as residue; with wet ESPs the separated dust merges with the rinsing water, being treated as waste water.

Depending on its source, the separated dust can be contaminated – e.g. dust originating from incineration might contain dioxins and/or heavy metals and their oxides. This type of dust might be classified as hazardous waste that has to be disposed of accordingly.

Monitoring [cww/tm/79]

A mass emission to assess the performance of an ESP can be determined by monitoring the particulate concentration in the effluent gas stream, using an isokinetic sampling probe or meters based on, e.g. UV/visible opacity, beta rays or particle impingement. The current and voltage across the ESP, the rapping rate and the temperature need to be routinely monitored. The dust outlet from the collection hopper has to be maintained free of blockages so that the hopper does not become overfilled and thus cause short circuiting of the ESP.

ESP need to be regularly inspected to detect any deterioration, e.g. corrosion, of the electrodes, insulating materials or rapping system. Hence, access to the precipitator needs to be free of obstruction, but within safety standards.

Economics

Type of costs	Costs			
	Dry wire-plate	Wet wire-plate	Dry wire-pipe	Wet wire-pipe
Capital costs [per 1000 Nm^3/h]	USD 8500-28000 [1]	USD 18000-36000 [2]	USD 18000-120000 [3]	USD 35000-180000 [4]
Annual operating costs [per 1000 Nm^3/h]	USD 2400-24000 [1]	USD 3500-27000 [2]	USD 2800-5600 [3]	USD 4200-7000 [4]
Cost effectiveness [per tonne pollutant controlled per year]	USD 45-280 [1]	USD 60-600 [2]	USD 55-950 [3]	USD 90-950 [4]
[1] [cww/tm/125] [2] [cww/tm/127] [3] [cww/tm/124] [4] [cww/tm/126]				

Costs can be substantially higher than the ranges shown for pollutants which require an unusually high level of control, or which require the ESP to be constructed of special materials such as stainless steel or titanium. In general, smaller units controlling a low concentration waste gas stream will not be as cost-effective as a large unit cleaning a high pollutant load flow.

3.5.3.4 Wet Dust Scrubber

Description

Wet dust scrubbing is a variation of wet gas scrubbing (see Section 3.5.1.4), using the same or equivalent techniques to abate or recover particulate matter additionally to gaseous compounds. The different scrubbers operated are mainly:

- **Fibrous Packing Scrubber**
  See Section 3.5.1.4. It is mainly suitable for gaseous contaminants. For particulate matter, it is restricted to collecting fine and/or soluble particulate matter, aerosols and mists. Insoluble and/or coarse particulate clogs the fibre bed.
- **Moving Bed Scrubbers**
  See Section 3.5.1.4.
- **Plate Scrubbers**
  See Section 3.5.1.4. Their primary application is for particle removal.

- **Spray Towers**
  See Section 3.5.1.4. Their primary application is particle removal. Spray towers are not as prone to fouling as packed-scrubbers, but very high liquid-to-gas ratios (>3 l/m^3) are required to capture fine particulate.

- **Impingement Entrainment Scrubbers**
  Impingement entrainment scrubbers contain a mechanism to accelerate the inlet gas stream towards a liquid surface and an entrainment separator. They are generally not suitable for mass transfer applications, e.g. trace gas removal, but to handle high or low gas streams and operate at lower pressure drops than venturi scrubbers.

  An example is given in Figure 3.80 [cww/tm/79].
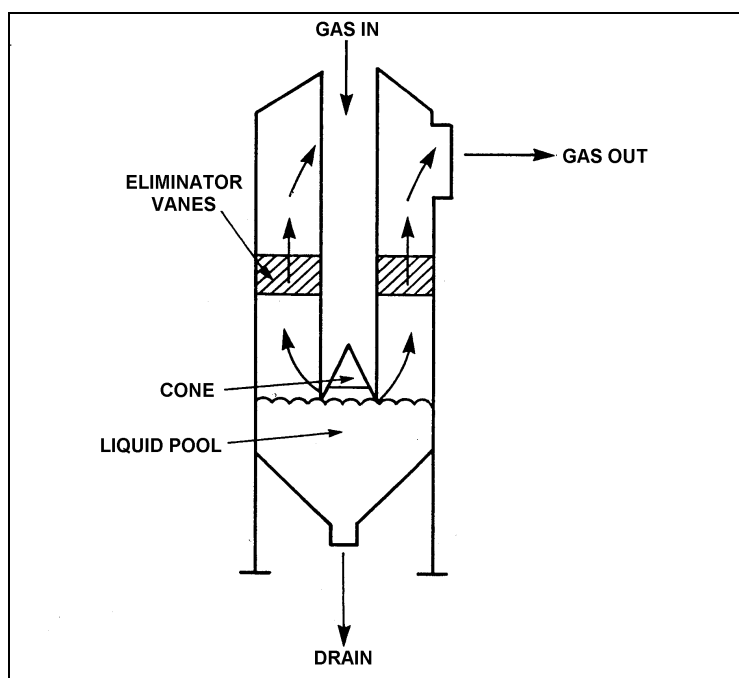
Figure 3.80: Impingement Entrainment Scrubber

- **Venturi Scrubbers**
  The characteristic feature of a venturi scrubber is the constriction of the duct – venturi throat – causing an increase in gas velocity. Liquid is introduced to the scrubber and forms a film on the walls, which is atomised by the gas stream in the venturi throat. Alternatively, with ejector venturi scrubbers, the liquid is sprayed into the venturi throat. Venturi scrubbers are highly efficient particle scrubbing devices, because they are suitable down to submicron particles. They can also be used to remove trace gases, particularly reactive slurries. An example is given in Figure 3.81 [cww/tm/79].

  A problem encountered with this technology is the erosion that can occur due to high throat velocities. The venturi throat is sometimes fitted with a refractory lining to resist abrasion by dust particles. A flooded elbow located after the venturi throat reduces wear from abrasive particles. The venturi is constructed of corrosion resistant material designed for maximum life expectancy. The final choice of material depends on factors such as:

  - temperature
  - abrasion
  - corrosion
  - chemical attack.

Collection efficiency increases with gas velocity and pressure drop. Several venturi scrubbers have been designed to allow velocity control by varying the width of the venturi throat.

Generally, no pretreatment is required for venturi scrubbers, though in some cases the waste gas is quenched to reduce the temperature for scrubbers made of materials that can be affected by high temperatures.

When the waste gas stream contains both particulate matter and gases to be controlled, venturi scrubbers can be used as a pretreatment device that removes the particulate matter to prevent clogging of a downstream waste gas treatment facility, such as a packed bed scrubber.
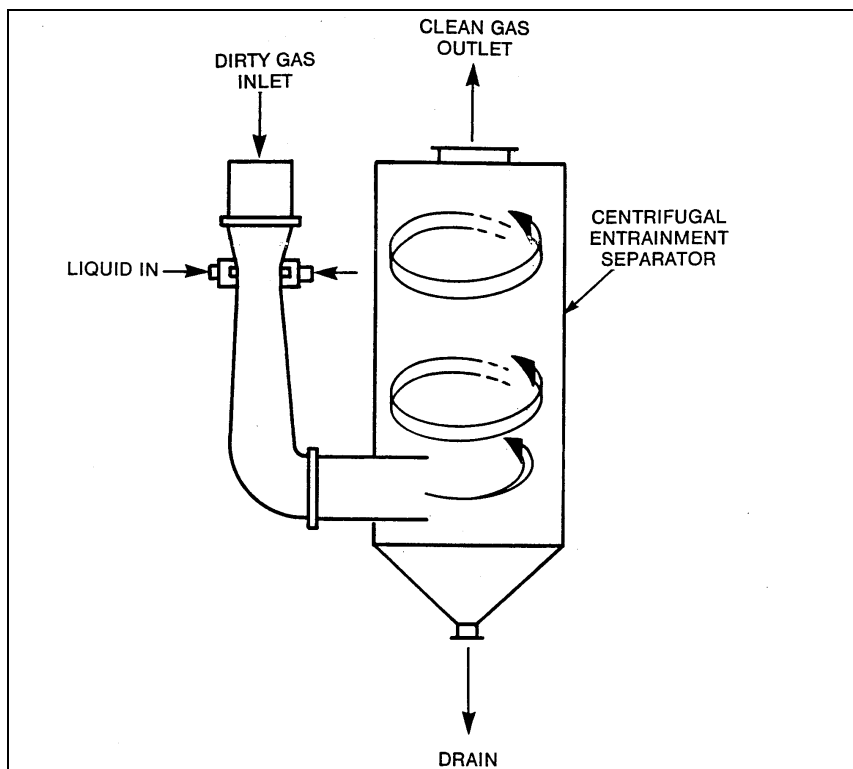
Figure 3.81: Venturi Scrubber

Application

See Table 3.16.

	Fibrous Packing	Moving Bed	Plate	Spray Towers	Impingement Entrainment	Venturi
	Collect fine and/or soluble PM As mist eliminator to collect liquid aerosols, inorganic and VOC Control aerosol emissions from chemical, plastics, asphalt, sulphuric acid, surface coating industry Only limited acceptance for dust collection		Collection of ≤PM_{10}, ≤$PM_{2.5}$, PM_{HAP} Inorganic fumes, vapours, gases, VOC;	Collection of ≤PM_{10}, ≤$PM_{2.5}$, PM_{HAP}, Inorganic fumes, vapours, gases, VOC; Often used as part of flue gas desulphurisation Only limited usage for fine PM	Collection of PM10-PM2; Used in pharmaceutical processing and packaging, manufacturing of chemicals, rubber, plastics, ceramics, fertilisers Processes controlled include dryers, cookers, crushing and grinding operations, spraying, ventilation, material handling	Collection of ≤PM_{10}, ≤$PM_{2.5}$, down to submicron Control PM emissions from utility, industrial, commercial and institutional boilers fired with coal, oil, wood and liquid waste Control emission sources in the chemical and related industries Typically applied where high collection efficiencies for fine PM are required
Gas flow [Nm^3/h]	1800–170000 [1]		1700–130000 [2]	2500–170000 [3]	1700–90000 [4]	720–100000 [5]
Temperature [°C]	<60 [1]		4–370 (PM) [2] 4–38 (gases) [2]	4–370 (PM) [3] 4–38 (gases) [3]	up to 150 [4]	4–370 [5]
Pollutant loading (PM) [g/Nm^3]	0.2–11 [1]		No limits	No limits	up to 23 [4]	1–115 [5]
[1] [cww/tm/110] [2] [cww/tm/111] [3] [cww/tm/114] [4] [cww/tm/112] [5] [cww/tm/115]						

Table 3.16: Application and Application Limits and Restrictions of Different Wet Dust Scrubbers

Advantages/Disadvantages

Advantages	Disadvantages
General • Can handle flammable and explosive dusts with little risk. • Provides cooling for hot gases. • Corrosive gases can be neutralised. • Simultaneous removal of dust and inorganic compounds.	General • Effluent liquid can create water pollution problems. • Waste product collected wet. • Protection against freezing required. • Collected PM may be contaminated and/or not recyclable. • Off-gas may require reheating to avoid visible plume.
Fibrous Packing Scrubber • Can handle mists. • Relatively low pressure drop.	Fibrous Packing Scrubber • High potential for corrosion problems. • Not really suitable to collect PM, only for fine and/or soluble PM.
Plate Scrubbers • Provides gas absorption and dust collection in a single unit. • Can handle mists. • Collection efficiency can vary. • Improves gas-slurry contact for SO_2 removal.	Plate Scrubbers • High potential for corrosion problems.
Spray Towers • Ability to collect PM as well as gases. • Relatively free from plugging. • Relatively small space requirements. • Relatively low pressure drop. • Operation in highly corrosive atmospheres possible with FRP construction.	Spray Towers • Relatively low mass-transfer efficiencies. • Relatively inefficient at removing fine PM. • With FRP construction, sensitive to temperature.
Impingement Entrainment Scrubbers • Can handle mists. • Relatively low water recirculation rate. • Collection efficiency can vary.	Impingement Entrainment Scrubbers • High potential for corrosion problems.
Venturi Scrubbers • Can handle mists. • Relatively low maintenance. • Simple in design and easy to install. • Collection efficiency can be varied. • Also removes reactive gaseous contaminants. • Free from clogging.	Venturi Scrubbers • High potential for corrosion problems. • Relatively high pressure drop, and hence high energy requirement. Noise may be a problem since gas velocity at the venturi throat is high. • Limited to PM and gases with high solubility.

Achievable Emission Levels / Performance Rates

The performance of scrubbing techniques is highly dependent on the size of the particulate matter and the aerosols to be collected. The performance rates are listed in Table 3.17.

Cross-media Effects

The consumables are listed in Table 3.17.

With a wet dust removal technique a secondary installation to separate the suspension is essential.

Depending on its source, the separated dust can be contaminated – e.g. dust originating from incineration might contain dioxins and/or heavy metals and their oxides. This type of dust might be classified as hazardous waste that has to be disposed of accordingly.

Parameter	Performance Rates [%]					
	Fibrous Packing	Moving Bed	Plate	Spray Tower	Impingement Entrainment	Venturi
PM	70->99 [1]		50–99 [2]	70->99 [3]	80–99 [4]	70->99 [5,7]
VOC	70->99 (mists) [1]			50–95 [3]		
SO2			80->99 [2]	80->99 [3]		
HCl						90 [7]
HF						90 [7]
NH3				94-99 [8]		94-99 [8]
Consumable	**Amount of Consumables**					
Scrubbing water [l/Nm³]				>3 [3]		0.5–5 [6]
Energy [kWh/1000 Nm³]					1–2 [6]	<0.5–6 [6,7]
Pressure drop [kPa]					1.5–2.8 [6]	2.5–20 [6,7]
Type of Costs	**Costs**					
Capital costs [per 1000 Nm³/h]	USD 600-1800 [1]		USD 1300-7000 [2]	USD 500-2200 [3]	USD 2800-10000 [4]	USD 1900-17000 [5]
						EUR 5000 [a,7]
Annual operating costs [per 1000 Nm³/h]	USD 1000-21100 [1]		USD 1500-41100 [2]	USD 800-28100 [3]	USD 2200-42000 [4]	USD 2400-70000 [5]
						b
Cost effectiveness [per tonne pollutant]	USD 40-710 [1]		USD 51-1300 [2]	USD 28-940 [3]	USD 88-1400 [4]	USD 84-2300 [5]

[a] at 10000 Nm³/h, scale-up factor to the power of 0.3
[b] EUR [2500 + 100 x (flow/1000)]
[1] [cww/tm/110]
[2] [cww/tm/111]
[3] [cww/tm/114]
[4] [cww/tm/112]
[5] [cww/tm/115]
[6] [cww/tm/132]
[7] [cww/tm/70]
[8] [cww/tm/138] fertiliser industry, phosphoric acid as scrubbing liquor

Table 3.17: Performance Rates, Consumables and Costs of the Wet Dust Scrubber Variants

Scrubbing devices are sources of noise that needs to be abated accordingly, e.g. by housing the equipment.

Monitoring [cww/tm/70]

A mass emission to assess the performance of a wet scrubber can be determined by monitoring the particulate concentration in the effluent gas stream, using an isokinetic sampling probe or a meter based on, for example, UV/visible opacity, beta rays or particle impingement. The pressure drop across the scrubber and the liquid/reagent flow rate and feed pressure need to be routinely monitored. Liquid-to-gas ratio, liquid blowdown rate and pH also need regular control. Wet scrubbers should be inspected regularly to identify any deterioration in the plant, such as corrosion or blockages. There should be ready access to the scrubber.

Economics

The cost ranges for wet dust scrubbers are listed in Table 3.17. The estimated costs are based on an assumed inlet loading of particulate matter of approximately 7 g/Nm^3. For applications which require expensive materials, solvents or treatment methods, actual costs can be substantially higher than the ranges shown. As a rule, smaller units controlling a low-concentration waste gas stream will be much more expensive (per unit flow rate) than a large unit cleaning a high pollutant load flow.

3.5.3.5 Fabric Filter

Description

In a fabric filter, waste gas is passed through a tightly woven or felted fabric, causing particulate matter to be collected on the fabric by sieving or other mechanisms. Fabric filters can be in the form of sheets, cartridges or bags (the most common type) with a number of the individual fabric filter units housed together in a group. The dust cake that forms on the filter can significantly increase the collection efficiency.

Operating conditions are important determinants of the choice of fabrics. Some commonly used fabrics are shown in Table 3.18.

Generic name of fibre	Chemical resistance to		Continuous operating temp. in moist heat [ºC]	Continuous operating temp. [°C]	Maximum peak temp. [°C]	Material supports combustion
	Acids	Alkalis				
Polyester	good	fair	94	132	150	yes
Copolymer Acrylic	good	fair	110	120	130	no
m-Aramide	good	good	177	200	240	no
Polyphenylensulphide	excellent	excellent	190	190	232	no
Ethylenechlorotrifluo-roethene	excellent	excellent	177	177	190	no
Polytetrafluorethene	excellent	excellent	260	260	290	no
Polyimide	good	good	240	260	280	no
Glass	very good	fair	260	260	290	no
Stainless Steel	good	excellent	550	550	600	no
Ceramic	very good	good	760	760	1204	no

Table 3.18: Commonly Used Fabrics

Practical application of fabric filters requires the use of a large fabric area to avoid an unacceptable pressure drop across the fabric. An unacceptable pressure drop can cause failure of the filter housing, resulting in fugitive dust emissions. Baghouse size for a particular unit is

determined by the choice of the ratio of volumetric air flow to cloth area (a/c ratio). The selection of a/c ratio depends on the particular loading and characteristics and the cleaning method used. A high particulate loading will require the use of a larger baghouse to avoid forming too heavy a dust cake, which would result in an excessive pressure drop.

Cleaning intensity and frequency are important variables in determining removal efficiency. Because the dust cake can provide a significant fraction of the fine particulate removal capability of a fabric, cleaning which is too frequent or too intense will lower the removal efficiency. If removal is too infrequent or too ineffective, then the pressure drop will become too high.

Common fabric filter types according to their cleaning method are:

- **reverse-air (or reverse-jet) cleaned fabric filter**, using a gentler but sometimes less effective cleaning mechanism than mechanical shaking. Typically, the bags are open on the bottom, closed on top, the dust being captured on the inside or the outside of the bags. To clean the filter, it is taken off-line and clean air is forced through it in the opposite direction, the dust cake falling off into the hopper. The typical cleaning cycle lasts about < 5 minutes per compartment. Reverse air cleaning alone is used only in cases where the dust releases easily from the fabric. In many instances, it is used in conjunction with shaking, pulsing or sonic horns.

- **mechanical shaker cleaned fabric filter**, using a simple and effective cleaning mechanism. The waste gas enters an inlet pipe equipped with a baffle plate, where large particles are removed when they strike the baffle plate and fall into the hopper. The laden gas is drawn from beneath a cell plate in the floor into the filter bags and passes from the inside to the outside, the particles collected on the inside bag surface. The tops of the bags are attached to a shaker bar, which is moved briskly to clean the bags.

- **pulse-jet cleaned fabric filters**, using a relatively new method that can treat high dust loads, operate at constant pressure drop and occupy less space than other fabric filter types. They can only operate as external dust collection devices. The bags are closed at the bottom, open at the top and supported by internal retainers. The laden gas flows from the outside to the inside of the bags, using diffusers to prevent oversized particles from damaging the bags, the particles being collected on the outside of the bags and dropping into the hopper. Pulse-jet cleaning means the injection of a short burst (0.03–0.1 seconds) of high pressurised (0.4–0.8 MPa) air into the bags. This mechanism ensures that the waste gas flow does not have to be stopped during cleaning. Felted, i.e. non-woven, fabrics are used in pulse-jet fabric filters because they do not require a dust cake to achieve high collection efficiencies. Woven fabrics are found to leak a great deal of dust after cleaning when they are used with pulse-jet fabric filters.

Sonic horns are increasingly being used to enhance the collection efficiency of mechanical shaker and reverse-air fabric filters. They are operated with compressed air (0.3–0.6 MPa). Sonic horn cleaning significantly reduces the residual dust load on the bags and decreases the pressure drop across the filter fabric by 20–60 % as well as the mechanical stress on the bags, resulting in a longer operational life.

Corrosion of filter and housing material can be a problem if the gas stream consists of acidic components, especially at temperatures below the dew point. For appropriate filter fabrics see Table 3.18.

Other near relatives of the fabric filter are:

- **Compact filter**, which is also known as cassette filter or envelope filter, and is a version of the fabric filter. The distinction lies in the compact way in which the filter material is fitted. It is pleated, e.g. like a concertina, to obtain a far larger specific filtration surface. The space saving, however, is partly cancelled out by the lower fabric load of this type of filter.
- **Improved compact filter**, which is also known as sintamatic, sinter lamellae filter or Spirot tube, is another version of the fabric filter. It consists of porous sintered material with pleated filter elements for the sintamatic or sinter lamellae filter, which provides a longer service life and thereby reduced maintenance costs.

The gas temperature needs to be above the dew point of any constituent because otherwise the filter fabric is clogged and the filtration process stops. To prevent this the baghouse might need to be insulated and possibly heated.

Systems with an elevated risk, such as explosion and fire, have to be equipped with safety facilities, such as explosion hatch or sprinkler system. On the inlet side of the filter, there should be an explosion relief that opens to a safe place, e.g. outside the building. A trap for very hot particles, released from boilers and furnaces, may be required to prevent fire and hence fabric damage. Sparks or flames must not be admitted.

Application

Primarily the fabric filter is used to remove particulate matter down to $<PM_{2.5}$ and hazardous air pollutants in particulate form (PM_{HAP}), such as metals (exception mercury). In combination with injection systems (including adsorption, dry lime / sodium bicarbonate injection and semi-dry lime injection) upstream of the baghouse, it can also be applied to remove specific gaseous contaminants.

Fabric filters are useful to collect particulate matter with electrical resistivities either too low or too high for ESP, hence they are suitable to collect fly ash from low-sulphur coal or fly ash containing high levels of unburnt carbon. The addition of a baghouse downstream of an ESP has been found to achieve very low particulate emissions.
When the waste gas loading consists of relatively large particulates, upstream mechanical collectors such as cyclones, ESP or spray coolers may be used to reduce the load for the fabric filter, especially at high inlet concentrations.

Application limits and restrictions are:

	Limits / restrictions
Typical waste gas flow [Nm³/h]	300–1800000 [1]
Temperature [°C]	see Table 3.18 above dew point of any condensable in the gas stream, otherwise filter is blinding <70 (improved compact filter) [2]
Pressure	range −6.4 to +6.4 kPa around atmospheric pressure [1]
Dust content [g/Nm³]	1–23 (typical) [1] 0.1–230 [1]
Particle properties	sticky dusts are difficult to remove from the bags, hence they need to be avoided
a/c ratio [a] [m/min]	≤1 [3] (reverse-air filter)
	<0.5 [3] (mechanical shaker filter)
	1–1.5 (2.0) [3] [b] (pulse-jet filter)
[a] recommended to ensure proper operation (see above) [b] higher value for special arrangements [1] [cww/tm/123] [2] [cww/tm/70] [3] personal information	

Advantages/Disadvantages

Advantages	Disadvantages
• In general, fabric filters provide high collection efficiencies for coarse and fine particles. • Efficiency and pressure drop of continuously cleaned filters are relatively unaffected by large changes in inlet dust loads. • Dust is separated dry without using consumables. The separated dust might be re-used in the preceding process. • Residual emissions are virtually independent of the intake concentration. • Relatively simple operation.	• No wet or sticky dusts allowed as input. • Static electricity may hinder the cake to be removed from the fabric. • There is an explosion risk. • Baghouse fires possible if very hot particles are released from furnaces or because of pyrophoric materials.

Achievable Emission Levels / Performance Rates

For a given combination of filter design and dust, the effluent particle concentration from a fabric filter is nearly constant, whereas the overall efficiency is more likely to vary with particulate loading. Thus, fabric filters can be considered to be constant outlet devices rather than constant efficiency devices.

Parameter	Fabric filter		Compact filter		Improved compact filter	
	Performance rate [%]	Emission level [mg/Nm^3]	Performance rate [%]	Emission level [mg/Nm^3]	Performance rate [%]	Emission level [mg/Nm^3]
PM	99-99.9 [1]	2-10 [1] 1 [a][2]		1-10 [2]		<1 [2]
[a] ceramic filter [1] [cww/tm/123] [2] [cww/tm/70]						

Cross-media Effects

Consumables are:

Consumable	Amount	Remarks
Filter fabric [m^2 per 1000 Nm^3/h]	11-17	a/c ratio 1–1.5 m/min
Precoating material (optional)		for sticky or static dust or as fabric protection
Compressed air [per 1000] [a] for 0.3-0.6 MPa (sonic horn) for 0.4-0.8 MPa (pulse-jet)	2–2.5 [1]	filter cleaning
Energy [kWh/1000 Nm^3]	0.2–1.2 [2] 0.5–2.0	
Pressure drop [kPa]	0.5–2.5 [2]	fabric filter
	0.5–1.8 [1]	compact filter and improved compact filter
	5–50	ceramic filter
[a] Nm^3/h compressed air per 1000 Nm^3/h gas [1] [cww/tm/70] [2] [cww/tm/64]		

The separated dust – possibly mixed with pre-coat material – is the only residue. Its quantity depends on the dust content of the incoming gas stream. Depending on its source, the separated dust can be contaminated – e.g. dust originating from incineration might contain dioxins and/or heavy metals and their oxides. This type of dust might be classified as hazardous waste that has to be disposed of accordingly.

Monitoring [cww/tm/79]

Performance and maintenance have to be carefully monitored. The mass emission to assess the performance of a fabric filter can be determined by monitoring the particulate concentration in the effluent waste gas stream, using an isokinetic sampling probe or a meter based on, e.g. UV/visible opacity, triboelectric flow, beta rays or particle impingement.

Temperature and pressure drop across the fabric filter need to be routinely monitored. The latter is used to indicate when the cleaning cycle has to start. Fabric filters should be inspected regularly to identify any deterioration of fabric or housing. Hence access to the fabric filter should be available. Each baghouse should be equipped with a bag leak detection system with alarm.

Economics

The working life of filter material is about 5 years for fabric filter and compact filter and 8 years for the improved compact filter.

Type of costs	Costs				
	Reverse-air	Mechanical shaker	Pulse-jet	Compact	Improved compact
Capital [per 1000 Nm³/h]	USD 5300-50000 [1] EUR 30000-55000 [c 4]	USD 4500-42000 [2]	USD 3700-15000 [3]	EUR 1000-4000 [4]	EUR 2500-4000 [4]
Plus sonic horn	USD 300-400 [1]	USD 300-400 [2]	--		
Plus reverse jet equipment	USD 600-1200 [1]	--	--		
Annual operating costs [per 1000 Nm³/h]	USD 4000-16000 [1] d [4]	USD 2600-14000 [2]	USD 3200-14000 [3]	a [4]	b [4]
Cost effective-ness [per tonne pollutant]	USD 58-372 [1]	USD 41-334 [2]	USD 46-293 [3]		

a EUR 2500 + 300 x flow/1000
b EUR 350 + 240 x flow/1000
c ceramic filter
d 350 + 300 x flow/1000
[1] [cww/tm/123]
[2] [cww/tm/121]
[3] [cww/tm/122]
[4] [cww/tm/70]

The cost estimates assume a conventional design under typical operating conditions and do not include auxiliary equipment such as fans and ductwork. Costs are primarily driven by the volumetric flow rate and pollutant loading of the waste gas stream. In general, a small unit controlling a low pollutant loading will not be as cost-effective as a large unit controlling a high pollutant loading. The costs presented are for flow rates between 3500 and 1700000 Nm³/h respectively, and a pollutant loading of 9 g/Nm³.

Pollutants that require an unusually high level of control or that require the fabric filter bags or the unit itself to be constructed of special materials will increase the costs of the system.

3.5.3.6 Catalytic Filtration

Description

Catalytic filtration is the elimination of gaseous components accompanied by particulate separation. It is comparable to the operation of fabric filters (see Chapter 3.5.3.5). The distinction is between the filter materials, the catalytic filter being loaded with a catalyst (titanium/vanadium system) that destroys pollutants by catalytical gas reaction. The separated dust will be removed and disposed of separately.

The catalyst filter consists of an expanded polytetrafluoroethene (ePTFE) membrane, laminated to a catalytic felt substrate. The catalyst is inserted into the felt substrate. It is installed as modules in a baghouse, shown in Figure 3.82 [cww/tm/85], in such a way that it can be easily fitted to an existing plant.
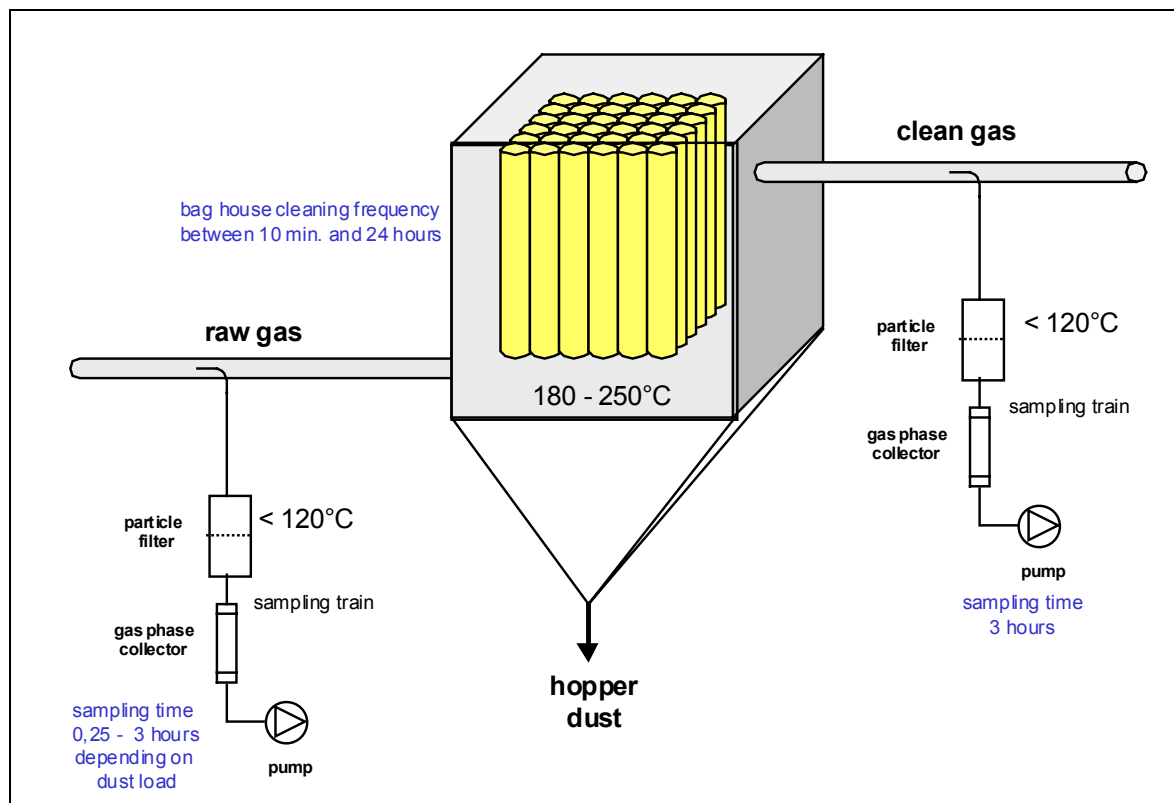
Figure 3.82: Catalytic Filter Baghouse, including Sampling Trains

<u>Application</u>

Catalytic filtration is used to separate particulates and eliminate hazardous contaminants from the gaseous phase. The chief contaminants this technology is applied to are dioxins and furans (PCDD and PCDF). But other contaminants such as polyaromatic hydrocarbons (PAH), polychlorinated benzenes (PCBz), polychlorinated biphenyls (PCB), VOCs and chlorinated phenols (PCP) can be eliminated as well.

Application limits and restrictions are:

	Limits / restrictions
recommended continuous operating temperature range	160–260 ºC [a]
ammonia content	<200 ppm
sulphur oxides content	<50 ppm
moisture content	5–35 %
filtration velocity	48–84 m/h
critical substances	deactivation by arsenium, potassium, calcium, sulphur
[a] The upper limit of the temperature range is determined by the maximum continuous operating temperature of the filter medium (260 ºC). The recommended maximum operating temperature is 250 °C to avoid over-temperature spikes. The lower limit of the temperature range is determined by the temperature at which dioxins and furans are adequately destroyed. Successful testing has been conducted at temperatures down to 155 °C.	

Advantages/Disadvantages

Advantages	Disadvantages
• Destruction of hazardous gaseous compounds without contaminated residues. • Reduction in the total release of hazardous pollutants to the environment. • Easily retro-fittable. • No additional operating and maintenance costs. • No additional solid waste to be disposed of. • No change in standard operating procedures. • Cost comparable to using powdered activated carbon.	• Restricted to a maximum continuous operating temperature of 260 ºC • Although the filter removes organics in general, and dioxins and furans specifically, at all temperatures, a minimum continuous operating temperature of 155 °C is recommended for adequate destruction of dioxins and furans. At lower temperatures, they are adsorbed on the catalyst.

Achievable Emission Levels / Performance Rates

Parameter	Performance rate [%]	Emission level	Remarks
Dust		<1 mg/Nm^{3} [1]	typical
PCDD/PCDF (TEQ)	>99 [a,1]	<0.004-0.040 ng/Nm^{3} [1]	waste incinerators
		<0.075 ng/Nm^{3} [1]	

[a] up to 99.8 % observed
[1] information from manufacturer

Cross-media Effects

The separated dust – fly ash possibly mixed with acid gas sorbent material – is the only residue for which disposal is required. The filtered dust contains up to 90 % less dioxins and furans than when activated carbon is used. The dust is normally classified as non-hazardous waste.

The main utilities and consumables are:

Consumable	Amount	Remark
Filter material		working life of filter and catalyst about 5 years or even longer
Catalyst		
Energy [kWh/1000 Nm^{3}]		
Pressure drop [kPa]		

Monitoring [cww/tm/79]

Performance and maintenance have to be monitored carefully. The mass emission to assess the performance of the filter can be determined by monitoring the particulate concentration in the effluent waste gas stream, using an isokinetic sampling probe or a meter based on, e.g. UV/visible opacity, beta rays or particle impingement. Catalyst activity can be monitored by testing an individual filter removed from the baghouse. If there are reasons to suspect a fall in catalytic activity, monitoring of dioxins and furans via stack sampling can be performed.

Temperature and pressure drop across the bag filter need to be routinely monitored. The latter is used to indicate if it is necessary to begin the cleaning cycle. Bag filters should be inspected regularly to identify any deterioration in the filter housing or filters. Hence access to the filter should be available.

Economics

Type of costs	Costs	Remarks
Capital costs [per 1000 Nm^3/h]		
Annual operating costs [per 1000 Nm^3/h capacity]		

3.5.3.7 Two-Stage Dust Filter

Description

The two-stage dust filter contains metal gauze as filter material. A filter cake is built up in the first filtration stage and the actual filtration takes place in the second stage. Depending on the pressure drop across the filter, the second stage is cleaned and the system switches between the two stages (step one becomes the second and vice versa). A mechanism to remove the filtered dust is integrated in the system. The dust drops to the bottom of the chamber where it has to be removed. An example is shown in Figure 3.83 [cww/tm/70].

Since metal gauze has a larger load capacity than a fabric filter, less filter area (i.e. less filter material) is required. This advantage, however, is usually eliminated because of the two-stage system.
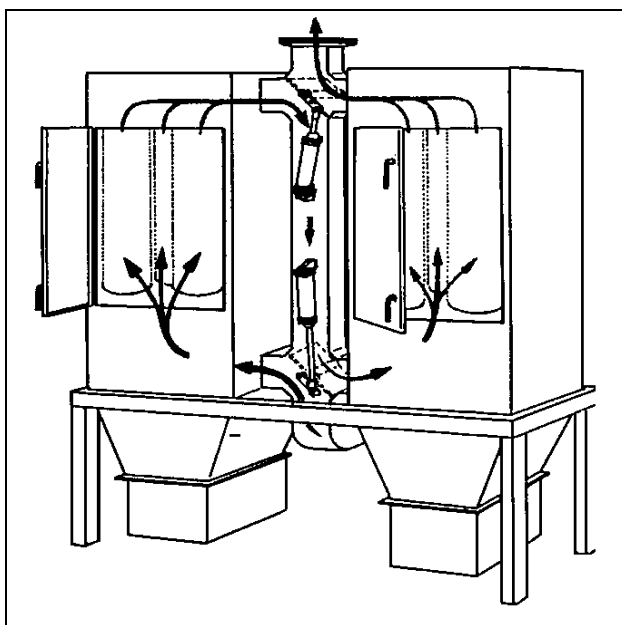
Figure 3.83: Two-stage Dust Filter

A special variant is the metal mesh filter with recaking process, which is illustrated in Figure 3.84 [cww/tm/168]. This filter is constructed to overcome the loss of filtration efficiency after cleaning by re-establishing the base cake before allowing the cleaned element back into the gas stream. In normal operation the filter works with only some of the filter chambers, the others being in stand-by operation (in the example three chambers are working, the fourth being in stand-by). The filter continues in this mode until a cleaning cycle has been signalled. Then the previously cleaned and recaked stand-by chamber(s) comes online. The chamber(s) needing cleaning is (are) taken offline and isolated for pulse cleaning, the dust collected in the dust hopper below. The cleaning process finished, the dust-laden gas is circulated to the just cleaned filter without being released to the outlet. This mode enables the re-establishing of a full filter cake on the cleaned filter while the other chambers are used as back-up filters to control

leakages. When the recaking is complete, the chamber(s) changes into stand-by mode to replace the next ones that need cleaning.
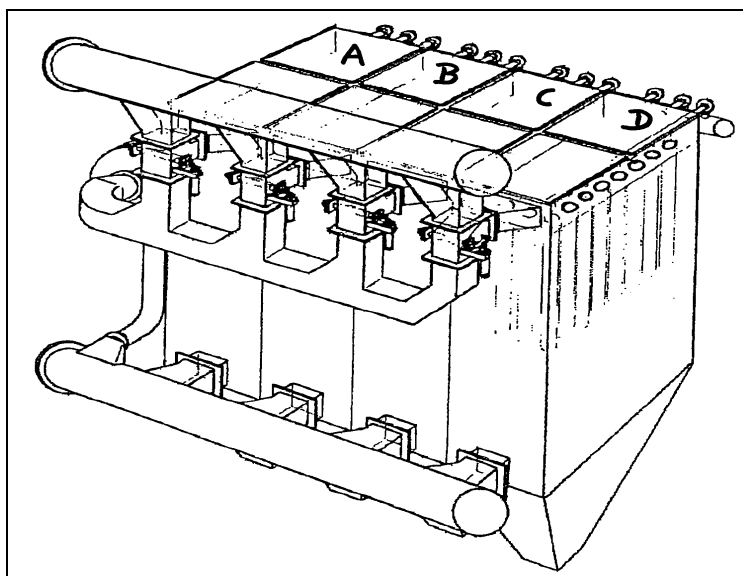
Figure 3.84: Metal Mesh Filter With Recaking Process

Systems with an elevated risk, such as explosion and fire, have to be equipped with safety facilities, such as explosion hatch or sprinkler system.

Application

Primarily the two-stage dust filter is operated to remove particulate matter. In combination with injection systems (including adsorption, semi-dry lime injection), it can also be used to remove specific gaseous contaminants.

	Limits / restrictions
Typical waste gas flow [Nm^3/h]	up to 75000 per module [1]
Temperature [°C]	up to approximately 500
Pressure	atmospheric [1]
Dust content [g/Nm^3]	no restrictions
[1] [cww/tm/70]	

Advantages/Disadvantages

Advantages	Disadvantages
• High efficiency for dust. • Solids recovery is possible. • Ventilated air re-usable as intake air. • Modular structure. • No extra filter material; steel-only design. • Filter load higher than for a fabric or compact filter. • Also for damp, sticky, fibrous or static dust. • Resistant to fire damage. • Offers the possibility of heat recovery (when operated at higher temperatures).	• Higher costs, compared to fabric and compact filter, when used under ambient temperature. Not valid for high-temperature applications. • Frequent switching between the two compartments (normal 2-stage filter). • Valve control necessary in a dusty environment. • There is an explosion risk.

Achievable Emission Levels / Performance Rates

The dust emission of a two-stage dust filter with metal gauze as filter medium is virtually independent of the inlet load.

Parameter	Emission level [mg/Nm^3]	Remarks
PM	≈ 1 [1]	virtually independent of inlet
[1] [cww/tm/70]		

Cross-media Effects

Consumables are:

Consumable	Amount	Remarks
Filter material (metal gauze or mesh)		
Compressed air (0.3–0.7 MPa)		filter cleaning
Energy [kWh/1000 Nm^3]	1.5 [1]	
Pressure drop [kPa]	0.5-2.5 [1]	
[1] [cww/tm/70]		

The separated dust is the only residue. Its quantity depends on the dust content of the incoming gas. Depending on its source, the separated dust can be contaminated – e.g. dust originating from incineration might contain dioxins and/or heavy metals and their oxides. This type of dust might be classified as hazardous waste that has to be disposed of accordingly.

Monitoring [cww/tm/79]

Performance and maintenance have to be carefully monitored. The mass emission to assess the performance of a two-stage dust filter can be determined by monitoring the particulate concentration in the effluent waste gas stream, using an isokinetic sampling probe or a meter based on, e.g. UV/visible opacity, beta rays or particle impingement.

Temperature and pressure drop across the fabric filter need to be routinely monitored. The latter is used to indicate when the cleaning cycle has to start. Fabric filters should be inspected regularly to identify any deterioration of filter material and housing. Hence access to the filter should be available.

Economics

Type of costs	Costs	Remarks
Capital costs [per 1000 Nm^3/h]	EUR 30000 [1]	based on a system of 1700 Nm^3/h
Annual operating costs	a	
labour [per year]	EUR 2000 [1]	about 1.5 hours per week
utilities [per 1000 Nm^3/h]	EUR 350 [1]	
[a] total annual operating costs are EUR 2000 + 350 x flow/1000 [1] [cww/tm/70]		

3.5.3.8 Absolute Filter (HEPA-Filter)[12]

Description

The filter medium is paper or matted glass fibre with high packing density. The waste gas stream is passed through the filter medium, where particulate matter is collected. The dust cake that forms on the filter medium can increase collection efficiency. The filter medium is pleated to provide a smaller a/c ratio (volume flow rate to surface area).

The most common designs are a box filter cell and a cylindrical filter cell. In a box cell, the pleated medium is placed in a rigid, square frame constructed of wood or metal. The air flows from the front to the back of the filter. In a cylindrical filter cell, a metal cap seals the medium at one end. The air flows from the outside to the inside of the filter.

The filter can be mounted directly in the duct or in a separate housing. It requires pre-filtering for large diameter particulate matter, hence HEPA filter systems are generally the final component in a removal system for particulate matter.

The number of filter cells used in a particular system is determined by the a/c ratio, the selection of which is based on the particulate loading characteristics and the pressure drop across the filter medium. Practical application of fibrous media filters requires the use of large media areas to minimise the pressure drop across the filter. The paper and non-woven filter media used have a larger pressure drop across the filter than the woven fabrics used in fabric filters. For this reason, HEPA filters are mainly used at lower air flow rates and lower particulate loadings than baghouse designs. Once the air flow rate through the filter system decreases to an unacceptable point, the filter must be replaced. They are generally not cleaned, because cleaning action may cause leakage of the filter medium.

Application

HEPA filters are applicable to submicron particulate matter between $PM_{0.12}$ and $PM_{0.3}$ as well as hazardous air pollutants that are in particulate form, such as most heavy metals (except mercury).

HEPA filters are best applied in situations where high collection efficiency of submicron particulate matter is required, where toxic and/or hazardous particulate matter cannot be cleaned by other filters, e.g. chemical and biological material. They are installed as the final component in a collection system, downstream from other devices such as ESP or baghouses.

	Limits / restrictions
Waste gas flow [Nm^3/h]	100-3600 per module [1,2]
Temperature [°C]	<200 [2] (commercial HEPA) <530 [2] (ceramic or glas packing) above dew point of waste gas
Pressure	atmospheric [1]
Dust content [g/Nm^3]	1-30 [2] <2 [3]
Relative humidity [%]	<95 [2]
[1] [cww/tm/70] [2] [cww/tm/106] [3] [cww/tm/64]	

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[12]   **H**igh **E**fficiency **P**article **A**ir Filter

HEPA filters require pre-filtering to remove large particulate matter, such as cyclones or venturi scrubbers to reduce large PM, standard baghouse or cartridge filters to filter out particulate matter >$PM_{2.5}$.

Advantages/Disadvantages

Advantages	Disadvantages
• Separation of very small fractions is possible. • Very high efficiency with very low residual emission. • Outlet air is very clean and can be recirculated within the plant. • Modular structure. • Not sensitive to minor fluctuations in the waste gas stream. • Relatively simple operation. • Usually no corrosion problems.	• Care has to be taken of explosive hazards. • High maintenance and frequent filter replacement required. • Not suitable for moist environments. • Not suitable for high dust loads. • Glass fibre medium is not suitable for waste gases containing alkalis.

Achievable Emission Levels / Performance Rates

Parameter	Performance rate [%]	Emission level [mg/Nm^3]
PM		>0.0001 [1]
$PM_{0.01}$	>99.99 [2]	
$PM_{0.1}$	>99.9999 [2]	
[1] [cww/tm/64] [2] [cww/tm/106]		

Cross-media Effects

Consumables are:

Consumable	Amount	Remarks
Filter material (e.g. paper, glass fibre)		
Energy [kWh/1000 Nm^3]	<0.1 [1]	
Pressure drop [kPa]	0.05–0.25 [1]	
[1] [cww/tm/70]		

The loaded filter elements have to be disposed of as waste. Each module can absorb approximately 1 kg of dust.

Monitoring [cww/tm/79]

Performance and maintenance have to be carefully monitored. The mass emission to assess the performance of an absolute filter can be determined by monitoring the particulate concentration in the effluent waste gas stream, using an isokinetic sampling probe or a meter based on, e.g. UV/visible opacity, beta rays or particle impingement.

Temperature and pressure drop across the fabric filter need to be routinely monitored. When the pressure drop reaches a point that prevents adequate air flow, the filter must be replaced and disposed of.

Economics

Type of costs	Costs	Remarks
Capital costs [per 1000 Nm^3/h]	USD 1800-2400 [1]	
Annual operating costs	a [2]	application-specific
annual labour costs	EUR 2500 [2]	about 2 hours per week
annual consumable [per 1000 Nm^3/h]	EUR 60-120 [2]	
a total annual operating costs EUR 2500 + 60 x flow/1000 [1] [cww/tm/106] [2] [cww/tm/70]		

3.5.3.9 High Efficiency Air Filter (HEAF)

Description

An HEAF is a flat bed filter in which aerosols combine into droplets. Highly viscous droplets remain on the filter fabric and can eventually clog the filter. When a pre-set value of pressure difference is reached, the filter fabric has to be replaced by a new and clean filter, which can be exchanged during continuous operation, because the filter fabric is set on a roll. The treated waste gas leaves the treatment device via a mist filter, which has to separate the entrained layer of viscous droplets.

Additionally a droplet separator is implemented for droplets with low viscosity. The design of the secondary droplet separator can be a lamellar type separator (inertia separator) or a mist filter.

Application

HEAF are normally applied to remove aerosols such as oil, plasticisers and condensable VOCs.

Application limits and restrictions:

	Limits / restrictions
Typical waste gas flow [Nm^3/h]	up to 25000 [1]
Pressure	atmospheric [1]
[1] [cww/tm/70]	

Advantages/Disadvantages

Advantages	Disadvantages
• Continuous process. • Suitable for highly viscous droplets.	• High pressure drop.

Achievable Emission Levels / Performance Rates

Parameter	Performance rate [%]	Remarks
Droplets	99 [1]	
Aerosols	99 [1]	
[1] [cww/tm/70]		

Cross-media Effects

Consumables are:

Consumable	Amount	Remarks
Filter material		
Energy [kWh/1000 Nm^3]	<0.1 [1]	
Pressure drop [kPa]	8 [1]	
[1] [cww/tm/70]		

Residues to be disposed of are the loaded filter rolls, containing the contaminants separated as droplets, aerosols and dust. They have to be disposed of as chemical or hazardous waste and are usually sent to waste incineration.

Economics

Type of costs	Costs	Remarks
Capital costs [per 1000 Nm^3/h]	EUR 5700 – 8000 [1]	
Annual operating costs [per 1000 Nm^3/h] annual labour costs	about EUR 3000 [1]	about 2.5 hours per week
[1] [cww/tm/70]		

3.5.3.10 Mist Filter

Description

The most common mist filters (mist eliminators, demisters) are mesh pads. Mesh pad filters usually consist of woven or knitted metallic or synthetic material monofilament in either a random or specific configuration and are operated as deep bed filtration, which takes place over the entire depth of the filter. Solid dust particles remain in the filter until it is saturated and thus has to be cleaned by flushing. When the mist filter is used to collect droplets and/or aerosols, it is usually self-cleaning, drained by the liquid. They work by mechanical impingement and are velocity-dependent. Baffle angle separators are also commonly used as mist filters.

The basis for the filter dimension is the waste gas flow rate, the outlet contents and the filter load.

Mist filters are designed to remove specific particle sizes. Because of the plugging potential of high-efficiency mesh pads, washing is necessary on a regular schedule. If washing is neglected, the contaminants can solidify deep inside the pads and further pad flushing becomes ineffective.

Most mist filters incorporate access doors to facilitate the cleaning process. Special care should be taken with reinstalling the media into the vessel to ensure that they properly fit and make certain that there remain no gaps between the media and the vessel wall. Because of the high pressure drop across the mesh pad, gaps, however small, can create a bypass for the waste gas stream to avoid the filter.

Application

Mist filters are used to remove misty pollutants, such as droplets and aerosols. When the filter material is cleaned in-situ, they are also applicable to solid particles soluble in liquids. Owing to clogging, they are less suitable for solid dusts and greasy vapours. They protect equipment from solid/liquid dust particles to prevent wear and friction on blower bearings and housings.

High-efficiency mist filters can be used as primary devices. They are an increasingly viable option with regard to removal efficiency, water saving and economics in many processes that evolve mists such as sulphuric acid, nickel compounds, sodium hydroxide, nitric acid and chromium compounds. Multi-stage mist filters to control mist emissions have been tested with good results. The rationale to use these kind of filters is to collect most of the particles in the first stage, thereby protecting the subsequent stages that are designed to handle the smaller particles. A good way to accomplish this is a three- or four-stage unit, using a monofilament and voids configuration in the first stages and gradually decreasing monofilament size and voids downstream from stage to stage. Each stage is flushed with fresh water. Individual drain chambers should be used to prevent the wash water with the highest concentration of contaminant from flowing into the next stage.

As secondary devices, mist filters are widely used as the final stage of wet scrubbers to prevent re-entrained scrubbing solution to be carried into the clean gas discharging into the air. A mist filter is situated at the top part of the column to collect the droplets, which coalesce and fall back into the column. The design of the mist filter is critical if low pollutant concentrations (high control efficiencies) are to be achieved and if solvent losses in absorbers, scrubbers or distillation equipment need to be reduced.

Application limits and restrictions [cww/tm/70]:

	Limits / restrictions
Typical waste gas flow [Nm^3/h]	up to 150000 [1]
Temperature [°C]	<170 [1]
Dust content [mg/Nm^3]	<1 [1]
Aerosols	a few g/Nm^3 [1]
[1] [cww/tm/70]	

Advantages/Disadvantages

Advantages	**Disadvantages**
• Self–cleaning systems for the collection of liquids. • Suitable for filtration of liquid aerosols, also as primary device.	• The cleaning of the filter results in a contaminated washing liquid. • High pressure drop with solid dust particles. • Clogging risk.

Achievable Emission Levels / Performance Rates

Parameter	Performance rate [%]	Remarks
Dust	99 [1]	
Aerosols	99 [1]	
[1] [cww/tm/70]		

Smaller monofilaments and tighter voids in mesh pads are more efficient in removing smaller particles (sizes 1–3 μm), but they have a greater potential for plugging and require more care and maintenance. The most effective mesh pad has a filament diameter and void space large enough to minimise plugging potential and have a functional liquid drainage capacity. This mesh pad configuration is usually effective on particles of 5–10 μm in diameter.

Cross-media Effects

Consumables are:

Consumable	Amount	Remarks
Filter material		
Washing liquid		for cleaning
Energy [kWh/1000 Nm^3]		
Pressure drop [kPa]	2.5 [1]	normal
	9.0 [1]	big loads
[1] [cww/tm/70]		

Residues to be disposed of are the washing liquid, which contains filtered dust, and the loaded filter material. The washing liquid either has to undergo waste water treatment or is disposed of as waste, e.g. incinerated. When the mist filter is installed after a wet scrubber, the washing liquid is usually recycled to the scrubber.

Monitoring

The pressure drop of each individual stage of the mist filter needs to be monitored, e.g. by magnahelic or photohelic gauge.

Economics

Type of costs	Costs	Remarks
Capital costs [per 1000 Nm^3/h]	EUR 2300 [1]	for small systems up to 2000 Nm^3/h
Annual operating costs [per 1000 Nm^3/h]	a [1]	
annual labour costs	EUR 2500 [1]	about 2 hours per week
consumables [per 1000 Nm^3/h]	EUR 250-600	
[a] annual total operating costs EUR 2500 + 450 x flow/1000 [1] [cww/tm/70]		

3.5.4 Recovery and Abatement Techniques for Gaseous Pollutants in Exhaust Gases

Pollutants in flue gas from high-temperature (e.g. thermal and catalytic oxidation) and chemical processes are particulates and gases such as sulphur dioxide, NO_x, hydrogen halides and, under special conditions, dioxins. Particulates and NO_x in flue gas are abated (see Sections 3.5.3 for particulates and 3.5.4.2 for NO_x). Hydrogen chloride and sulphur dioxide, however, can be recovered. The treatment of hydrogen chloride and sulphur dioxide often follows a two-stage process:

- wet scrubbing with water (see Section 3.5.1.4) to produce a concentrated hydrochloric acid
- various desulphurisation processes (see Section 3.5.1.4 and 3.5.4.1) to produce gypsum or sulphuric acid.

Common flue gas treatment techniques in the chemical sector, additional to wet gas scrubbing (Sections 3.5.1.4 and 3.5.3.4), are described below.

3.5.4.1 Sorbent Injection as FGD[13] Techniques

Description

The reaction principle of FGD sorbent injection is the introduction of reactive material to, and its dispersion in, the waste gas stream. This material reacts with SO_x species to form a solid, which has to be removed afterwards from the waste gas stream. The most used sorbents are:

- lime
- sodium hydrogencarbonate (sodium bicarbonate)
- sodium carbonate (soda.).

The choice of the sorbent depends on its availability. It is in most cases a naturally occurring material, such as limestone, dolomite or hydrated compounds derived from these raw materials.

These sorbents are also effective in removing other acid gases, particularly hydrogen chloride and fluoride. If these acid gases are intended to be recovered, the waste gas needs to be pretreated (water scrubbing, see Section 3.5.1.4).

There are three types of sorbent injection techniques:

- dry sorbent injection
- semi-dry (or semi-wet) injection
- wet injection of lime milk.

With **dry sorbent injection**, the fine powdered sorbent is either injected into the flue gas stream or added to a reaction tower, the latter being the more efficient method. When the sorbent is injected into the gas stream, this can be done at various positions according to the temperature and conditions at which it is most reactive. This is illustrated in Figure 3.85 [cww/tm/79].
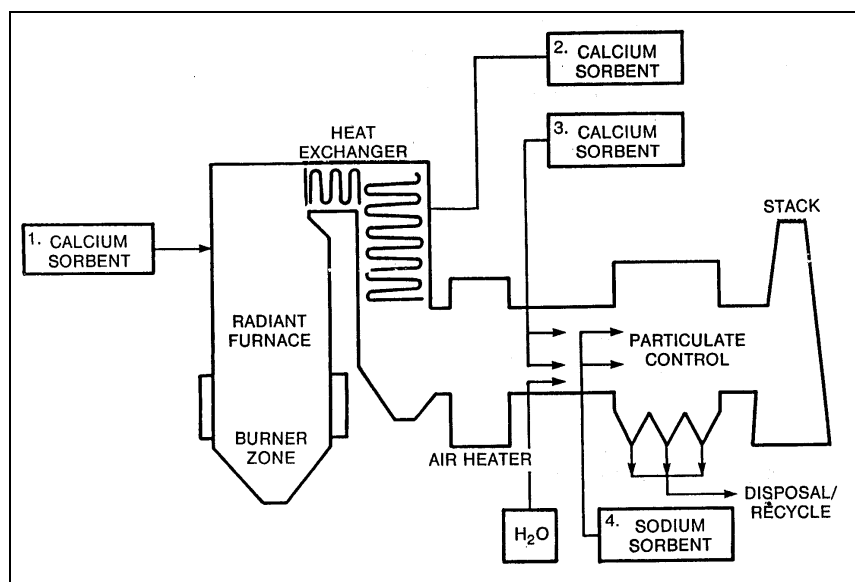
Figure 3.85: Dry Sorbent Injection for Sulphur Dioxide Removal (Injection Positions)

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[13]   **F**lue **G**as **D**esulphurisation

Commonly used injection positions and adequate sorbents are [cww/tm/79]:

- furnace injection of limestone at temperatures between 1100 and 1250 ºC
- heat exchanger injection of slaked lime at temperatures of about 550 ºC
- post-furnace injection of slaked lime at relatively high humidity at temperatures of 5–15 ºC above flue gas saturation
- post-furnace injection of sodium-based compounds, e.g. sodium bicarbonate, between heat exchanger and particulate abatement device, at a temperature range between 130 and 180 ºC or, when the filter medium allows it, up to 400 °C.

With **semi-dry sorbent injection**, the sorbent is added as a suspension or solution (droplets) in a reaction chamber in such a way that the liquid is continuously evaporating during the reaction. The result is a dry product, collected at the base of the chamber or in a particulate abatement device. The technique is illustrated in Figure 3.86 [cww/tm/79] using a fabric filter as particulate abatement, which can be replaced by an ESP.

The semi-dry system consists of:

- the spray dryer, i.e. atomiser and reaction chamber (a tower or duct, droplets and flue gas flowing co-currently)
- associated slurry/liquid equipment (lime slurries or sodium carbonate/bicarbonate solutions)
- a particulate collection device
- a particulate recycling device.
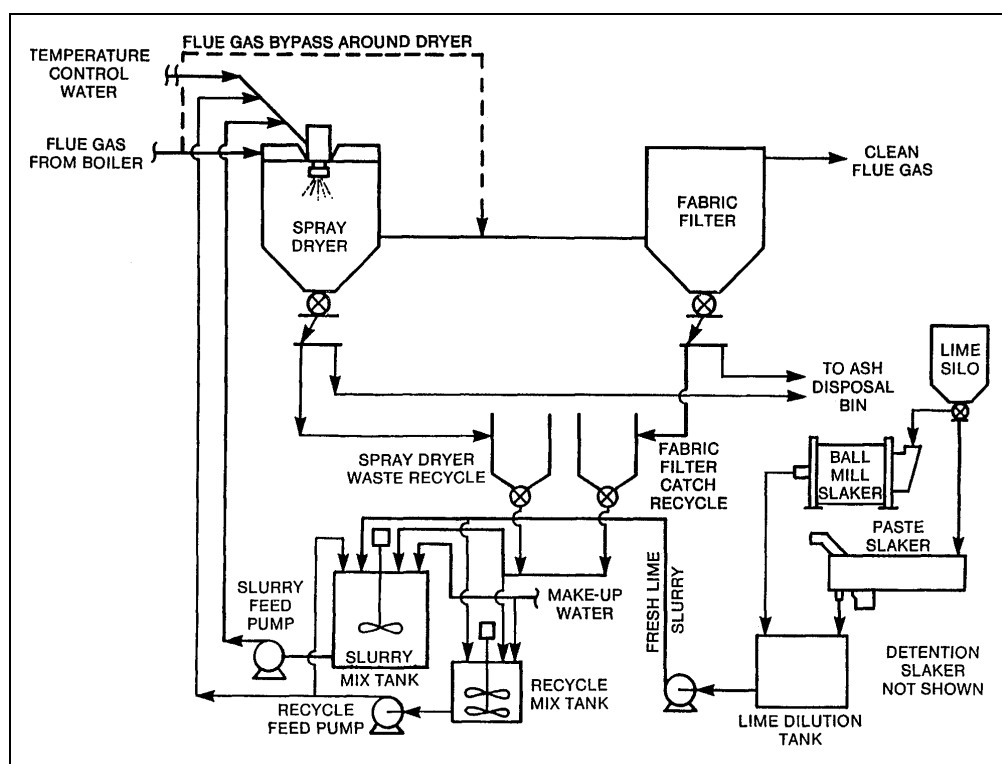
Figure 3.86: Spray or Semi-dry FGD System

With **wet injection**, SO_2 is removed from the flue gas in the FGD absorber by direct contact with an aqueous suspension of finely ground limestone (lime milk), after having left the particulate control system and passed through a heat exchanger. The scrubbed flue gas passes through a mist eliminator and is released to the atmosphere by a stack or cooling tower. The reaction products are withdrawn from the absorber and sent for dewatering and further processing.

The process is divided into:

- absorption of SO_2 by the scrubbing liquid in the pH range of 4-5.5, the primary product being calcium bisulphite [$Ca(HSO_3)_2$]
- oxidation of the bisulphite to sulphate
- crystallisation of the formed gypsum ($CaSO_4 \cdot 2\ H_2O$)
- separation of the gypsum crystals from the solution.

The technique is illustrated in Figure 3.87.
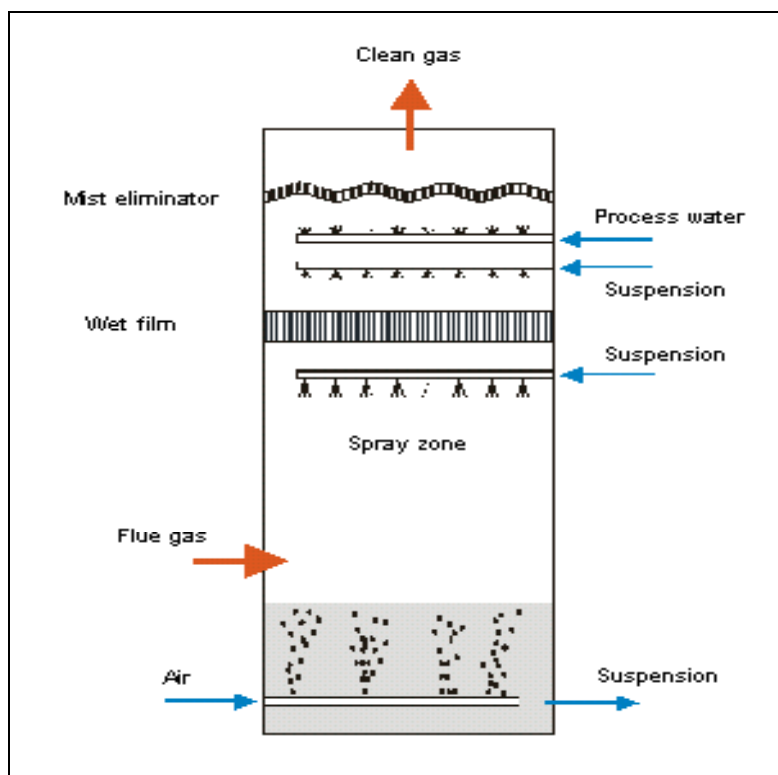
Figure 3.87: Wet FGD System: Lime Milk Scrubber

The solid part of the scrubber cycle is principally gypsum with a concentration of 100-120 g/l. Modern incineration units operate with a fairly rich mix, the oxygen content of the flue gas often not sufficient to complete the bisulphite oxidation, which requires the blowing of air into the scrubber sump. To prevent fouling of the clean gas channel, FGD units are normally equipped with mist eliminators.

The level of desulphurisation depends on the liquid to gas (L/G) ratio. The transverse turbulence between liquid and gas can be increased with high gas stream rates, by which the mass transfer and – consequently – the level of desulphurisation are improved. On the other hand it is characteristic for co-current units that high gas rates reduce the residence time and thus the level of desulphurisation.

To reduce the chloride concentration in the scrubbing liquid below 30 g/l, part of it is separated from the process and treated to remove heavy metals and COD. Fresh lime milk is added to replace the blowdown.

The treated flue gas leaves the FGD unit in a more or less saturated state. To ensure that the dew point is exceeded, a reheating stage (normally a regenerative gas preheater) and sufficient up-draught in the stack or cooling tower are required.

The adequate particle abatement techniques to remove the dry material both from dry and semi-dry systems are ESP or fabric filters. If fabric filters are used, the flue gas normally requires cooling, either by heat exchanger or cooling air, to keep the temperature below 200 °C (except with fabrics suitable for higher temperatures, such as ceramics or metal gauze/mesh).

The temperature at which maximum abatement efficiency is achieved varies from component to component. Furthermore, there is a different reactivity of waste gas pollutants with the various absorbents and competing reactions occur between the different species, especially if the ratio of reagent to acidic gases is relatively low. Therefore, the different absorption rates are dependent on the specific amount of absorption agent, waste gas composition (such as pollutants, humidity, oxygen content) and reaction temperature. The absorption rates due to the nature of the gas/solid reaction are highly dependent on the active specific area of the absorbent and the residence time. Therefore, it is normally necessary to have an over-stoichiometric ratio of absorbent.

The abatement rates for species such as HCl and SO_2 decrease drastically with decreasing temperature and are at a minimum in the range between 200 and 280 °C. Below 200 °C, the abatement rates increase and can achieve good results for most pollutants.

Application

Dry and semi-dry sorbent injection are typically used to reduce emissions of acidic gases. The dry variant is also suitable for smaller plants or for retrofitting applications where the capital expenditure for other systems might be very high. To reduce other contaminants, grained carbon (GAC) can be added to the dry sorbent.

Application limits and restrictions [cww/tm/70]:

	Limits / restrictions
Typical waste gas flow [Nm^3/h]	10000–300000 (dry sorbent)
	up to 1000000 [1] (semi-dry sorbent)
	50-500000 [1] (wet sorption)
SO_x concentration	wide range
Hydrogen halide concentration	wide range
[1] [cww/tm/70]	

Advantages/Disadvantages

Advantages	**Disadvantages**
Dry sorbent variant • No extra installations are necessary, since a dust removal system is usually installed. • High efficiency if a well designed reaction chamber or tower is installed. • Low cost system compared with others.	Dry sorbent variant • The added sorbent can, by interacting with fly ash, cause fouling of heat exchanger surfaces. • Large surplus of sorbent that has to be disposed of.
Semi-dry sorbent variant • Relatively simple installation. • Cheaper than wet scrubbing. • No waste water produced.	Semi-dry sorbent variant • Low particulate separation performance in the reaction chamber. • Humidity can be a disturbance, if fabric filter is used as subsequent particulate abatement.
Wet sorbent variant • Very high efficiencies. • Compact equipment. • Can operate at relatively high temperatures (50-80 °C). • Indirect monitoring through stoichiometric dosing of chemicals (if pH controlled). • Re-usable product, when lime is used (gypsum).	Wet sorbent variant • Arising of waste water. • High water consumption, compared with dry and semi-dry variant.

Achievable Emission Levels / Performance Rates

As mentioned above, the reductions achieved depend on different factors including waste gas temperature, the molar ratio between sorbent and pollutant and the dispersion of the sorbent. Various efficiencies under various conditions are given in Table 3.19 - Table 3.22.

Pollutant	Performance rate [%]		
	ESP		Bag filter
	about 400 °C	200–280 °C	130–240 °C
SO_2	50	10	10
SO_3	80	90	95
HCl	70	35	80
HF	95	95	95
Ref.: VDI Guidelines 2578, Nov. 1997			

Table 3.19: Dry Sorption Performance Rates for Lime as Sorbent with Different Temperatures and Dust Abatement Systems

Molar ratio Ca/S	SO_x abatement rate [%]	
	130–140 °C	170–180 °C
1	30	22
2	50	40
3	70	55
Ref.: Les techniques de désulfuration des procédés industriels, ADEME 1999		

Table 3.20: Dry Sorption SO_x Abatement Rates for Lime with Different Temperature Ranges and Ca/S Molar Ratios

Molar ratio Ca/S	SO_x abatement rate [%]
1	80
1.5	90
2	92
Ref.: Les techniques de désulfuration des procédés industriels, ADEME 1999	

Table 3.21: Semi-dry Sorption SO_x Abatement Rates for Lime with Different Ca/S Molar Ratios

Pollutant	Abatement rates [%]	
	Dry sorption [a]	Semi-dry sorption
SO_2	<50	90–95
SO_3	90	
HCl	50–75	>90
HF	10-40	>85
[a] temperature range 300–400 °C		

Table 3.22: Abatement Rates for Dry and Semi-dry Sorption with Sodium Carbonate

Under normal conditions achievable emission levels / performance rates are:

Contaminant	Dry sorption		Semi-dry sorption		Wet sorption	
	Performance rate [%]	Emission level [a] [mg/Nm^3]	Performance rate [%]	Emission level [mg/Nm^3]	Performance rate [%]	Emission level [mg/Nm^3]
SO_x	40-80 [1 b]	<40	85->90 [1,2]	<40	90-97 [c]	<40 [2]
HCl		<10 [2]	>99 [1]	<10 [2]		<10 [2]
HF		<1 [2]		<1 [2]		<1 [2]
[a] achievable emission levels, but normally dry sorption is not used for such low concentrations, where wet scrubbing or sorption might be the preferred technique						
[b] use of fabric filters can increase abatement efficiency by about 10 % [1]						
[c] dependent on L/G ratio (90 % with 8 l/Nm^3, 95 % with 14 l/Nm^3, 97 % with 20 l/Nm^3)						
[1] [cww/tm/79]						
[2] [cww/tm/70]						

An effect on NO_x emissions has been reported when using sodium carbonate or hydrogencarbonate in the semi-dry process, for sodium hydrogencarbonate the optimal range is between 120 and 160 °C. The efficiency depends on the SO_2/NO_x ratio. The abatement rate is favoured by a high ratio and moderate temperatures [BREF on Glass Manufacturing Industry, 2000].

Cross-media Effects

Consumable	Amount		
	Dry sorption	**Semi-dry sorption**	**Wet sorption**
Sorbent [a] [Ca/S molar ratio]	3 and more (for lime)	1.5–3 (for lime)	<1.1 [1]
Water [b] [l/Nm^3]	-	0.027–0.04 [2]	8-20 [c]
Energy [kWh/1000 Nm^3]	dependent on dust removal system	1 [3]	
Pressure drop [kPa]	dependent on dust removal system	2.5 [3]	
[a] sodium hydrogencarbonate requires a considerable smaller excess [b] L/G ratio [c] 8 l/Nm^3 corresponding with 90 %, 14 l/Nm^3 with 95 % and 20 l/Nm^3 with 97 % desulphurisation [1] [cww/tm/132] [2] [cww/tm/79] [3] [cww/tm/70]			

In the case of dry and semi-dry sorption, the residue is a mixture of the original sorbent and the reaction products and, if it cannot be recovered or recycled, has to be disposed of. Included are all pollutants that have not been destroyed during the incineration process, such as heavy metal compounds and/or dioxins, depending on the input of the incineration installation. Sometimes the dust is partially recycled.

With wet sorption, the residue is gypsum of high purity (>99 % $CaSO_4$ in the solid) [cww/tm/132], which can be used elsewhere.

Monitoring [cww/tm/79]

The performance of the dry sorbent and semi-dry sorbent injection system is examined by determining the acidic gas concentration and particulate abatement efficiencies.

Temperature and pressure drop (and liquid / gas flow ratio with the semi-dry variant) are routinely monitored across the (bag) filter. When an ESP is used, electric current and field strength are monitored to give warning of any malfunction in the particulate abatement device.

Economics

Type of costs	Costs		
	Dry sorption	**Semi-dry sorption**	**Wet sorption**
Capital costs [per 1000 Nm^3/h]		EUR 11000 [1 c]	
Annual operating costs [per 1000 Nm3/h]	a [1]	d [1]	
annual labour costs	EUR 2500 [1 b]	EUR 20000 [1 e]	
annual utilities cost	EUR 150 + sorbent [1]	EUR 250 + sorbent [1]	
[a] annual total operating costs EUR 2500 + 300 x flow/1000 + sorbent [b] estimated 2 hours per week [c] based on 100000 Nm^3/h [d] annual total operating costs EUR 20000 + 400 x flow/1000 + sorbent [e] estimated 1 day per week [1] [cww/tm/70]			

3.5.4.2   Selective Reduction of NO_x (SNCR and SCR)[14]

Description

Selective reduction of NO_x involves the injection of NH_2-X compounds (with X = H, CN or $CONH_2$) into the flue gas stream, reducing nitrogen oxides to nitrogen and water. The most common reduction agent is a 25 % aqueous solution of ammonia or pure ammonia. Other reaction agents are urea solutions, nitrolime or cyanamide.

There are different variants of selective NO_x reduction:

- selective non-catalytic reduction (SNCR)
- selective catalytic reduction (SCR).

With **SNCR**, the reduction agent is injected in the area where the exhaust gases have reached a temperature between 930 and 980 ºC, whereas urea is injected in an area where the gas temperature is between 950 and 1050 ºC. The injection occurs after combustion and before other treatment. Temperature, NH_3/NO_x molar ratio and residence time are the main parameters for optimum reduction efficiency. Temperatures below the level mentioned above cause unconverted ammonia to be emitted (ammonia slip); temperatures significantly above the level oxidise ammonia to NO_x. SNCR is operated with a NH_3/NO_x molar ratio range of 0.5–0.9. At higher levels (>1.2) ammonia slip can also occur, generating aerosols of ammonium chloride and sulphate, which pass through the filter and cause visible white plumes above the exhaust gas stack. The residence time and mixing quality are decisive for the reaction efficiency. Too short a residence time will cause ammonia slip.

With **SCR**, the exhaust gas stream and the injected agent are passed over a catalyst, with operation temperatures between 200 and 500 °C, dependent on the catalyst. The optimum mixing, i.e. NH_3/NO_x molar ratio, over the catalyst is vital. The molar ratio level is usually kept below 1.1 to limit the potential for ammonia slip.

The considerably lower temperatures compared to SNCR make possible the installation of SCR downstream of other treatment devices such as dust abatement and FGD. With this "cold" Denox process, a mixture of air (to control optimum oxygen content) and ammonia is added after FGD. The desulphurised flue gas stream needs to be reheated at the necessary reaction temperature. The advantage of this procedure is that, because there is no adsorption to dust, there is no potential for ammonia slip.

The equipment of SNCR and SCR consists of:

- aqueous ammonia (or other agents) storage tank
- the vaporiser
- a carrier gas supply, steam or compressed air
- injector nozzles
- the catalyst bed (with SCR).

The main components of catalysts are titanium dioxide with vanadium, tungsten and molybdenum compounds.

There are other techniques that treat sulphur dioxide and NO_x in either consecutive or simultaneous operations, such as [cww/tm/50]:

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[14]   **S**elective **N**on-**c**atalytic **R**eduction and **S**elective **C**atalytic **R**eduction

- Desonox process, where the dedusted flue gas is mixed with ammonia and passed at 450 °C over a catalyst to reduce NO_x and then over a catalyst to convert SO_2 to SO_3, which reacts to sulphuric acid
- absorption of NO (90 % of NO_x in flue gas is NO) and SO_2 with chelates (to bind NO) in sodium bicarbonate solutions and redox reaction of NO-complex with sulphite to nitrogen gas.

Application

SNCR and SCR are used to abate nitrogen oxides from processes such as chemical production, combustion or process furnaces. High dust, low dust and tail end configurations are available with SCR.

Application limits and restrictions:

	Limits / restrictions	
	SNCR	**SCR**
Typical waste gas flow [Nm^3/h]	>10000	up to 1000000 [1]
NO_x concentration	in the range of g/Nm^3 [1]	in the range of g/Nm^3 [1]
Temperature [°C]	800–1100 (dependent on agent)	200–500 (dependent on catalyst)
Pressure	atmospheric [1]	atmospheric [1]
Residence time [s]	1–2	
NH_3/NO_x molar ratio	<1.2	<1.1
[1] [cww/tm/70]		

Advantages/Disadvantages

Advantages	Disadvantages
General - Both SNCR and SCR are generally proven techniques.	General - Safety is of paramount importance when liquid ammonia systems are used.
SNCR - Under correct conditions good NO_x reduction achievable. - Relatively simple installation, though much know-how is needed to locate the ammonia injectors properly. - Low capital costs compared to alternatives. - Low energy requirements.	SNCR - High temperature necessary. - Fly ashes contain ammonia. - Outside the operational condition range (temperature, NH_3/NO_x ratio, residence time) ammonia slip or increased NO_x emission.
SCR - Very high NO_x reduction efficiency, higher than with SNCR, and lower NO_x emissions. - Reduces NO_x from all sources, not only flue gas. - Low temperature and hence lower energy consumption for heating. - Because of less dust content, less ammonia slip with the fly ash than with SNCR.	SCR - Outside the operational condition range (temperature, NH_3/NO_x ratio, residence time) ammonia slip, lower NO_x destruction efficiency. - Pressure drop to be considered. - High space requirement. - Relatively high capital costs, compared with SNCR.

Achievable Emission Levels / Performance Rates

Parameter	SNCR		SCR	
	Performance rate [%]	Emission level [mg/Nm³]	Performance rate [%]	Emission level [mg/Nm³]
NO$_x$ (gas boilers/heaters)	40-70	150-200	90-94	<20
NO$_x$ (liquid fuel boilers/heaters)	40-70	150-300	90-94	55-150
NO$_x$ (from nitric acid production)	–	–	80-97 [1]	74-100 [3]
NH₃		<5 [2]		<5 [2]
[1] lower value information from the Netherlands, upper end [cww/tm/137]				
[2] measurements in Austria; value for new catalysts, but higher NH₃-emissions occur as the catalyst ages				
[3] lower value information from the Netherlands, upper value [cww/tm/157 a]				

Cross-media Effects

Consumables are:

Consumable	Amount	
	SNCR	SCR
Ammonia [kg/tonne NO$_x$ removed]	570 [1]	370–450 [1,2]
Steam to evaporate ammonia (from aqueous solution)		
Energy [kWh/1000 Nm³]		
Pressure drop [kPa]	-	0.1-1 [1]
[1] [cww/tm/70]		
[2] upper value information from Italy		

The catalyst has a service life under regular conditions of 5-10 years, or >10 years when clean waste gas is involved, e.g. waste gas from nitric acid plants. After this time, it cannot be regenerated but will normally be recycled by the manufacturer.

Monitoring

The performance of the SNCR / SCR systems can be monitored by analysing the nitrogen oxides content before and after the treatment and the ammonia and oxygen content of the effluent gas stream.

The temperature and pressure drop (with SCR) are routinely monitored.

Economics

Type of costs	Costs	
	SNCR	SCR
Capital costs [per 1000 Nm³/h]	EUR 2300–3900 [1]	EUR 7500–32000 [1]
Operating costs [per tonne NO$_x$ removed]	EUR 700–1200	EUR 500–5000 [1,2]
[1] [cww/tm/70]		
[2] [comment]		

Cost-effectiveness parameter in the case of SNCR is the consumption of ammonia or urea; in the case of SCR it is the catalyst. The retrofitting of SNCR is relatively easy because there is no other equipment to install than the injection items and the storage tank for the agent. Retrofitting of SCR can require radical modifications of the existing installation and thus demand high capital costs.

4 BEST AVAILABLE TECHNIQUES FOR WASTE WATER / WASTE GAS TREATMENT / MANAGEMENT IN THE CHEMICAL SECTOR

4.1 Introduction

In understanding this chapter and its contents, the attention of the reader is drawn back to the preface of this document and in particular the fifth section of the preface: "How to understand and use this document". The techniques and associated emission and/or consumption levels, or ranges of levels, presented in this chapter have been assessed through an iterative process involving the following steps:

- identification of the key environmental issues for the sector.
- examination of the techniques most relevant to address those key issues;
- identification of the best environmental performance levels, on the basis of the available data in the European Union and world-wide;
- examination of the conditions under which these performance levels were achieved; such as costs, cross-media effects, main driving forces involved in implementation of the techniques;
- selection of the best available techniques (BAT) and the associated emission and/or consumption levels for this sector in a general sense all according to Article 2(11) and Annex IV of the Directive.

Expert judgement by the European IPPC Bureau and the relevant Technical Working Group (TWG) has played a key role in each of these steps and in the way in which the information is presented here.

On the basis of this assessment, techniques and, as far as possible emission and consumption levels associated with the use of BAT, are presented in this chapter that are considered to be appropriate to the sector as a whole and in many cases reflect current performance of some installations within the sector. Where emission or consumption levels "associated with best available techniques" are presented, this is to be understood as meaning that those levels represent the environmental performance that could be anticipated as a result of the application, in this sector, of the techniques described, bearing in mind the balance of costs and advantages inherent within the definition of BAT. However, they are neither emission nor consumption limit values and should not be understood as such. In some cases it may be technically possible to achieve better emission or consumption levels but due to the costs involved or cross-media considerations, they are not considered to be appropriate as BAT for the sector as a whole. However, such levels may be considered to be justified in more specific cases where there are special driving forces.

The emission and consumption levels associated with the use of BAT have to be seen together with any specified reference conditions (e.g. averaging periods).

The concept of "levels associated with BAT" described above is to be distinguished from the term "achievable level" used elsewhere in this document. Where a level is described as "achievable" using a particular technique or combination of techniques, this should be understood to mean that the level may be expected to be achieved over a substantial period of time in a well maintained and operated installation or process using those techniques.

Where available, data concerning costs have been given together with the description of the techniques presented in the previous chapter. These give a rough indication about the magnitude of costs involved. However, the actual cost of applying a technique will depend strongly on the specific situation regarding, for example, taxes, fees and the technical characteristics of the installation concerned. It is not possible to evaluate such site-specific factors fully in this

document. In the absence of data concerning costs, conclusions on economic viability of techniques are drawn from observations on existing installations.

It is intended that the general BAT in this chapter are a reference point against which to judge the current performance of an existing installation or to judge a proposal for a new installation. In this way they will assist in the determination of appropriate "BAT-based" conditions for the installation or in the establishment of general binding rules under Article 9(8). It is foreseen that new installations can be designed to perform at or even better than the general BAT levels presented here. It is also considered that existing installations could move towards the general BAT levels or do better, subject to the technical and economic applicability of the techniques in each case.

While the BAT reference documents do not set legally binding standards, they are meant to give information for the guidance of industry, Member States and the public on achievable emission and consumption levels when using specified techniques. The appropriate limit values for any specific case will need to be determined taking into account the objectives of the IPPC Directive and the local considerations.

Identification of a Horizontal BAT
The horizontal approach to waste water and waste gas treatment and management in the entire chemical sector is based on the premise that the options for emissions prevention or control can be assessed independently of the particular production process(es), and that, on this basis, BAT can be identified that embrace the most effective and suitable measures to achieve a high general level of protection of the environment as a whole against the emissions mentioned above. Because this is a horizontal BREF, BAT needs to be determined more broadly than for a vertical BREF, particularly to embrace more than just technology.

BAT used in this document includes both:

- the methodology to prevent waste water / waste gas discharge, identify the need for and carry out emissions improvement and find the best option for waste water / waste gas collection and treatment (effluent management)
- the identification of the best and most suitable [in the sense of Art. 2(11)] treatment technologies.

Thus this chapter contains:

- a generic part describing a general BAT for environmental management methodology
- a specific part describing BAT for specific waste water / waste gas management methodologies and a rationale that leads to decisions on waste water and waste gas treatment techniques.

The chemical Sector
The chemical industry sector covers a wide range of enterprises: at one end the one-process-few-products small enterprises with one or few waste water / waste gas release sources and, at the other, the multi-production-mix enterprises with many complex waste water / waste gas streams. Although there are probably no two chemical sites that are totally comparable in production range and mix, environmental situation and the quantity and quality of their emissions is it possible to describe BAT for waste water and waste gas treatment for the chemical sector as a whole.

Implementation of BAT
The implementation of BAT in new plants is not normally a problem. In most cases it makes economic sense to plan production processes and their waste water / waste gas releases to minimise emissions and material consumption. With existing sites, however, the implementation of BAT is not generally an easy task, because of the existing infrastructure and local circumstances (see Section 3.2.2). Nevertheless, this document does not distinguish between BAT for new and existing installations. Such a distinction would not encourage the

operators of industrial sites to move towards adopting BAT and it would not reflect the commitment of the chemical industry to continuous improvement of environmental conditions.

On the other hand, it is obviously not feasible or viable to implement all techniques identified as BAT at once. What is feasible, however, is integrating BAT in existing installations when major alterations are planned, or implementing BAT that influences the whole site in a step-by-step construction programme over a period of time. Such programmes challenge operator and regulator to come to an agreement on time scale and priority setting for the required changes.

Key ideas for priority setting programmes at existing sites would be, e.g.:

- consideration of the current quality of the receiving media
- consideration of the degree of the current local impact
- consideration of the effectiveness of the measures in terms of overall pollutant reduction in relation to cost and hazard.

4.2   General BAT

BAT for General Environmental Management
The task of environmental management is to:

- define environmental goals for the operator's activities
- ensure an environmental optimum operation and ever-improving performance of these activities
- control the compliance with these environmental goals.

The management tools described in Section 2.2 are to consider in the determination of BAT and should be reflected as conditions or requirements when deciding on a permit. These tools are not restricted to dealing with waste water and waste gas, but they are a prerequisite of best performance as required under the Directive. BAT for general environmental management as described below follows the same principles for all kinds of enterprises, i.e. small or big ones. In contrast to big companies, the general environmental management of small- and medium-size enterprises (SME) is less complex.

BAT is to:
- implement and adhere to an environmental management system (EMS) or HSE-system, the whole content of which is detailed in Section 2.1 (such as ISO 9001 / 14001, EMAS, Responsible Care®, ICC Business Charter for Sustainable Development, CEFIC Guidelines for Protection of the Environment). Elements of a good EMS could include:
    - implementation of a transparent hierarchy of personnel responsibility for EMS concerns including effluent discharge, the persons in charge reporting directly to the top management level
    - preparation and publication of an annual environmental performance report (e.g. as part of EMAS or ISO 9001 / 14001) to enable the dissemination of performance improvements to the public, which can also serve as a vehicle for information exchange according to Art. 16(2) of the Directive
    - setting internal (site- or company-specific) environmental targets, reviewing them regularly as detailed in Section 2.2.2.2 and publishing them in the annual report
    - holding a regular audit to secure compliance with the principles of EMS
    - regular monitoring of performance and progress towards the achievement of EMS policy
    - practising risk assessment on a regular basis to identify hazards, as detailed in Section 2.2.3.1

- practising benchmarking on a regular basis and challenging the processes (production and waste water / waste gas treatment) on their water and energy consumption, waste generation and cross-media effects as described in Section 2.2.3.2
- implementation of an adequate training programme for staff and instructions for contractors working on the site on HSE and emergency issues, as mentioned in Section 2.2.4.2
- application of good maintenance practices to ensure proper operation of the technical devices.

BAT for Waste Water / Waste Gas Management
The task of waste water / waste gas management is to fit the situation of the waste water / waste gas releases generated on the industrial site to legal and permit requirements, the given local environmental and hygienic conditions and the continuous improvement of environmental conditions, which is also implemented in CEFIC's Responsible Care programme. It detects and assesses options for preventing or reducing the generation of emissions or their impact to the environment. The results of waste water / waste gas management considerations and decisions are the identification and implementation of:

- potential emissions reduction in the production process
- means to avoid unnecessary contamination of otherwise unpolluted releases
- best suitable waste collection systems
- best suitable emission control systems
- best monitoring systems to check compliance with targets or legal regulations

Again, as with general environmental management, BAT for waste water / waste gas management follows the same principles for all kinds of enterprise sizes. Whereas waste water / waste gas management for enterprises with one or very few production lines and effluent sources is a relatively easy and simple task, it is normally very complex for large sites with a multi-production mix (see Section 2.1, Figure 2.3).

BAT is to:
- implement a waste water / waste gas management system or waste water / waste gas release assessment for the entire chemical site with reference to Section 2.1 and Figure 2.2 by using an appropriate combination of:
    - using a site inventory and a stream inventory or register. These inventories provide the necessary information for the following assessment steps, as described in Section 2.2.1.1 and 2.2.1.2.
    - pursuing systematically the internal mass streams by applying EMFA (see Section 2.2.1.3) – adequately to the complexity of the waste water / waste gas system – to draw the necessary conclusions for optimisation; for sites with only one or very few emission arising points the application of EMFA can be obsolete or very simple
    - checking and identifying the most relevant emission sources for each medium and listing them according to their pollutant load. The resultant ranking of emission sources is the basis for an improvement programme which gives priority to those sources that offer the greatest potential reduction efficiency
    - checking the receiving media (air and water) and their tolerance of the emissions, using the results to determine the extent to which stronger treatment requirements are needed or if the emissions can be accepted at all
    - performing assessment of toxicity and, subject to available methods, persistence and potential bioaccumulation of waste water to be discharged into a receiving water body, as described in Section 2.2.1.2.1, to identify potentially hazardous effects on the ecosystem and share the results with the competent authorities
    - checking and identifying relevant water-consuming processes and listing them according to their water usage. The resultant ranking is the basis for improvement of water consumption
    - pursuing options for improvement (such as options for waste prevention or reduction, improvement of effluent collection and control and/or options for process-integrated

measures), focusing on streams with higher concentrations and loads, their hazard potential and impact on the receiving water body, as detailed in Section 2.1 in connection with Figure 2.2

> **Split view**
> One Member State expressed the opinion that the statements on BAT for waste water and waste gas management are partly too general and they refer to examples for streams with higher concentrations and loads (as mentioned in Section 2.2.2.3.1).

- assessing the most effective options by comparing overall removal efficiencies, overall balance of cross-media effects, technical, organisational and economic feasibility etc., as detailed in Section 2.1

The waste water / waste gas release assessment is the basis for all decisions on stream segregation, reduction strategies, process improvements (see the vertical BREFs on the chemical and related sectors with respect to cleaner process technology, clean raw material, improved process equipment, control of leakages etc.) and control techniques. An example of an efficient waste water management - as reported from Germany - which follows the outlined strategy for chemical sites carrying organic loads from the production of organic chemicals has as a reasonable target an overall COD-removal performance (including pretreatment) of at least 90 %. BAT for the measures to be adopted in the light of the results of waste water / waste gas release assessment are dealt with in Section 4.3.

- assess impact on the environment and the effects on treatment facilities when planning new activities or alterations to existing activities, comparing the future environmental situation with the existing one and indicating whether substantial changes are to be expected
- practice emission reduction at source by stream segregation, installation of adequate collection systems and construction measures (see Section 4.3)
- link production data with the data on emission loads to compare the actual and calculated releases. If the data obtained do not match, the processes responsible for unexpected releases need to be identified
- treat contaminated waste water / waste gas streams at source in preference to dispersion and subsequent central treatment, unless there are good reasons against it. Most treatment techniques work most efficiently when the pollutant content is high. It is also economical to treat relatively small tributary streams with small, high-efficiency treatment devices than to have large central facilities with high hydraulic load
- use quality control methods, as described in Section 2.2.2.6, to assess the treatment and/or production processes and/or prevent them running out of control
- apply good manufacturing practice (GMP) for equipment cleaning to reduce emissions to water and to air
- implement facilities / procedures to enable timely detection of a deviation that could affect the downstream treatment facilities, so as to avoid an upset of those treatment facilities, enable identification of the source of deviation and eliminate its cause; in the meantime the arising waste water can be diverted into retention facilities and the waste gas to adequate safety facilities, e.g. a flare
- install an efficient central warning system that will give notice of failures and malfunctions to all concerned; when the accident could have a significant effect on the environment and/or the neighbourhood, the competent authorities need to be part in the information chain
- implement a monitoring programme in all treatment facilities to check that they are operating properly, to enable detection of any irregularities or operating failures that might influence the receiving media and give information on the actual emissions of pollutants

- the implementation of a monitoring programme to detect the emissions is required by Art. 9(5) of the Directive, with the information obtained serving as information to the public under Art. 15(2) of the Directive. The monitoring programme needs to include the contaminants and/or surrogate parameters relevant to the treatment facility. The frequency of the measurements depends on the hazard risk of the pollutants in question, the failure risk of the treatment facility and the variability of the emissions
- put in place strategies for dealing with fire-fighting water and spillages, as described in Section 2.2.4.1
- put in place a pollution incident response plan to enable the most rapid and appropriate response to internal accidents and operating failures, as described in Section 2.2.4.2
- allocate costs of treatment associated with production.

4.3   Specific BAT

Once this foundation of management methodology has been laid, the next step towards integrated pollution prevention and control is the implementation of technical measures.

4.3.1 Waste Water Section

This section is devoted to the determination of BAT for waste water treatment on a chemical industry site, including necessary prevention and reduction techniques in addition to control (end-of-pipe) techniques.

BAT for Process-integrated Measures
As already mentioned in Sections 1.3.1 and 3.3.1, process-integrated measures are the preferred method for preventing or reducing the amount of waste water and/or contamination. They are, however, generally production- or process-specific and their applicability requires special assessment, which is within the scope of the vertical BREFs on the chemical and related sectors. Conclusions on BAT for process-integrated measures in this document therefore refer to the general need to implement these measures within a production line and consider only the measures for processes such as product washing, equipment cleaning, vacuum generation and cooling that are commonly applied to most production lines.

BAT is an appropriate combination of:
- using process-integrated or waste water or contaminant-recovering measures in preference to end-of-pipe techniques when there is a choice
- assessing existing production installations for options of retrofitting process-integrated measures and implement them when feasible or at latest when the installation undergoes major alterations
- using process water in a recycle mode whenever feasible for economic and quality reasons, with a maximum number of recycles before discharge, as described in Section 3.3.1.2
- optimising product washing processes by avoiding once-through processes whenever feasible for quality reasons, as mentioned in Section 3.3.1.1
- avoiding direct contact cooling systems whenever feasible, as detailed in Section 3.3.1.3
- using closed-circuit vacuum generation instead of water jet or vapour jet pumps whenever feasible, e.g. when their use is not prohibited by safety or corrosion issues as mentioned in Section 3.3.1.4
- assessing whether water-based waste gas treatment processes can be replaced by other measures, as described in Section 3.3.1.5. Waste gas treatment techniques using relatively high amounts of water (such as scrubbing or cooling medium) are of special significance in regions where water is in short supply. Examples of such measures, which can be of high importance in regions with water shortage, are:
  - removal of solid matter by dry techniques rather than by wet scrubbing
  - reduction of SO_x in flue gas by secondary measures rather than by systems that include wet scrubbing.

BAT for Waste Water Collection

An adequate waste water collection system plays an essential role in effective waste water reduction and/or treatment. It ducts the waste water streams to their appropriate treatment device and prevents mixing of contaminated and uncontaminated waste water.

BAT is to:
- segregate process water from uncontaminated rainwater and other uncontaminated water releases. This minimises the amount of water requiring treatment and the hydraulic load sent to treatment facilities. It enhances the cost and performance efficiency of treatment devices. If existing sites do not yet operate water segregation, it can be installed – at least partially – when major alterations are made to the site
- segregate process water according to its contamination load: organic, inorganic without or with insignificant organic load or insignificant contamination. It ensures that a treatment facility receives only those pollutants it can cope with
- install a roof over areas of potential contamination by, for example, spillage or leakage - wherever feasible. It prevents rainwater falling on these areas and mixing with contaminants that would otherwise increase the amount of waste water requiring treatment
- install separate drainage for areas of contamination risk, containing a sump to catch leakage or spillage losses, as described in Section 3.3.4.4. They prevent the discharge of rainwater contaminated by product losses. The separately captured rainwater is released after adequate monitoring and discharged, according to the results, either directly to the drainage system for uncontaminated rainwater or to appropriate treatment facilities
- use overground sewers for process water inside the industrial site between the points of waste water generation and the final treatment device(s). If climatic conditions do not allow overground sewers (temperatures significantly below 0 °C), systems in accessible underground ducts are a suitable replacement. Both provide easy and economical leak detection, maintenance work and options for retrofitting new equipment into existing installations. Many chemical industry sites are still provided with underground sewers and the immediate construction of new sewer systems is normally not viable, but work can be done in stages when major alterations at production plants or the sewer system are planned
- install retention capacity for failure events and fire-fighting water in the light of a risk assessment, choosing one, two or all of the following options:
  - decentralised retention for detected failure events, whenever possible close to the production plants and large enough to prevent the release of substances into the sewer during the process undergoes a controlled shut down
  - central retention to collect waste water from failure events that has already entered the sewerage system instead of ducting it to the central WWTP, as described in Section 3.3.3. Although there are several kinds of retention systems in operation that can be considered to be BAT, the most secure systems are those where the tank is flooded only in the case of a failure event (see Figure 3.2) or where two tanks are filled alternately (see Figure 3.1)
  - retention for fire-fighting water, either used in isolation or in combination with local containment. Experience has shown that fire-fighting water can amount to thousands of cubic metres (for example about 15000 m^3 highly contaminated fire-fighting water) and the retention capacity needs to be large enough to cope with it to protect both surface and waste water drainage systems
  - drainage system for hazardous and inflammable substances, e.g. to transport them from the fire zone.
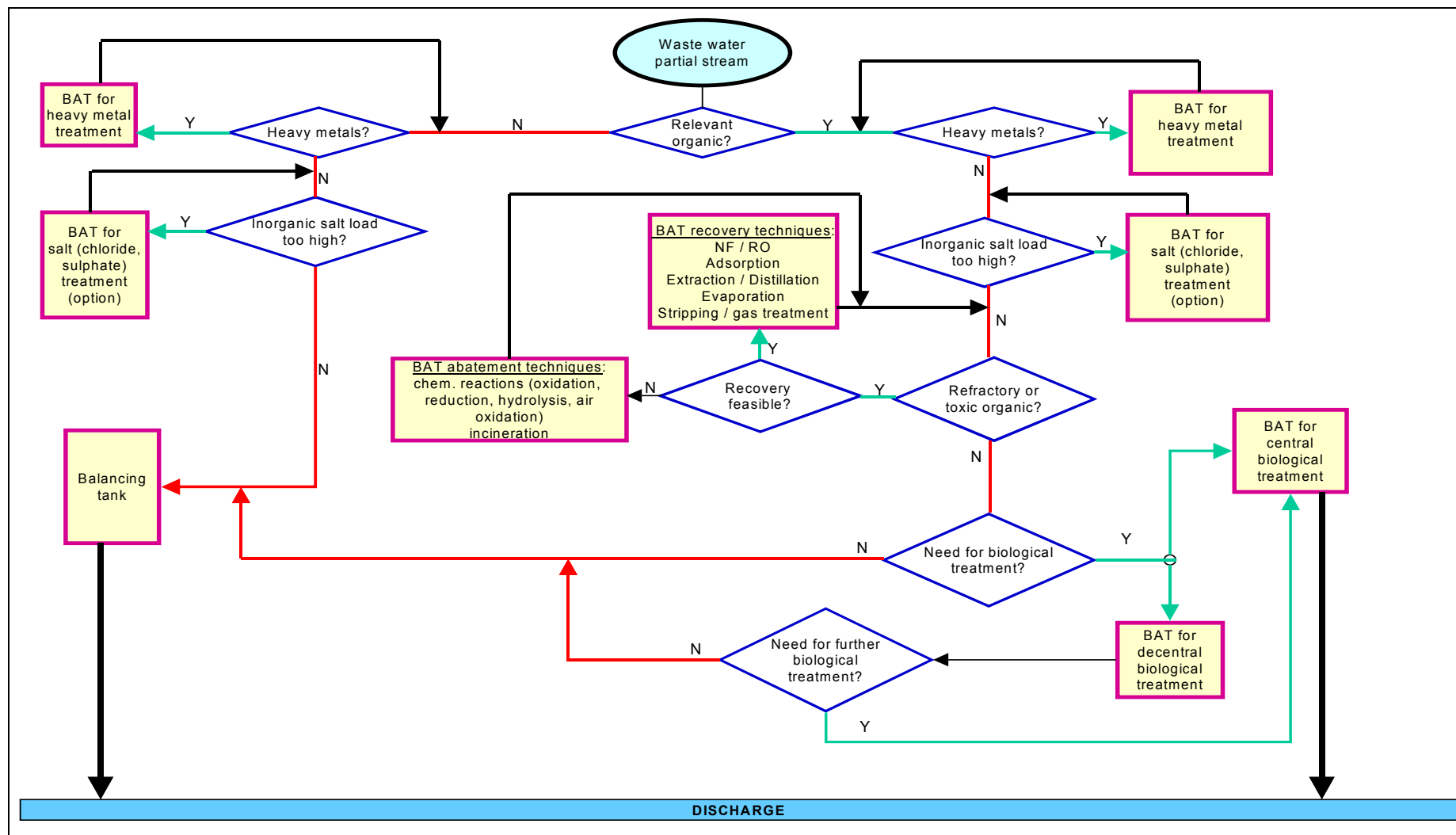
Figure 4.1: Decision Pathway for Waste Water Treatment on a Chemical Industry Site: Basis for BAT Conclusions

BAT for Waste Water Treatment

Waste water treatment in the chemical sector follows at least four different strategies:

- central final treatment in a biological WWTP on site
- central final treatment in a municipal WWTP
- central final treatment of inorganic waste water in a chemical-mechanical WWTP
- decentralised treatment(s).

This document gives no preference to any of those. All four strategies are to consider as BAT when properly applied to the actual waste water situation, otherwise none of them is BAT.

The BAT conclusions follow the path of the contaminants to be controlled, as described in Figure 4.1. It is assumed at this stage that the appropriate effluent management decisions have been made, the impact on the receiving water body has been assessed, all practical options for prevention and reduction of waste water have been exploited and all safety measures have been taken into account, i.e. from this point on, only end-of-pipe solutions are considered.

It needs to be mentioned that region-specific issues can require treatment techniques especially developed for a site, or they can invalidate well-known and commonly used techniques for this special case. The following approach to come to BAT conclusions for waste water treatment gives guidance on finding and installing the appropriate technique, including how to cope with these peculiarities typical to waste water treatment. The approach follows a decision pathway to come to BAT conclusions for appropriate waste water treatment for a chemical site, which is illustrated in Figure 4.1.

- General
  BAT is to:
  - allocate contaminated waste water streams according to their pollutant load. Inorganic waste water without relevant organic components is segregated from organic waste water and ducted to special treatment facilities (see special sections on heavy metals and inorganic salts, discussed later in this chapter). Organic waste water with a relevant portion of inorganic and refractory or toxic organic compounds is directed to special pretreatment devices (see sections on heavy metals, inorganic salts and pollutants unsuitable for biological treatment later in this chapter).

- Rainwater
  BAT is to:
  - duct uncontaminated rainwater directly to a receiving water, by-passing the waste water sewerage system
  - treat rainwater from contaminated areas by using techniques described in Sections 3.3.4.1.1, 3.3.4.4.1 and 3.3.4.4.2, see Table 4.1, before discharging it into a receiving water.
  In some cases the use of rainwater as process water to reduce fresh water consumption may be environmentally beneficial.

  The techniques listed in Table 4.1 are to consider as BAT, when applied to the respective situation. The table lists the restrictions for the different techniques

	Grit chambers			Retention pond / sedimentation tank (see Table 4.3)	Sand filter
	Channel-shaped	**Circular**	**Aerated**		
Purpose	Removal of sand and grit only Protection of treatment process Protection of equipment against abrasion			Clarification and cleaning of rainwater and catching of hydraulic load from heavy rainfall to protect receiving river (retention pond) Clarification of rainwater before discharge or re-use (sedimentation tank)	Treatment of rainwater run-off from lightly contaminated surfaces, either to discharge or re-use
Application	As part of the WWTP applied to rainwater treated in the WWTP (rainwater from heavily contaminated surfaces) Flow rate 0.3 m/s thus only sand and coarse material is separated			Removal, from lightly contaminated surfaces, of suspended solids	Removal of suspended solids
Application limits	Suitable for highly fluctuating waste water flow	Less suitable for high fluctuations in waste water flow	Suitable for fluctuating waste water flow	Not suitable for rainwater from heavily contaminated surfaces Not suitable for regions with long periods of dryness and/or high temperature, because long residence time together with heat causes odour emissions	Not suitable for rainwater from heavily contaminated surfaces
Consumables	Energy for pumps	Compressed air Energy for pumps and air jet	Compressed air Energy for pumps and air jet		Energy for pumps From time to time replacement of filter medium
Cross-media effects	Noise emissions Odour emissions Sand to dispose of			**Retention pond**: Disposal of sludge Depending on hydraulic residence time, odour emissions possible	Disposal of backwashed sludge
Space requirement	Comparatively low Part of the WWTP			Large area required	Low space requirement
Achievable performance [% pollutant removal]				Retention pond: TSS 50-90	TSS 80-83
Retrofittability	Easily retrofittable, if not already part of equipment			Retrofittable when space available	Easily retrofittable

Table 4.1: Rainwater Treatment Techniques as Described in Chapter 3

- Free Oil / Hydrocarbons
  BAT is to:
  - remove oil / hydrocarbons when they appear as large slugs and where these are incompatible with other systems, with the aim of maximising recovery, by applying an appropriate combination of:
    - oil/water separation by cyclone, MF or API, when large slugs of free oil or hydrocarbons can be expected, otherwise PPI and CPI are alternatives, details in Section 3.3.4.1.6
    - MF, granular media filtration or gas flotation, which are described in Section 3.3.4.1.5, 3.3.4.1.4 and 3.3.4.1.3 respectively
    - biological treatment (see section on biodegradable substances), either in a central biological WWTP, a municipal WWTP or a separate treatment plant for this special waste water stream.

  The BAT-associated emission levels for oil / hydrocarbons removal are given in Table 4.2.

Parameter	Concentration [a] [1] [mg/l]
total hydrocarbon content	0.05-1.5
BOD$_5$	2-20
COD	30-125
[a] monthly average [b] There is disagreement on the analytical methods to assess hydrocarbons which could not be solved within the TWG. [1] Taken from Draft BREF for Mineral Oil and Gas Refineries, dated October 2001	

Table 4.2: BAT-associated Emission Levels for Free Oil / Hydrocarbons Discharged into a Receiving Water

- Emulsions
  BAT is to:
  - break emulsions at source and recover the separated constituents. The addition of flocculating and/or coagulating chemicals can be necessary to support separation; treatment at source enables recovery and prevents adverse effects on downstream sewerage systems; or
  - remove emulsions at source when they cannot be broken and can have adverse effects on downstream facilities. Suitable treatment techniques are such as air oxidation, evaporation, incineration (when the heat value of the emulsion allows autothermal operation) or biological degradation. Often it is not permitted to discharge emulsions into public sewerage systems.

- Total suspended solids (TSS)
  The measures for TSS removal used in this section do not include those for activated sludge or heavy metal compounds, which are dealt with in other sections.

  BAT is to:
  - remove TSS from waste water streams when they can cause damage or failure to downstream facilities such as abrasion and clogging in pumps and pipes or clogging and plugging in treatment facilities. Downstream treatment facilities, which might be damaged, are items such as filters, adsorption columns, membrane filters, oxidation vessels using UV irradiation or the central and municipal WWTP. The techniques are listed in Table 4.3.The ranking of treatment techniques is:
    - 1st step: sedimentation / air flotation to catch the main TSS load and to protect subsequent filter systems from clogging or high frequencies of backwashing. Sedimentation or air flotation is normally sufficient to prevent abrasion and clogging in pumps and pipes (provided emulsions and inseparable solids have been treated successfully)

> ➢ 2nd step: mechanical filtration as an option, if the solid content has not been reduced enough to prevent clogging in subsequent treatment facilities, such as membrane filtration, adsorption, chemical oxidation reaction using UV irradiation
> ➢ 3rd step: MF or UF as an option, if the waste water stream needs to be solid-free to prevent clogging, for example, in NF or RO facilities, or free of other particles that cannot be removed by other filtration techniques

- remove TSS from waste water streams before discharging into a receiving water. As long as no hazardous substances are included in TSS, the common techniques are:
  > ➢ sedimentation / air flotation
  > ➢ filtration, only if required because of insufficient separation by the preceding techniques
- remove TSS from waste water streams using a technique that enables recovery in preference to abatement techniques whenever it is feasible and viable to re-use the solids
- apply flocculating and/or coagulating agents when finely dispersed or otherwise inseparable material is present to produce flocs large enough to settle
- cover or close the treatment device when odour and/or noise are an issue, duct the exhaust air to further waste gas treatment if necessary and implement the necessary safety devices when explosion risk can be expected in the closed treatment device
- dispose of the sludge appropriately either by handing it to a licensed contractor or by treating it on site (see section on sludge treatment).

The techniques to consider as BAT, depending on the application, are those described in Sections 3.3.4.1.2 - 3.3.4.1.5 and listed in Table 4.3.

- Heavy Metals
  As heavy metals are chemical elements that cannot be destroyed, recovery and re-use are the only ways to prevent them being released into the environment. Any other option causes them to be transferred between the different media: waste water, waste air and landfilling. Waste water streams carrying a significant load of heavy metals are those that originate from production processes where heavy metal compounds are produced or used (e.g. as catalyst), or from cleaning processes of equipment used in such production.

  BAT is to:
  - segregate waste water containing heavy metal compounds as far as possible and
  - treat the segregated waste water streams at source before mixing with other streams and
  - prefer techniques that enable recovery. The techniques that can be applied to achieve these requirements are listed in Table 4.4 and
  - facilitate further elimination of heavy metals in a final WWTP (chemico-mechanical stage for inorganic productions, biotreatment for organic productions) as a polishing step, with subsequent treatment of sludge, if necessary.

  The TWG could not provide BAT-associated emission levels for heavy metals in tributary waste water streams that would be applicable to the chemical sector as a whole for the reasons detailed in Section 3.3.4.2.1. The emission levels resulting from the application of BAT mentioned above are dependent on the production process from which the heavy metal pollutants originate.

	Sedimentation	Air flotation	Filtration	MF/UF
Purpose	Clarification of collected rainwater from suspended solids Clarification of process water from suspended solids or floc	Clarification of process water when sedimentation is not appropriate	Final separation stage after sedimentation or air flotation to achieve low particulate emissions	Clarification down to solid-free waste water for downstream treatment facilities (e.g. RO)
Application	Separation of solids from waste water In principle TSS recoverable	Separation of unsettleable solids and oil / grease Separated material can be recovered	Separation of solids from waste water stream Material recovery depends on filter type	Separation of all solid material, colloidal particles, bacteria, viruses Very suitable to material recovery
Application limits	Particles need to be settleable No limits to TSS content No stable emulsions	No foaming detergents No limits to feed concentration, but not bulk free oil	Finely dispersed and slimy solids to avoid High TSS load causes clogging	Membrane material vulnerable to chemical attacks Feed of TSS needs to be low because of clogging and plugging
Consumables	Chemicals: 0.5-100 g/m^3 Energy: 0.5-1.5 kW (tank diameter 25-35 m)	Compressed air: 0.53-0.55 m^3/m^3 Flocculant: 2.4-4.7 kg/tonne TSS Energy: 20.6 kWh/1000 m^3	Filter aids Pressure drop Energy	Antiscaling, antifouling and backwashing chemicals Energy related to flow rate and pressure drop: 2-20 kWh/m^3 (MF) [1] 1-10 kWh/m^3 (UF) [1] Pressure drop: 0.02-0.5 MPa (MF) 0.2-1 MPa (UF)
Cross-media effects	Sludge disposal Noise emissions from pumps and sludge / scum removal system Odour emissions (e.g. VOC) when tank is not closed	Sludge disposal Noise emissions from pumps and air jet Odour emissions (e.g. VOC) when tank is not closed, higher than with sedimentation	Sludge disposal after backwashing Closed filters might need connection to waste gas abatement systems	Residue disposal Noise emissions from pumps
Space requirement	Dependent on device (flat tank or lamina settler)	Less than with sedimentation		Module arrangement Space requirement low compared to other techniques
Achievable performance [% pollutant removal]	TSS 60-90 Settleable solids 90-95	TSS 85-98 HM sulphides: 95 higher treatment stability with feed fluctuations	Dependent on filter medium and filter aids TSS 50-99.99	TSS close to 100
Achievable emissions [mg/l]	TSS <10	TSS 10-20 Oil 2-10	TSS <10 Free oil <5	
Retrofittability	Dependent on available space	yes	yes	yes

[1] It seems rather surprising that MF, the process with the lowest pressure drop, consumes more energy than the processes with high pressure drops. The reason is the occurrence of concentration polarisation and fouling. In MF, and to a lesser extent in UF, this phenomenon is very severe and it results in a drastic flux decline [cww/tm/161].

Table 4.3: Treatment Techniques Associated with BAT for Suspended Solids

- Inorganic Salts and/or Acids (Ionic Particles)

  The inorganic salt and/or acid content of waste water can influence both the biosphere of a receiving water, e.g. small rivers when they are confronted with high salt loads, and the operation of sewerage systems, e.g. corrosion of pipes, valves and pumps or malfunction of downstream biological treatment. The control measures used in this section for inorganic salts do not include those for heavy metal salts, which were dealt with in the previous section, and for ammonium salts, which are controlled by other means.

  BAT is to:
  - control the inorganic salt and acid content of waste water streams with negative impact on the biosphere of receiving water appropriately, if necessary preventing its discharge. When treatment is required, it is more cost-effective if done at source
  - control the inorganic salt content (mainly chloride and sulphate) by treatment at source when it could cause damage, failure and/or malfunction of the on-site or municipal sewerage system
  - choose a treatment technique that enables recovery and re-use of the treated contaminants whenever it is feasible and suitable, taking into account cross-media effects and the impact of the pollutants.

  Appropriate treatment techniques are listed in Table 4.5, the actual choice depending on the given situation.

	Precipitation / sedimentation or air flotation / filtration	Crystallisation	Ion exchange	NF / RO
Purpose	Transferring dissolved heavy metal compounds to insoluble compounds and separating them from the waste water stream	Growth of heavy metal compounds on granular seed material in a fluidised bed	Replacement of heavy metal ions in the aqueous phase by other ions from ion exchange resin	Separation of heavy metal ions by membrane permeation Separation of most other contaminants
Application	Removal of heavy metals from waste water streams, preferably for higher concentrations Recovery possible in principle	Removal of heavy metals from waste water streams by producing conditions that enable precipitation Recovery is the purpose	Solutions containing heavy metal ions with low feed concentrations Recovery is possible	Achieving high grade of purity to recycle and re-use the water Concentration increase of contaminants for further treatment requirement Recovery is possible
Application limits	Avoid complex-forming agents pH adjustment is important Not applicable when concentration lower than solubility of precipitate		High ionic strength to be avoided Temperature limit about 60 °C Corrosive agents damage resin	Concentrations with osmotic pressures too high to operate Low thermal and chemical resistance
Consumables	Precipitation agent Flocculant / coagulant Energy for pumps	Crystallisation chemicals Energy	Regeneration liquid Fouling suppressors Energy	Chemicals for cleaning Energy: 1-3 kWh/m^3 (NF) 1-3 kWh/m^3 (RO) Pressure drop: 0.5-3 MPa (NF) 2-100 MPa (RO)
Cross-media effects	Disposal of sludge Odour emissions possible	Over-dosage of crystallisation chemicals can result in a higher salt load Normally no waste or sludge generation	Regeneration returns high concentrations of heavy metal solutions (recovery or disposal)	Concentrate needs further treatment, e.g. ion exchange
Space requirement		Comparable to ion exchange and NF/RO	Comparable to crystallisation and NF/RO	Comparable to crystallisation and ion exchange
Achievable performance [% pollutant removal]			80-99	inorganic Hg >90 (NF) organic Hg >90 (NF) Cd compounds >90 (NF) close to 100 % with RO
Achievable emission levels [mg/l]	for heavy metals highly dependent on production process from which they originate	Zn 1 Ni 1	0.1–10	very low (near to zero) with RO
Retrofittability	yes		relatively easy	
^{1} packed height of 1 m, diameter 1 m, including vessel, valves and resin				

Table 4.4: Treatment Techniques Associated with BAT for Heavy Metals

	Evaporation	Ion exchange	Reverse osmosis	Biological sulphate removal
Purpose	Distillation of water leaving a concentrate as bottom residue	Replacement of cations by H^+ and anions by OH^- ions thus replacing salts by water	Separation of all water contaminants by membrane permeation	Anaerobic reaction of sulphate to sulphur via sulphide
Application	Making inorganic salts to crystallise and separate them from waste water Concentrate other non-volatile substances as well In principle substance recovery possible	Solutions containing salts, also with heavy metals Recovery is possible	Achieving high grade of purity to recycle and re-use water Concentration increase of contaminants for further treatment or recovery requirement Recovery is possible	Removal of sulphate from waste water containing a large amount of it Can also remove heavy metals as sulphides Recovery of the sulphur generated
Application limits	Avoid foam generating substances	High ionic strength to be avoided Temperature limit about 60 °C Corrosive agents can damage resin	Concentrations too high result in osmotic pressure too high to operate Low thermal and chemical resistance	Very slow reaction, i.e. long residence time COD/sulphate needs to be at least 1:1
Consumables	Chemicals when pretreatment is necessary Steam 5-16 kg water/kg steam Energy	Regeneration liquid Fouling suppressors Energy for pumps	Chemicals for cleaning Energy: 1-3 kWh/m^3 Pressure drop: 2-100 MPa	Chemicals (neutralising agent, COD delivering substance, flocculant) Energy
Cross-media effects	Condensate might need further treatment Noise emission	Recovery returns high concentrations of salt removed (recovery by treatment of aqueous waste or disposal)	Concentrate needs further treatment, e.g. ion exchange to enable recovery	Sulphur to be used for production processes (sulphuric acid)
Space requirements	Comparatively low	Comparatively low	Comparatively low	
Achievable performance [% pollutant removal]	Complete salt removal	80-99	Close to 100 %	sulphate: 94 zinc: 99.8 cadmium: >99
Achievable emission levels [mg/l]		0.1-10	very low (near to zero)	sulphate: 75 zinc: 0.05-0.15 cadmium: <0.01
Retrofittability		relatively easy		
[1] packed height of 1 m, diameter 1 m, including vessel, valves and resin				

Table 4.5: Treatment Techniques Associated with BAT for Inorganic Salts (Heavy Metals not Included)

- <u>Pollutants Unsuitable for Biological Treatment</u>
  Apart from the contaminants discussed in the previous sections there are tributary waste water streams that are not suited to biological treatment because they contain:

  - COD not or only poorly biodegradable
  - toxic substances that inhibit the biological process.

  Thus their discharge into a biological treatment plant needs to be prevented. It is not possible to forecast which contaminants are inhibitors for biological processes in a WWTP, because this depends on the adaptation to special contaminants of the micro-organisms working in this plant. There is no difference if the waste water is ducted to a central biological WWTP inside of the chemical industry site or to a municipal WWTP. The conditions for pretreatment of pollutants unsuitable for biological treatment are in both cases the same.

  BAT is to:
  - avoid the introduction of waste water components into biological treatment systems when they can cause malfunction of such systems
  - treat tributary waste water streams with relevant non-biodegradable part by adequate techniques, described in Section 3.3.4.2 and listed in Table 4.6, before or instead of a final biological treatment. The actual choice of the appropriate treatment technique depends on the actual situation, the composition of the waste water stream, the situation of the biological WWTP (if operated) and the adaptation of its micro-organisms and the requirements of the receiving water. It is a site-specific issue in every case

  > **Split view**
  > One Member State expresses a view that the criterion 'relevant non-biodegradable part' needs to be more closely defined by giving a set of indicative values for recalcitrant TOC (see Section 3.3.4.2) to waste water streams.

  - use techniques that enable substance recovery whenever feasible, such as (see Table 4.6):
    - ➢ NF / RO
    - ➢ adsorption, using the most suitable variant (for details, see Section 3.3.4.2.9)
    - ➢ extraction
    - ➢ distillation / rectification
    - ➢ evaporation
    - ➢ stripping
  - remove relevant ammonia content from waste water streams at source, using, e.g. air or steam stripping, as described in Section 3.3.4.2.14
  - use techniques that do not need additional fuel, when other abatement techniques achieve sufficient results and if recovery is not feasible. When a final biological WWTP is operated, it can suffice to break down refractory organic load into biodegradable substances, using techniques such as (see Table 4.6):
    - ➢ chemical oxidation (making a thorough assessment whether organic chlorides are generated when chlorine-containing oxidation agents are used)
    - ➢ chemical reduction
    - ➢ chemical hydrolysis
  - use air oxidation and incineration only when there is no other choice to abate toxicity or inhibitory effects or when the process can be operated on a self-sustaining basis or it is the only way to meet discharge requirements without biological treatment
  - take into account water consumption with treatment techniques such as:
    - ➢ extraction
    - ➢ distillation / rectification
    - ➢ evaporation
    - ➢ stripping,

either requiring considerable amounts of cooling water or needing wet scrubber systems to recover the contaminants from the gaseous phase, when this could be an environmental issue. When water shortage is an important factor, second best treatment techniques can become preferable in the consideration for BAT.

- Biodegradable Substances
  BAT is to:
  - remove biodegradable substances from waste water using biological treatment systems as described in Section 3.3.4.3 and Table 4.7 or an appropriate combination of them. When anaerobic processes are applied, a subsequent aerobic treatment step is often required
  - use biological pretreatment when relevant tributary streams carry a high biodegradable organic load to relieve the final central WWTP, if this is a feasible option. Anaerobic treatment can be a choice to use the energy offered by the generation of methane, which can be combusted. Another advantage of anaerobic pretreatment is the considerable overall reduction of excess activated sludge in the downstream biological WWTP. When COD removal efficiency of the overall waste water treatment processes is high, but the concentration to be discharged is considerable higher than the BAT-associated level in Table 4.8, it is an indication that high-loaded tributary streams may need biological pretreatment
  - use pretreatment or polishing facilities, as described in Table 4.7, if compounds with low biodegradability (but not recalcitrant or toxic compounds) are not sufficiently removed by central biological waste water treatment. Suitable techniques are fixed-bed reactors, which enable a longer residence time and hence higher degradation rates
  - implement nitrogen removal techniques (nitrification / denitrification) as described in Section 3.3.4.3.4 when the waste water contains a relevant nitrogen load, which might cause considerably higher concentrations than the BAT-associated emission level in Table 4.8. Both described techniques are BAT. Under favourable conditions they are easily retrofittable into existing central WWTP. When only tributary streams carry considerable nitrogen loads (ammonium, nitrate, nitrite, Kjeldahl-N) it is preferable to treat those separately, which saves cost because small equipment for nitrification / denitrification is not excessively expensive.

- Central Chemical-mechanical WWTP
  When there are no biodegradable contaminants, it is BAT to:
  - use a combination of chemical treatment (for neutralisation and precipitation of waste water components) and mechanical treatment (for the elimination of undissolved substances, including screening, clarification and filtration) as chemical-mechanical stage.

- Central Biological WWTP
  When a central biological WWTP is used, it is BAT to:
  - avoid the introduction of non-biodegradable waste water pollutants into the central biological treatment plant, when they could cause malfunction of the treatment system and when the plant is not suitable to treat them
    buffer the incoming waste water streams upstream of the treatment section to equalise the contaminant load and to use synergetic effects
  - treat the incoming waste water, as described in Section 3.3.4.3.5, by using a combination of:
    - ➢ primary clarifier with preceding mixing station
    - ➢ one- or two-stage aeration device (basin or tank) with subsequent clarifier
    - ➢ filtration or air flotation to protect the receiving water from excess activated sludge floc not easily separable, e.g. bulking sludge
    - ➢ alternatively to 2nd and 3rd indent: aeration basin or tank with dipped MF- or UF-membrane.
    - ➢ additional option as final treatment a fixed-bed biofilter to treat refractory COD if necessary because of regulatory requirements.

  In general the BAT-associated emission level for BOD after central biological treatment is <20 mg/l. In the case of activated sludge a typical application is a low-loaded biological stage with a daily COD load of ≤0.25 kg/kg sludge

	Chemical reactions			Air oxidation	
	Oxidation	**Reduction**	**Hydrolysis**	**Wet air oxidation**	**Super-critical water oxidation (SCWO)**
Purpose	Conversion of pollutants by H_2O_2 with UV or ferrous salts, O_3, O_3/UV, Cl_2, ClO_2, OCl^-	Conversion of pollutants by SO_2, $NaHSO_3$, $FeSO_4$, NaHS	Reaction of organic and inorganic pollutants with water, breaking into smaller compounds	Reaction with O_2 in aqueous phase, high temperature and high pressure, normally in the presence of catalyst (see Section 3.3.4.2.4)	Wet air oxidation in the super-critical region of water, i.e. pressure >22.1 MPa, temperature >374 °C
Application	Oxidise inorganic material Oxidise organic material to protect biological WWTP or transfer it into biodegradable matter Can replace biological treatment	Reduction of inorganic material	Destruction of substances non-biodegradable into smaller biodegradable compounds Wide concentration range (1 mg/l – 100 g/l)	Oxidise organic compounds Protect biological WWTP against recalcitrant material Transfer refractory COD into biodegradable Can replace biological treatment	Destroy contaminants with low biodegradability and/or high toxicity Can replace biological treatment
Application limits	UV irradiation requires solid-free solutions Careful with Cl-containing oxidation agents and organic pollutants to be treated	Limited number of applications Strict control of pH and ORP	Not suitable for pollutants with low solubility in water	Not recommendable for low COD concentrations Fluoride < 10 mg/l Low salt loads (corrosion)	
Consumables	Oxidation agent Agent to destroy surplus oxidant Energy	Reduction agent Agent to destroy surplus reduction agent Energy	Steam / hot water for heating Chemicals to adjust pH and redox potential Energy	Air or oxygen Energy for temperature and pressure	Air or oxygen Energy for temperature and pressure
Cross-media effects	Cl-containing oxidation agents can create additional AOX with organic pollutants	Off-gas releases need to be ducted to downstream treatment	Release of odorous or volatile substances possible	Aqueous and off-gas releases might need further downstream treatment	Aqueous and off-gas releases might need further downstream treatment
Space requirement					
Achievable performance [% pollutant removal]	TOC: >90 (see Section 3.3.4.2.3)			COD: 60-90 (low pressure) 99 (high pressure) (more see Section 3.3.4.2.4)	organic compounds: >99
Achievable emission levels [mg/l]					
Retrofittability					

Table 4.6: Treatment Techniques Associated with BAT for Contaminants Unsuitable for Biological Treatment

	NF / RO	Adsorption	Extraction
Purpose	Separation of most contaminants	Transfer of soluble pollutants from the water phase to a solid adsorbent	Transfer of soluble pollutants from the water phase into a solvent
Application	Achieving high grade of purity to recycle and re-use the water Concentration increase of contaminants for further treatment requirements Recovery is possible	Remove organic not biodegradable, coloured, odorous and/or toxic pollutants Concentration enrichment for further treatment options (e.g. incineration) Recovery is possible	Remove organic non-biodegradable and/or toxic pollutants at high concentration Pretreatment to adsorption to reduce feed load Recovery is possible Not suitable as final treatment
Application limits	Concentrations with osmotic pressures too high to operate Low thermal and chemical resistance	Low pollutant load, otherwise adsorbent is spent too fast Limited TSS because of clogging Efficiency dependent on physical properties of the pollutant (low efficiency with low molecular mass, high polarity, high solubility)	Waste water preferably free of TSS and emulsions Dependent on suitability of solvent, thus limited applications
Consumables	Chemicals for cleaning High energy requirement	Adsorbent Chemicals for regeneration Energy for pumps and regeneration process (elevated temperature)	Replacement of solvent losses Energy for pumping Energy for subsequent solvent recovery (e.g. distillation / rectification)
Cross-media effects	Concentrate needs further treatment, e.g. extraction, incineration (if not recovered)	Off-gases during regeneration require treatment Regeneration generates residue (if not recovered)	Waste water needs treatment to get rid of dissolved solvent, e.g. stripping Bottom residue from solvent recovery, if not recovered, to incineration Off-gas from extraction and recovery needs waste gas treatment, e.g. adsorption or incineration
Space requirement		Normally at least two columns per application	
Achievable performance [% pollutant removal]	High efficiency (see Section 3.3.4.2.8)	High efficiency, depending on pollutant (see Section 3.3.4.2.9)	Good efficiency for special pollutants with high feed concentration
Achievable emission levels [mg/l]			
Retrofittability			

Table 4.6: continued

	Distillation / rectification	Evaporation	Stripping	Waste water incineration
Purpose	Transferring volatile contaminants from the waste water phase into the vapour phase, the enriched vapour phase condensed afterwards	Distillation of water leaving a concentrate a bottom residue	Transference of volatile pollutants into the gaseous phase by blowing air or steam through the waste water	Thermal oxidation of pollutants and simultaneous evaporation of water, operated with or without catalyst
Application	Recovery of bulk contaminants from waste water Pretreatment to remove the main contaminant before sending it to further treatment Restricted use	Concentration of waste water streams to recycle valuable substances or before thermal exploitation	Removal of volatile organic and inorganic compounds Recovery is possible	Removal of harmful or inhibitory pollutant that cannot be treated otherwise or is not sufficiently concentrated to make incineration self-sustaining Abatement technology
Application limits	Large feed concentration required Boiling point difference between water and volatile pollutant needs to be large enough	Avoid foam-generating substances Not applicable to volatile pollutants	Liquid needs low TSS content Restricted to volatile pollutants	Halogen and sulphur content require special waste gas treatment
Consumables	Steam for heating Energy	Chemicals when pretreatment is necessary Steam 5-16 kg water/kg steam Energy	Anti-fouling agents When steam used: 0.1-0.3 tonne/m^3 Energy 680 kW/m^3	Supporting fuel (with low TOC concentration) Energy
Cross-media effects	Further treatment required Off-gas needs to be ducted to waste gas treatment, e.g. incineration	Condensate might need further treatment Noise emission	Gas streams need treatment (scrubbing, adsorption, catalytic oxidation, incineration)	With low TOC content high energy consumption Flue gas releases
Space requirements		Comparatively low		
Achievable performance [% pollutant removal]	Good performance for special pollutants under special conditions	Nearly complete pollutant removal, provided no volatile substances are present	Good efficiency (see Section 3.3.4.2.14)	Nearly 100 % removal efficiency of organic compounds
Achievable emission levels [mg/l]				
Retrofittability				
[1] sour water stripper, 30-32 m^3/h				

Table 4.6: continued

	Anaerobic biology	Aerobic biology			
		Activated sludge (mix) / membrane bioreactor	Trickling / percolating filter	Expanded-bed	Biofilter fixed-bed
Purpose	Conversion of organic content by micro-organisms and exclusion of air (oxygen)	Conversion of organic content by micro-organisms in the presence of dissolved oxygen, injected as air or pure oxygen (for details see Section 3.3.4.3.3)			
Application	Pretreatment of high organic load and streams of constant quality	Pretreatment of high organic load Final treatment in tributary streams Used as central WWTP	As part of a central WWTP (first or pretreatement stage) to reduce the most easily degradable contaminants and improve the sludge quality	Pretreatment of high organic loads Final treatment of smaller streams	Direct pretreatment step or polisher after activated sludge process in central WWTP Good conditions for slow-growing micro-organisms
Application limits	Prevention of toxic substances because process is very sensitive	High concentrations, even of non-toxic substances, to be avoided Inhibitor needs to be avoided, though well-adapted micro-organisms can cope with inhibitor concentrations not too high Maximum temperature 30-35 °C Salt concentrations should be <30 g/l			
Consumables	Neutralisation chemicals Energy	Air or oxygen Neutralisation chemicals Flocculants: 300-550 kg per tonne COD Nutrients: 23-42 kg/tonne COD Energy: 9.5 kWh/m^3	Air Neutralisation chemicals Energy	Air Neutralisation chemicals Energy	Air Neutralisation chemicals (when used as pretreatment) Energy
Cross-media effects	Biogas with 70 % CH_4 can be used as combustible gas Only 10 % of excess sludge compared with aerobic biology	Excess sludge about 10 times the amount from anaerobic biology, needs treatment High energy input because of aeration Emission of odour and noise	Excess sludge	Excess sludge	Excess sludge No emission of odour
Space requirements	Less than aerobic treatment	Large for central WWTP	Comparatively small	Comparatively small	Comparatively small
Achievable performance [% pollutant removal]	COD: 75-90 in combination with aerobic COD: 95-97 BOD: 99-99.8	BOD: 97-99.5 COD: 76-96 90-96 (membrane) Phenol index: >99 total inorg. N: 82 (membrane) NH_4-N: 96 (membrane)	BOD: 40-90 (1-stage) 85-95 (2-stage)	BOD: >98 COD: 90	refractory COD: 26-68 Phenol index: 75-98 AOX: 55-98 total inorg. N: 4-50
Achievable emission levels [mg/l]		TSS: 10 (central WWTP)			
Retrofittability	Need of gas vessels or flare to cope with methane	dependent on size	easy	easy	easy

Table 4.7: Treatment Techniques Associated With BAT for Biological Treatment Techniques

- Waste Water Discharge into Surface Water
  After the treatment procedures mentioned in the preceding sections of this chapter the treated waste water is discharged into a receiving water body (river, lake or sea).

  BAT is a suitable combination of:
  - avoiding a discharge situation such as excessive hydraulic load or toxic waste water that can cause damage to the river bed, the embankment or the biosphere of the receiving water
  - choosing, whenever it is possible, a discharge point into surface water where the waste water is most efficiently dispersed. This minimises the impact on the aqueous biosphere. This measure is not intended to replace treatment techniques
  - balancing waste water not coming from a central WWTP to reduce the impact on the receiving water body and to meet discharge requirements before discharging it
  - implementing a monitoring system to check the water discharge with adequate monitoring frequency (e.g. between 8 and 24-hours sampling)
  - performing toxicity assessment as a complementary tool with the aim of obtaining (more) information on the effectiveness of the control measures and/or on the hazard assessment for the receiving water body. The application of toxicity assessment, such as the actual need, the methods to be used and programming should be determined on a case-by-case basis.

  BAT-associated emission levels for final waste water discharge into surface water are listed in Table 4.8. These values are to understand as emission without dilution with rainwater and/or uncontaminated cooling water. For a better comparability of strategies with or without central biological WWTP, COD-performance is based on the raw contaminant load, i.e. the load before treatment and recycling / recovery procedures.

Parameter [a]	Performance rates [%]	Emission levels [mg/l] [b]
TSS		10-20 [c]
COD	76-96 [d]	30–250
total inorganic N [e]		5-25
total P		0.5-1.5 [f]
AOX		
[a] for BOD see preceding section on central biological treatment [b] daily average, exception TSS [c] monthly average [d] low performance rates for low contaminant concentrations [e] sum of NH_4-N, NO_2-N and NO_3-N (a more recommendable parameter would be total N. Because of the lack of information on total N, total inorganic N is used here) [f] lower range from nutrient feed in biological WWTP, upper range from production processes		

Table 4.8: BAT-associated Emission Levels for Final Waste Water Discharge into a Receiving Water

No BAT-associated emission levels for heavy metals could be identified that would represent the chemical sector as a whole. The reasons for this situation include:

➢ achievable emission levels of heavy metals after treatment at source are highly dependent on the production process where they are produced
➢ the levels depend on the actual waste water matrix
➢ the discharge concentrations depend on the site-specific waste water mixture from the various production processes, since there exists no further treatment after treatment at source.

As compensation for the lack of BAT-associated emission levels for waste water discharge of heavy metals, examples of such discharges are given in Annex 7.6.4. These examples are meant to show the range of heavy metal emissions from chemical sites of various complexities.

Split view

One Member State insists on naming BAT-associated emission levels for heavy metals based on the examples given in Annex 7.6.4. In their view, when following the strategy of prevention, pretreatment and central treatment as outlined above (see section on heavy metals), it is possible to name BAT-associated emission values for heavy metals which are valid for many chemical sites. The following long term mean values (yearly of 24 h-mixed samples) in some examples of chemical sites at the discharge point/last waste water treatment stage could be reached (without dilution of the waste water with rain and cooling water): Cd $0.02 - 0.833$ µg/l; Hg $0.01 - 0.84$ µg/l; Pb $10 - 100$ µg/l; Cr 10 - 30 µg/l; Cu $20 - 60$ µg/l; Ni $10 - 80$ µg/l; Zn $4 - 174$ µg/l. They further state that the values are influenced by the portion of productions relevant to heavy metals and hence are dependent on the production mix, which can cause higher values in special cases, especially in fine chemicals production. With regard to releases into public sewerage systems, the effect of the WWTP would have to be taken into account in so far as it would be ensured that the heavy metals are not shifted to other media.

The TWG did not follow this request, stating that it would not be useful to name BAT-associated emission levels which are influenced by particular combinations of waste water streams on individual production sites, resulting in values which might or might not be valid in real-life cases. A split view is therefore recorded.

The situation with BAT-associated emission levels of AOX is comparable to that with heavy metals. The specific production-mix on a given site greatly influences the amount of AOX discharged, hence levels valid for the chemical sector as a whole are not obtainable. Further more, AOX is not yet a regulatory parameter in most Member States. This might be the reason why only one Member State reported AOX data for final waste water discharge. AOX will have to be reported routinely under EPER by the year 2003. Thus, the duty to routinely monitor and report AOX might be a driver to make emission levels available from that time on. Until then, however, the TWG cannot come to a conclusion on BAT-associated emission levels for AOX. Nevertheless, the necessity for this parameter is emphasised.

Split view

One Member State insists on naming BAT-associated emission levels for AOX based on the examples given in Annex 7.6.2. They state that in this Member State on some chemical sites with production of chloro-organic chemicals and central waste water treatment plants, AOX emission levels between 0.16 and 1.7 mg/l are achieved.

The TWG did not follow this request. The examples presented (see Annex 7.6.2) were interpreted as consisting of different statistical data sets which did not allow naming BAT-associated emission levels. It was even mentioned that one of the lowest AOX emission values reported as examples represented poor performance, whereas the highest emission value came from a site with very good performance. Under these conditions the TWG saw it to be unsuitable to give BAT-associated emission levels for AOX. A split view is therefore recorded.

The BAT-associated emission levels listed in Table 4.8 reflect the emission levels after central biological treatment. When the waste water is ducted to a municipal WWTP, it needs to be demonstrated by, e.g. appropriate laboratory tests or other knowledge, that equivalent results can be achieved. The decentralised treatment strategy is equivalent to final biological treatment when it achieves comparable results.

- BAT for Sludge Treatment
  When sludge from waste water facilities is treated on the chemical industry site, it is BAT to:
  - operate the techniques described in Section 3.4, also taking into account landfilling
  - concentrate sludge using the techniques described in Section 3.4.1
  - stabilise sludge for further treatment or disposal using the techniques described in Section 3.4.2
  - use waste energy from chemical production processes as far as possible when thermal sludge treatment, e.g. drying, as described in Section 3.4.3 is operated
  - operate appropriate waste gas treatment when sludge incineration is used as described in Section 3.4.3.

  Off-site treatment is not taken into account because it is not within the scope of the document. This is by no means a BAT conclusion against off-site treatment by third-party contractors.

4.3.2 Waste Gas Section

This section is devoted to the determination of BAT for waste gas treatment on a chemical industry site.

BAT for Process-integrated Measures
As with waste water, process-integrated measures are the preferred method for preventing or reducing the amount of waste gas and exhaust air contamination, but they are generally production- or process-specific and their applicability requires special assessment, which is within the scope of the vertical BREFs on the chemical and related sectors. Conclusions on BAT for process-integrated measures in this document therefore refer to the general need to implement these measures within a production line.

BAT is to:
- use process-integrated measures in preference to end-of-pipe techniques when there is a choice (e.g. in the case of NO_x from combustion processes, the use of primary reduction techniques such as low-NO_x burners, in preference to secondary treatment techniques)
- assess existing production installations for options of retrofitting process-integrated measures and implement them when feasible or at latest when the installation undergoes major alterations. The observation of safety rules is a crucial point when assessing existing production lines for retrofitting options, because some might not allow the implementation of process-integrated measures due to explosion or corrosion risk
- assess existing production installations for options of source reduction of gaseous contaminants and implement these options if feasible (also under safety conditions). Contaminant reduction at source reduces the amount of waste gas to be treated. Large amounts of unnecessary waste gas mean installing larger equipment than necessary, which is not cost-effective
- consider as far as possible all options for source reduction when planning a new installation or major alterations.

BAT for Waste Gas Collection
Waste gas collection systems are installed to route gaseous emissions to treatment systems. They consist of the emission source enclosure, vents and pipes.

BAT is to:
- minimise the gas flow rate to the control unit by encasing the emission sources as far as possible. However, process operability, safety issues, product quality and hygiene concerns take precedence, as mentioned in Section 2.2.2.4.2
- prevent explosion risk by:

- installing a flammability detector inside the collection system when the risk of occurrence of a flammable mixture is significant
- keeping the gas mixture securely below the LEL by adding air sufficient to limit it to 25 % of LEL, by adding inert gas, such as nitrogen, instead of air or by working under inert atmosphere in the production vessel. The other option is to keep the gas mixture securely above HEL.

- install appropriate equipment to prevent the ignition of flammable gas-oxygen mixtures or minimise its effects, such as detonation arrestors and seal drums.

BAT for Waste Gas Treatment

The approach to reaching BAT conclusions follows the pathway of pollutants as in Section 3.5 and illustrated in Figure 3.45. Regional issues, such as climate, availability of water, energy, raw material and/or existence of waste disposal or treatment facilities, shortage of water, energy or raw material, inaccessibility of the site or difficulties of waste disposal, can render commonly used techniques unsuitable for a chemical industry site, which may require treatment techniques to be especially developed.

According to treatment, the sources for waste gases are distinguished as:

- low-temperature sources, such as production processes, handling of chemicals (including storage activities causing emissions), work-up of products
- high-temperature sources, such as combustion processes, which include facilities such as boilers, power plants, process incinerators and thermal and catalytic oxidisers.

The releases of both groups have special contaminants to consider. The first group can consist of:
- dust alone, i.e. solid raw material or products finely dispersed in air
- VOC from compounds used in production or evaporated from a tank, with or without dusty content
- inorganic volatile compounds from production or work-up, with or without dusty content
- mixture of VOC and inorganic compounds, with or without dusty content
- mists.

The order of treatment techniques used in these cases is:
- 1st step: remove considerable amounts of solid material or mists before further treatment of gaseous components if this treatment is not suitable for high dust or mist concentrations
- 2nd step: remove the gaseous pollutants
- 3rd step: if the second step cannot achieve the required emission levels, further abatement is necessary as a final polishing stage.

The second group – high-temperature processes – consists of a mixture of:
- particulate matter
- halogen compounds (mainly HCl, HF and Cl_2)
- carbon monoxide
- sulphur oxides (mainly SO_2)
- NO_x
- possibly dioxins.

BAT for treatment of waste gases originating from production processes, material handling and product work-up

- Dust
  BAT is an adequate combination of:
  - removing particulate matter and aerosols / droplets from waste gas streams, using techniques or combinations of techniques described in Section 3.5.3 and Table 4.9 according to the given situation

- using pretreatment to prevent final facilities from damage or overloading. Damage is done by e.g. hard or large particles or particles that clog filters, adsorption columns, scrubber surfaces, membrane surfaces, catalysts
- using high-efficiency techniques to remove considerable amounts of submicron particulate matter
- implementing downstream mist filter when wet scrubbers are used as final treatment device (with a HEAF the use of a mist filter downstream is already included)
- operating techniques in their appropriate pressure range (a/c ratio, flow rate/surface ratio) to prevent damage to the vessel or dust emissions from vessel leaks
- using material recovery wherever feasible
- taking into account energy consumption by critically assessing the use of energy-intensive techniques and comparing the results with energy-free or low-energy techniques
- taking into account water consumption, most of all in regions where water shortage is an issue. The use of wet scrubbing needs to be assessed and the results compared with water-free techniques
- using scrubbing water in a recycle mode with a maximum number of recycles when it is feasible and does not lead to abrasion or corrosion in the scrubber vessel.

- VOC
  BAT is an appropriate combination of:
  - removing VOC from waste gas streams, using techniques (or a combination thereof) described in Sections 3.5.1 and 3.5.2 and listed in Table 4.10.
  - using recovery techniques such as condensation, membrane separation or adsorption whenever feasible to regain raw material and solvents. Waste gas streams with high VOC concentrations are best pretreated by techniques such as condensation or membrane separation / condensation to recover the main load before sending them to adsorption, wet scrubbing or combustion. In the case of adsorption and combustion this can also be a safety issue, keeping VOC concentration below 25 % LEL
  - taking into account water consumption (process and cooling water) with techniques such as wet scrubbing, condensation (when water is used as cooling medium), adsorption (when water is used in regeneration processes or to cool the waste gas stream before entering the adsorption column) or biological treatment (where water is used as reaction medium). The use of those techniques needs to be assessed and compared with the results of water-free techniques. When water shortage is an important issue these techniques can become unsuitable under special local conditions
  - using abatement techniques only when recovery is not feasible, e.g. because of very low VOC concentrations causing expenditure of energy or material disproportionate to the ecological benefit derived
  - assessing existing waste gas abatement if material recovery is feasible and implement the appropriate technique, if the response is positive
  - preferring biological treatment of low-concentration waste gas streams to incineration processes if applicable (i.e. when content and composition of the waste gas as well as climate characteristics are suitable, see Section 3.5.2.1) and if water saving allows it. The consumption of supporting fuel for the incineration of low VOC concentrations is a disadvantage that can, however, be counterbalanced if no other treatment is feasible to achieve the environmental targets set, for example, by legal restrictions
  - using combustion of waste gas streams, especially when autothermal operation is possible, when hazardous compounds need to be abated or when other, likewise efficient techniques are not available
  - preferring catalytic oxidation whenever feasible and ecologically favourable compared to thermal oxidation. The much lower NO_x-content in the emitted flue gas, the lower operation temperature and energy requirement may render it more advantageous than thermal oxidation
  - operating combustion techniques with energy recovery (gas engine, regenerative and recuperative incinerator) when feasible

- using thermal incineration when catalytic incineration is not applicable, e.g. because of poisonous effects of the waste gas content, or the lower destruction efficiency of catalytic oxidation is not sufficient to abate the respective VOC appropriately
- implementing combustion exhaust gas treatment after incineration when considerable amounts of exhaust gas contaminants are to be expected because of the waste gas contaminants exposed to incineration, such as SO_2, HCl, NO_x, whereas dioxins are normally not an issue in waste gas combustion
- using flaring only to dispose safely of surplus combustible gases from, e.g. maintenance events, upset systems or remote vents without connection to abatement systems
- using ground flares only when there are no hazardous substances expected in the flue gas. When flares are needed, despite the foregoing conclusion, the options for heat recovery and low-NO_x burning have to be assessed and, when the result is positive, the respective equipment has to be implemented.

- Other compounds than VOCs
  BAT is to
  - remove these waste gas pollutants (hydrogen halides, Cl_2, SO_2, H_2S, CS_2, COS, NH_3, HCN, NO_x, CO, Hg) by applying the appropriate techniques listed in Table 4.10. Appropriate techniques are:
    ➢ wet scrubbing (water, acidic or alkaline solution) for hydrogen halides, Cl_2, SO_2, H_2S, NH_3
    ➢ scrubbing with non-aqueous solvent for CS_2, COS
    ➢ adsorption for CS_2, COS, Hg
    ➢ biological gas treatment for NH_3, H_2S, CS_2
    ➢ incineration for H_2S, CS_2, COS, HCN, CO
    ➢ SNCR or SCR for NO_x.
  - recover hydrogen chloride whenever feasible by using water as scrubbing medium in the first scrubbing stage to produce a solution of hydrochloric acid to be used as raw material
  - recover NH_3 whenever feasible, using a technique that enables its recovery.

  The techniques to consider as BAT are listed in Table 4.10.

The TWG did not come to conclusions on BAT-associated emission levels for waste gases from production processes. It was recommended to leave this task to the appropriate vertical BREFs, because these levels were identified as process-specific and hence no levels could be given that consider the whole chemical sector.

	Separator	Cyclone (dry and wet)	ESP (dry and wet)	Wet scrubber [a]
Purpose	Gravity separation	Gravity separation supported by centrifugal forces	Separation by electric field	Mass transfer from gaseous phase into liquid phase
Application	Preliminary (not stand-alone technique) to various filter systems to prevent entrainment or abrasion Not suitable for flue gas Recovery possible in principle	Control of PM as precleaners for ESP or fabric filters (not stand-alone technique) After spray drying, crushing, grinding and calcining operations Suitable for flue gas Recovery possible in principle	Control of PM as final treatment After boilers, in chemical manufacture, refineries, incineration and injection systems Applicable for wet and sticky material, flammable mixtures (see Section 3.5.3.3), acid mists (wet ESP) Recovery possible in principle	Control of PM as final treatment Dependent on variant for PM down to $<PM_{2.5}$ and PM_{HAP} Application see Table 3.16 Recovery possible in principle Also applicable to gas removal (VOC, inorganic compounds)
Application limits	Flow rate: up to 100000 Nm^3/h Dust content: no restriction Particulate size: $> PM_{50}$, but also down to PM_{10} Temperature dependent on vessel material, normally up to 540 °C	Flow rate: up to 100000 Nm^3/h (single unit) up to 180000 Nm^3/h (multiple units) Dust content: up to 16000 g/Nm^3 Particulate size: down to $PM_{2.5}$ Temperature dependent on vessel material, can be >1200 °C	Flow rate: very high, dependent on variant up to 1800000 Nm^3/h Dust content: 1-10 g/Nm^3 (wire-pipe) 2-110 g/Nm^3 (wire-plate) Particulate size: $>PM_{1.0}$ Temperature: up to 700 °C (dry) <90 °C (wet) Resistivity: $5x10^3$-$2x10^{10}$ ohm cm Not applicable to Hg	Flow rate: dependent on variant up to 170000 Nm^3/h Dust content: see Table 3.16 High dust loading with plate scrubber, spray tower, impingement-entrainment scrubber, venturi-scrubber Temperature: see Table 3.16
Consumables	Energy: only for fan Pressure drop: <0.5 kPa	Energy: 0.25-1.5 kWh/1000 Nm^3 Pressure drop: 0.5-2.5 kPa	Water with wet ESP Energy: 0.5-2 kWh/1000 Nm^3 Pressure drop: 0.05-0.5 kPa	Scrubbing water: 0.5-5 l/Nm^3 Energy: 1-6 kWh/1000 Nm^3 Pressure drop: 3-20 kPa (venturi)
Cross-media effects	Disposal of dust	Disposal of dust Emission of noise	Disposal of dust or waste water (wet ESP)	Suspension needing further separation treatment Emission of noise
Space requirement	Low			
Achievable performance [% pollutant removal]	10-90 (dependent on particle size and feed concentration)	PM 80-99 PM_{10} 60-95 PM_5 80-95 $PM_{2.5}$ 20-70	PM 99-99.2 PM_{10} 97.1-99.4 $PM_{2.5}$ 96-99.2 (dry and wet ESP)	PM 50-99 depending on variant VOC 50-95 depending on variant SO_2 80-99 (see Table 3.17)
Achievable emission levels [mg/Nm^3]			dust: 5-15	
Retrofittability	Normally integrated			
[a] details in the corresponding chapter				

Table 4.9: Treatment Techniques Associated With BAT for Particulate Treatment from Normal Waste Gas Streams

	Fabric filter	Two-stage dust filter	HEPA-filter	HEAF	Mist filter
Purpose	Filter technique, filter cake improving efficiency	Filter technique, material metal gauze, metal mesh	Filter technique, material paper or matted glass fibre with high packing density	Filter technique, flat-bed filter	Filter technique, mesh pad filters of metallic or synthetic monofilament
Application	Removal of PM <$PM_{2.5}$ as final treatment Collect PM unsuitable for ESP With injection systems (flue gas) Suitable for flue gas Recovery possible in principle	Removal of PM as final treatment With injection systems (flue gas) Suitable for flue gas Recovery possible in principle	Removal of submicron PM between $PM_{0.12}$ and $PM_{0.3}$ Downstream after ESP or fabric filters as final treatment when high collection efficiency required Recovery possible in principle	Removal of aerosols such as oil, plasticisers, condensable VOC Downstream mist filter and droplet separator required	Removal of aerosols and droplets Protection of downstream equipment to prevent wear and friction Primary collection device to leave smaller particles to other treatment techniques After wet scrubber
Application limits	Large particles to be collected upstream Flow rate: up to 1800000 Nm^3/h Temperature dependent on fabric (see Table 3.18), above dew point Dust content up to 230 g/Nm^3 Sticky dust to be avoided	Flow rate: up to 75000 Nm^3/h per module Temperature: up to 400 °C Dust content: no restrictions	Flow rate: up to 3600 Nm^3/h per module Temperature: <200 °C <530 °C (ceramic) above dew point Dust content: 1-30 g/Nm^3 Avoid moist environment	Flow rate up to 25000 Nm^3/h	Flow rate up to 150000 Nm^3/h Temperature <170 °C Dust content <1 mg/Nm^3
Consumables	Compressed air Energy: 0.2-2 kWh/1000 Nm^3 Pressure drop: 0.5-2.5 kPa 5-50 kPa (ceramic)	Compressed air Energy: 1.5 kWh/1000 Nm^3 Pressure drop: 0.5-2.5 kPa	Energy: <0.1 kWh/1000 Nm^3 Pressure drop: 0.05-0.25 kPa	Energy: <0.1 kWh/1000 Nm^3 Pressure drop: 8 kPa	Energy Pressure drop 2.5-9.0 kPa
Cross-media effects	Dust disposal	Dust disposal	Disposal of loaded filter modules	Disposal of loaded filter rolls	Disposal of washing liquid and loaded filter material
Space requirement					
Achievable performance [% pollutant removal]	dust 99-99.9		$PM_{0.01}$ >99.99 $PM_{0.1}$ nearly completely	droplets 99 aerosols 99	dust 99 aerosols 99
Achievable emission levels [mg/Nm^3]	dust 2-10 1 (ceramic filter)	dust 1 (independent of feed)	PM 0.0001		

Table 4.9: continued

	Wet scrubbing (see Section 3.5.1.4)	Adsorption	Condensation	Membrane separation
Purpose	Mass transfer from gaseous phase into liquid phase	Material transfer from gaseous phase to solid surface	Liquefaction by cooling	Permeation through membrane surface
Application	Control of VOC, inorganic compounds and also of dust, dependent on variant and scrubber liquid (water, acidic and alkaline solution), 1- or 2-stage Application see Section 3.5.1.4 In principle, recovery possible by desorption	Removal of VOC, odorous substances, dioxins, etc. Guard filter after final treatment Different variants, see Section 0 In principle recovery possible after regeneration	Recovery of VOC from concentrated waste gas stream Pretreatment before adsorption, scrubbing, abatement systems Post-treatment of enriched gas streams from membranes or waste water stripping	Recovery of VOC or fuel vapours Enrichment of VOC gas streams to make them available for treatment such as condensation or valuable for incineration
Application limits	Flow rates see Section 3.5.1.4 Temperatures best below 40 °C for gas scrubbing with water without chemical reaction Dust load: dependent on variant, see Section 3.5.1.4	Flow rate: up to 100000 Nm^3/h Temperature: <80 °C (GAC) < 250 °C (zeolites) VOC content: <25 % LEL Dust load: low	Flow rate: up to 100000 Nm^3/h <5000 $Nm3$/h (for cryogenic version) Temperature: <80 °C Limitations because of freezing and subsequent blocking Dust load: low (<50 mg/Nm^3)	Flow rate: dependent on membrane surface area Temperature and pressure dependent on membrane material Dust load: very low VOC load: no limit
Consumables	Scrubbing water, cooling water Chemicals (acid, caustic, oxidant) Energy 0.2-1 kWh/1000 Nm^3 Steam for stripping (desorption) Pressure drop 0.4-0.8 kPa	Steam or nitrogen (desorption) Cooling water (condensation) Energy 35-260 kWh/tonne solvent Pressure drop: 2-5 kPa	Cooling medium (air, water, brine, ammonia-brine, liquid nitrogen) Energy: 70 kWh/1000 Nm^3 (crogenic) Pressure drop: 0.1-0.2 kPa	Energy: 250 kWh/1000 Nm^3 Pressure drop: 0.1-1 MPa
Cross-media effects	Waste water to be treated Energy and emission of regeneration	Waste water from regeneration Disposal of adsorbent	Further treatment normally required after condensation	Further treatment of permeate
Space requirement				
Achievable performance [% pollutant removal]	VOC 50-99 inorganic compounds 90-99 SO_2 80-99	VOC 80-95 Odour 80-95 H_2S 80-95		VOC up to 99.9
Achievable emission levels [mg/Nm^3]	HF <1 HCl <10 (<50 with water) SO_2 <40	Hg <0.05 Dioxins <0.1 ng/Nm^3 TEQ	see Section 3.5.1.2	
Retrofittability	relatively easy	relatively easy	see Section 3.5.1.2	

Table 4.10: Treatment Techniques Associated With BAT for Treatment of VOC and Inorganic Compounds from Normal Waste Gas Streams

	Biological treatment (filtration / scrubbing / trickling)	Thermal oxidation	Catalytic oxidation	Gas engine / steam boiler
Purpose	Biological degradation by micro-organisms	Oxidation with oxygen (air) by heating a gas stream above its auto-ignition point	Oxidation with oxygen (air), using catalyst to lower auto-ignition point	Incineration of waste gas to recover energy
Application	Removal of low pollutant concentrations soluble in water: NH_3, amines, hydrocarbons, H_2S, toluene, styrene, odour	Emissions from all VOC sources, most suitable for autothermal VOC concentrations and final treatment for hazardous substances	Same application as thermal incineration, contaminants restricted to non-poisonous ones With or without heat recovery	Waste gas streams suitable for gas engine, downstream generator to produce electricity (see Section 3.5.2.4)
Application limits	see Sections 3.5.2.1 to 3.5.2.3 not suitable for changing content NH_3 can cause problems frost, rain high ambient temperatures affect the filter material	Flow rate: up to about 86000 Nm^3/h Temperature range: 800-1000°C 980-1200 °C (hazardous substances) VOC: <25 % LEL	Flow rate: up to about 86000 Nm^3/h Temperature range: 300-500 °C VOC: <25 % LEL	Relatively low combustion temperature limitations from waste gas com-position when corrosive compounds or precursors are included
Consumables	Water (scrubbing and trickling water) Chemicals (nutrients, pH adjustment) Energy: <1 kWh/1000 Nm^3 Pressure drop: 0.2-2 kPa	Fuel during start-up and non-autothermal conditions Energy: 3-8 kWh/1000 Nm^3 Pressure drop: 1-5 kPa	Fuel during start-up and non-autothermal conditions Energy: 1-2 kWh/1000 Nm^3 Pressure drop: 1-5 kPa	Coupled with steam boiler to produce steam
Cross-media effects	Disposal of filter material Waste water from scrubbing and biotrickling Emission of odour from scrubbing and biotrickling	CO and NO_x in flue gas Cl- and S-content require flue gas treatment dioxins are usually no problem with optimised conditions (see 3.5.2.4)	Very low NO_x in flue gas (about 15 mg/Nm^3) Cl- and S-content require flue gas treatment dioxins are usually no problem	Low combustion temperature with low NO_x CO in flue gas reduced by catalyst
Achievable performance [% pollutant removal]	VOC 75-99 Inorganic 80-95 (all) Odour 70-95 Details see Sections 3.5.2.1 to 3.5.2.3	VOC 95-99	VOC 90-99 CO >98 Odour 80-95	
Achievable emission levels [mg/Nm^3]		TOC 1-4		

Table 4.10: continued

BAT for Combustion Exhaust Gas Treatment
BAT for dust removal is to
- implement ESP or bag filter (after heat exchanger at 120-150 °C) or
- implement catalytic filtration or
- implement wet scrubbing

BAT for removal of HCl, HF and SO_2 is to
- recover them when feasible by using two-stage wet scrubbing, using in the first stage water or acidic solution as scrubber medium in recycle mode to remove HF and HCl, using in the second stage calcium carbonate suspension to remove SO_2 as calcium sulphate (after air injection). Both HCl and calcium sulphate can be recovered as enriched raw hydrochloric acid and gypsum respectively. Two-stage wet scrubbing is also used without material recovery to separate chloride and fluoride ions before desulphurisation or
- remove them by dry or semi-dry or wet sorbent injection as described in Section 3.5.4.1, the generated dust being removed together with the incineration dust. Wet scrubbing, however, is normally the most efficient technique for abatement as well as for recovery.

There are more FGD techniques, mainly used in power plants, which are within the scope of the BREF on large combustion plants.

BAT for removal of NO_x is to
- implement SCR instead of SCNR (at least for larger installations) because it has better removal efficiency and environmental performance (see Section 3.5.4.2). For existing installations which operate SNCR devices, the time to consider exchange might be when major alterations are planned for the incineration plant. Although SCR is BAT in the general sense, there are individual cases (typically smaller installations) where SNCR is the technically and economically best solution. Assessment needs to be made if other measures achieve better overall improvement instead of retrofitting SNCR.

There are more DeNOx processes in use, e.g. several simultaneous removal techniques of SO_2 and NO_x, which are also BAT when they achieve similar performance.

When dioxins can be expected it is BAT to
- abate dioxins by using a GAC filter (adsorption) at the end of flue gas treatment.

Techniques that achieve comparable results (see Table 4.11) are also considered as BAT.

BAT-associated emission levels and reduction performance of combustion exhaust gas treatment are listed in Table 4.11.

Parameter	Emission levels [mg/Nm³] [1]
dust	<5-15
HCl	<10
HF	<1
SO_2	<40-150 [2]
NO_x (gas boilers/heaters)	20-150 [3]
NO_x (liquid boilers/heaters)	55-300 [3]
NH_3 [4]	<5 [5]
dioxins	0.1 ng/Nm³ TEQ

[1] ½ hourly average, reference oxygen content 3 %
[2] lower range for gaseous fuel, upper range for liquid fuel
[3] higher value for small installations, using SNCR
[4] NH_3 slip with SCR
[5] value for new catalysts, but higher NH_3 emissions occur as the catalyst ages

Table 4.11: BAT-associated Emission Levels and Performance Rates for Combustion Exhaust Gas Treatment in the Chemical Sector

5 EMERGING TECHNIQUES

An emerging technique as understood in this document is a technique that has not yet been applied on a commercial basis or outside of pilot plant operation, but that can be expected to be applicable in the future in larger scale-operations in the chemical sector.

The techniques shown below are already operated to a certain degree under specified conditions in other sectors. There is no evidence yet that they have been successfully implemented in the chemical sector under existing working conditions, but they are expected to be so in the future.

BIOLOGICAL SULPHUR DIOXIDE REMOVAL FROM EXHAUST GAS

The biological sulphur dioxide removal system is a combination of a waste gas scrubber (absorber) and a biological waste water treatment facility. In the absorber, the waste gas stream containing sulphur dioxide is brought into contact with washing water. A mixture of sulphite and sulphate is formed. In a subsequent anaerobic biological process, this mixture is converted biologically into sulphide. The ensuing aerobic step converts sulphide into elemental sulphur, which is separated, and the supernatant water recycled to the scrubber.

Because of the presence of sulphide ions, heavy metals are precipitated as sulphides and can be removed as well.

LOW-TEMPERATURE NO$_x$ OXIDATION

The low-temperature NO$_x$ Oxidation is a combination of an oxidation process (ozone as oxidation agent) and gas scrubbing (with water or alkali as scrubbing liquid). Ozone (generated on-site in a high-voltage system) reacts with NO and NO2 in a reactor duct to obtain highly soluble N$_2$O5, which is subsequently removed in a wet gas scrubber by formation of nitric acid. Very low emission levels of NO$_x$, SO$_x$ and HCl are expected (5, 5-10 and 5-10 ppm respectively).

The main environmental issues are the energy need for the ozone generation and, when necessary, for the generation and/or storage of pure dry oxygen, and the need for an essential amount of water as scrubbing liquid.

6 CONCLUDING REMARKS

This chapter covers:

- the timing of the work
- sources and availability of information
- extent of consensus within the TWG
- recommendations for future work.

TIMING OF THE WORK

The work on this BREF took nearly 3 years, the major steps being:

- 12th-14th April 1999: first Technical Working Group (TWG) meeting in Sevilla.
- May 2000: a first draft was sent to the TWG members for consultation, covering Chapters 1 – 3. It included
    - general basic information on waste water and waste gas
    - information on waste water and waste gas management
    - information on common treatment technology, including treatment performance data
    TWG members delivered additional information during the consultation.
- March 2001: a second draft was sent to the TWG members for consultation, covering Chapters 1-5 plus Annexes. Because of the information received as comments from TWG consultation on the first draft and further information sources, the chapters on general information and on management were completely redrafted and additional data were added to the chapter on treatment technology. A chapter on BAT conclusions was included based on the information in the preceding three chapters.
- 27th-29th June 2001: second TWG meeting in Sevilla
    A range of issues, mainly those relating to Chapter 4, BAT conclusions, was discussed in detail. Four split views were recorded, partly because one Member State had the impression that the BAT conclusions on management were too general and should be supported with figures and partly because they wanted BAT-associated emission levels for heavy metals and AOX at the final waste water discharge point, based on the information they had provided.
- August 2001: an excerpt of the redrafted document as the result of the second TWG meeting was sent out to TWG members for final consultation.
- 15th-16th November 2001: the final draft document was presented to DG Environment at the 10th Meeting of the IPPC BAT Information Exchange Forum (IEF) in Brussels.
    The IEF found that the document accurately reflected the exchange of information in the TWG and that it was in line with the BREF Outline and Guide. The document was accepted by DG Environment with some editorial changes.

SOURCES OF INFORMATION AND AVAILABILITY OF INFORMATION

Several sources were used while writing the BREF. The main sources were textbooks, ULLMANN's Encyclopedia of Industrial Chemistry and publications on special techniques. Further information was taken from the internet website of the US Environmental Protection Agency (EPA), providing technical data sheets on waste gas treatment techniques, including information on costs, and the Environmental Technology Best Practice Programme, providing information on several waste water and waste gas control techniques.

Single Member States, European industry organisations (CEFIC and CONCAWE) and one chemical company supplied BAT documents, guidance notes, technical background material and real-life performance data on various issues, which are quoted in the Reference list of this document. Some manufacturers delivered information on their technology. Most of the documents were provided at very late stages of the work. The first and second documents on the chemical sector arrived in November / December 1999, others between the issuing of the first draft and a date one week before the second meeting.

EXTENT OF CONSENSUS

This BREF has met support from the majority of the TWG members, although on four BAT conclusions split views were noted. One Member State expressed their opinion on the lack of close definitions for the BAT conclusions on environmental management and of BAT-associated emission levels for heavy metals and AOX at the final discharge point. Details are found in Chapter 4.

RECOMMENDATION FOR FUTURE WORK

The main drawback in the information exchange was the lack of information on useful performance data in combination with operational data (such as energy consumption and use, use of auxiliary substances, cross-media effects). When, to name one example, the expert group concluded that emission levels for heavy metal control techniques, covering the whole chemical sector, do not exist, because those levels depend strongly on the source process, no data were made available that could support their view. Thus, the BREF cannot present achievable emission levels – or BAT-associated emission levels – for heavy metal control techniques.

There is a notable lack of information on cost data. Since the chemical industry (except CONCAWE) did not deliver any data, the BREF resorted to the existing sources, mainly the US-EPA data sheets, the Dutch paper on BAT for waste gas treatment and the VITO database on waste water techniques, still leaving big gaps. Thus, no sufficiently qualified, reliable and comparable cost data have yet been made available. It was generally not known what exactly was included within the cost data from the named sources and how the calculation was performed. The relative cost data (per m^3 waste water, per 1000 Nm^3 waste gas or per mass unit pollutant) presented in this BREF, therefore, are to be seen as indicators of magnitude and not as exact figures. The relatively few cost data in the BREF are delivered as they were received, i.e. national currencies are not converted into Euros. It is suggested to leave it to the BREF on economics and cross-media effects to make a decision on a conversion system for cost data. To fill and correct this gap will be a task for future work.

The obvious recommendation for future work is therefore to fill all the gaps still existing within the present BREF. Issues that will merit fuller consideration when this document is reviewed include:

- focus on technical performance, not just on performance rates and emission levels, giving more attention to cross-media and energy issues and providing the necessary data
- examples of real-life treatment systems in the context of the joint operation of the various techniques on chemical sites, providing the necessary data and rationale for the operator's decision, not just a list of the existing treatment plants or statements using "good" figures as examples for management decisions without a proper, understandable rationale or explanation
- selected examples of good engineering practice should be given as a demonstration of what is behind terms such as 'good manufacturing practice', 'adequate safety issues' or 'risk assessment'
- focus on the main objective of the BREF process, i.e. to support and give guidance to a regulator reaching a decision on a permit, not providing her/him only with a list of techniques ('shopping list') or trying to steer her/him towards a decision. Taking into account the preceeding three bullets might be helpful
- a more consistent approach to measurement of total nitrogen would assist comparison and conclusions in this respect. In this work data was primarily available for total inorganic nitrogen which is not a universally accepted parameter.

The EC is launching and supporting, through its RTD programmes, a series of projects dealing with clean technologies, emerging effluent treatment and recycling technologies and management strategies. Potentially these projects could provide a useful contribution to future BREF reviews. Readers are therefore invited to inform the EIPPCB of any research results which are relevant to the scope of this document (see also the preface of this document).

As to reviewing the BREF, the recommendation is to wait until all the vertical BREFs in the chemical sector are finalised. This will ensure that all the necessary information for the horizontal BREF has been collected before the review process starts. This does not mean, however, that it would be sufficient to give the same input to the Common Waste Water and Waste Gas BREF as to the vertical BREFs and simply repeat the results. To do that would call into serious question the need for a horizontal waste water / waste gas BREF.

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7 ANNEXES

The Annexes supplement the information provided in the document. They are:

Annex I   Joint Operation of Industrial and Municipal WWTP
Annex II   Pinch Technology as Example of EFMA
Annex III   Monitoring of a Central Biological WWTP
Annex IV   Monitoring Standards
Annex V   Pollution Incident Response Plan
Annex VI   Examples of Waste Water Treatment and Waste Gas Treatment
Annex VII   Legislation Applied to Waste Water and Waste Gas in the Chemical Sector

7.1 Annex I. Joint Operation of Industrial and Municipal WWTP

Conditions of Joint Treatment of Municipal and Industrial Waste Water (Example from France)

The general case in the chemical industry in France is that effluents are treated on-site. Joint municipal and industrial waste water treatment, however, is sometimes encountered, e.g. in biochemical productions (such as vitamins or antibiotics via biochemical pathways), and in formulation and conditioning activities for which the flow rate and the load of the effluent remain manageable by a municipal treatment plant. In this case, a study of the impact of industrial streams on the municipal treatment plant (impact on operation and sludge disposal) is done and an "industrial release agreement" is signed between industry and the local waste water management authority.

A Municipal Decree is issued that generally contains the following main provisions of the agreement:
- pH of the effluent comprised between 5.5 and 8.5 (eventually 9.5)
- temperature of the effluent <30°C
- effluent not containing substances hazardous to the personnel of the municipal WWTP, the collecting network, the WWTP itself and its operation, the environment downstream of the WWTP and the further handling of the waste water sludge
- either maximum flows and pollution loads to be discharged (BOD, COD, TSS, total Kjeldahl-N, (NO_2+NO_3)-N, non-biodegradable N, nitrification inhibitors, total P, other substances that might impact on the operation of the WWTP and the further handling of sludge) or provisions concerning pretreatment / recovery installations to be operated by the industrial site prior to discharge in the municipal sewer
- financial conditions

The discharge convention further describes the technical conditions of the discharge agreement fixed by the municipal decree. These generally include the following:
- provisions concerning the private network of the industrial site, in order to prevent unwanted discharge to the public network
- description of any private pretreatment facilities that have to be operated in order to handle properly flow variations, start-up / shut down of the plant, have to be monitored (monitoring results to be sent to the municipal authority)
- technical conditions for the connections between private and public networks
- various obligations of the industrial site, such as:

- no dilution of the effluent
- exceptionally high discharges (e.g. in case of maintenance) have to be smoothed over 24 hours
- effluents need to be monitored, connections periodically inspected. The local authority can monitor the effluent on their own initiative and check the monitoring equipment in cooperation with the industrial operator.
- water consumption is monitored and the results sent to the local authorities
- action plan for an emergency (e.g. the closure of connections between municipal sewage system and industrial site)
- the obligations of the local authority are:
  - to accept the discharge when it is within the limits fixed in the agreement
  - to inform the industrial site in the case of operational problems at the municipal WWTP
- economic and administrative questions

Example of Cooperation Between Municipal and Industrial WWTP with Positive Synergetic Effect (Germany)

In Section 1.3.2.1, it was mentioned that there are normally neither advantages nor disadvantages with the joint treatment of industrial and municipal waste water. An example where this is not the case is described briefly here.

In the past, two WWTPs – one a municipal and the other a chemical industry plant – each operating a central biological treatment, had separate discharge points into a small receiving river. They now operate jointly in the following manner:

- nitrogen-rich and poorly degradable filtrate from sludge treatment devices of the municipal WWTP is treated in the industrial WWTP, which has micro-organisms adapted to cope with this kind of waste water
- in return, the industrial WWTP sends an equal amount of waste water to the municipal WWTP

Figure 7.1 and Figure 7.2 show, respectively, the processes before and after the move to joint operation.

This cooperation has economic and environmental advantages. The use of equipment on only one site saves capital and the mutual discharge reduces the nitrogen load (sum of ammonium, nitrite and nitrate) into the receiving river by 1000 kg per day, compared to the separated discharges before.

7.2   Annex II. Example of EFMA: Pinch Technology

A widespread and well known EMFA tool is Pinch technology, used to optimise production processes, save energy and water consumption and decrease the impact of waste discharge. Two of those – the optimisation of water consumption and waste discharge – are within the scope of this BREF. Optimisation of production processes is covered by vertical BREFs and other references [cww/tm/132].

Pinch Technology is a methodology for optimising the consumption of consumables in processes and on sites by introducing process integration techniques. It was primarily used as an energy saving tool to improve thermal efficiency in the chemical and process industries. Recently this method has been transferred to water and waste (water) minimisation.
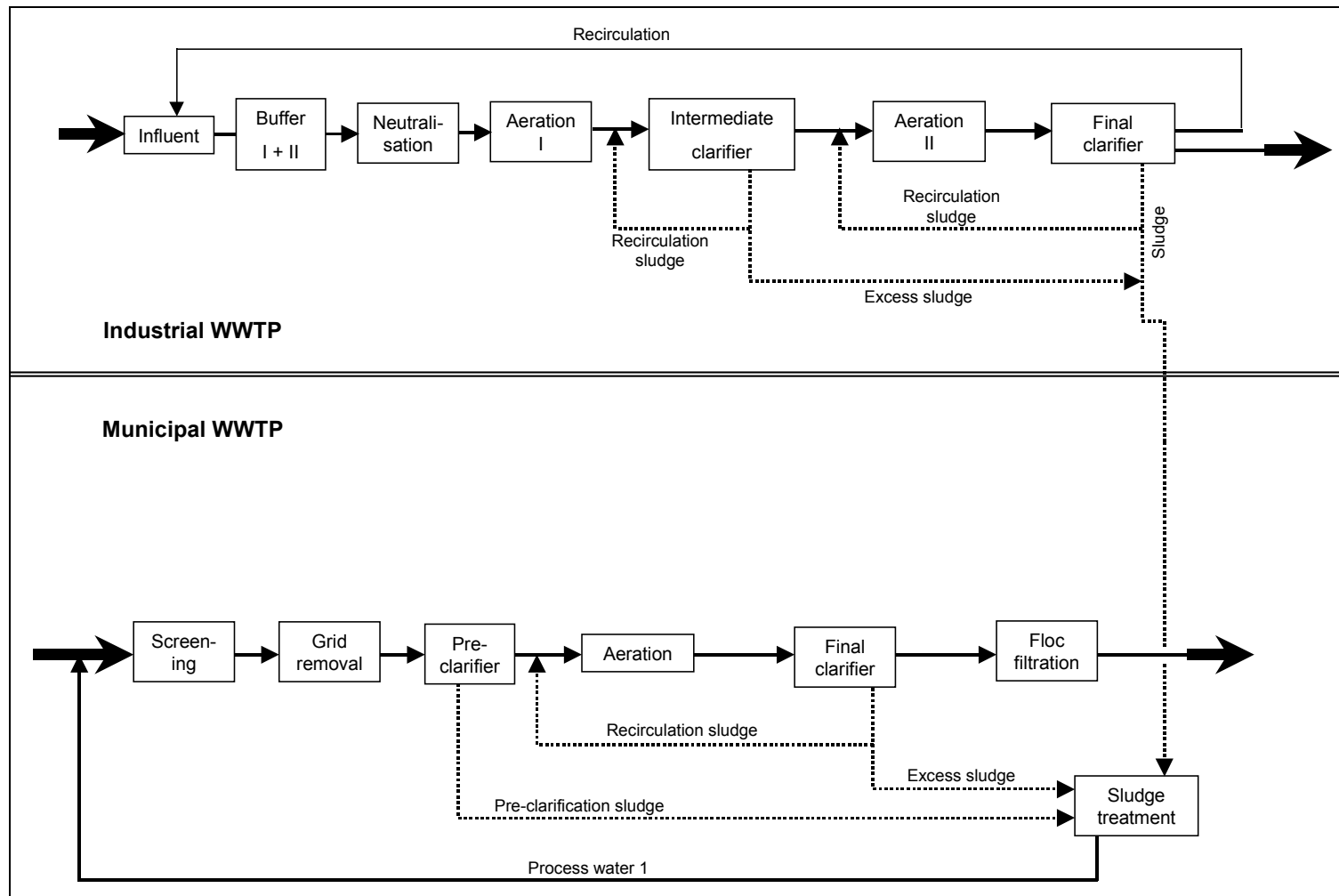
Figure 7.1: Cooperation Between an Industrial and a Municipal WWTP: Situation Before
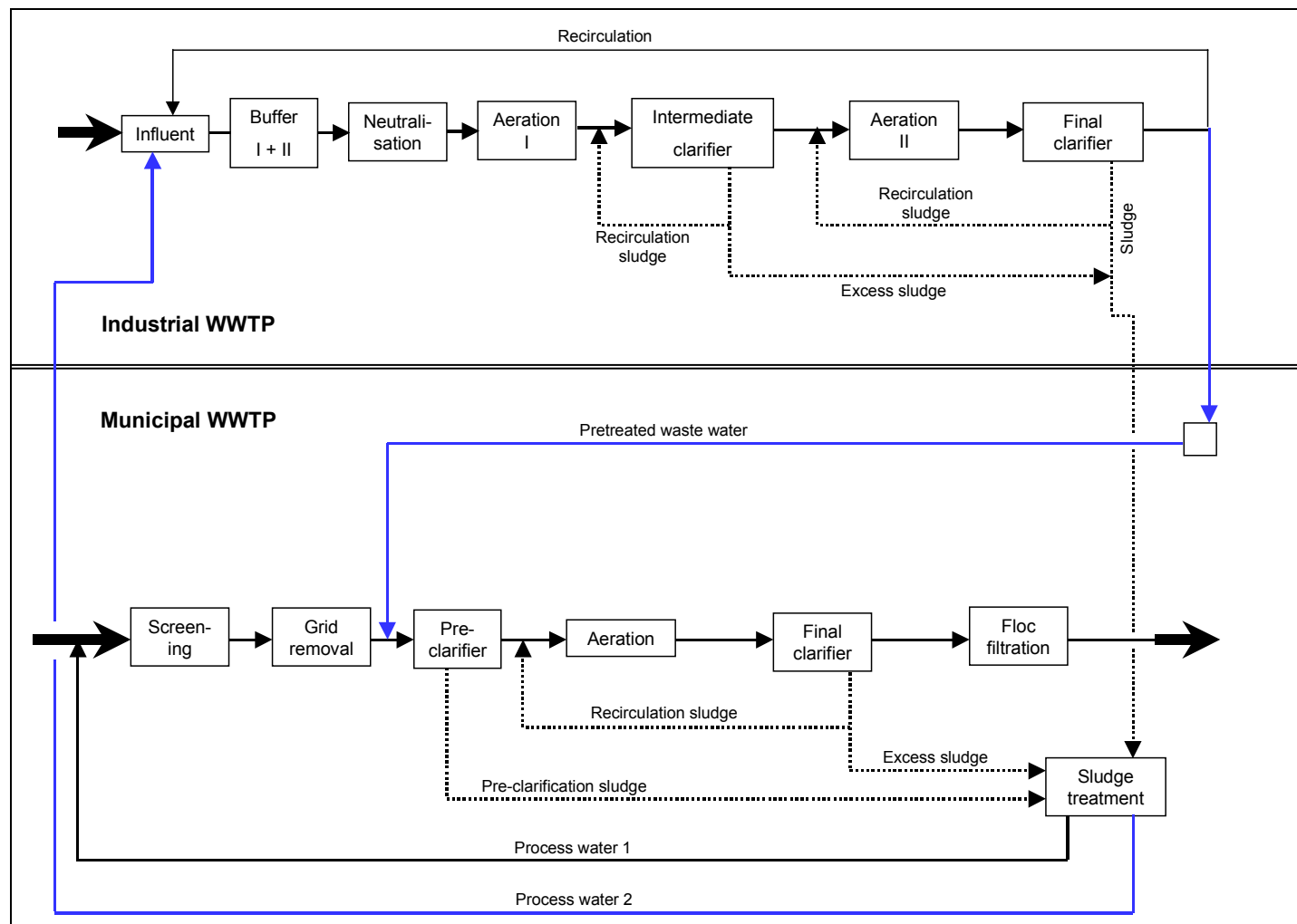
Figure 7.2: Cooperation Between an Industrial and a Municipal WWTP: New Situation

Its concept is to define and find water saving potential by, e.g. piping and control changes, and to minimise waste water discharge by process modifications, thus enabling selective waste water regeneration and reducing treatment costs. It is also used to design or re-design distributed effluent treatment so as to lower capital costs by reducing the hydraulic load of a central WWTP.

Its application can be broken down into four steps [cww/tm/86]:

Step 1:
Drawing a flowsheet of the entire water system (supply, discharge) that shows all places where water is used, and all points where waste water is generated.
Developing a water balance accurate to within 10 % of the amounts of the larger streams.
Defining the appropriate data for the analysis by determining water sources and water sinks.

A profile is presented in Figure 7.3 [cww/tm/86].
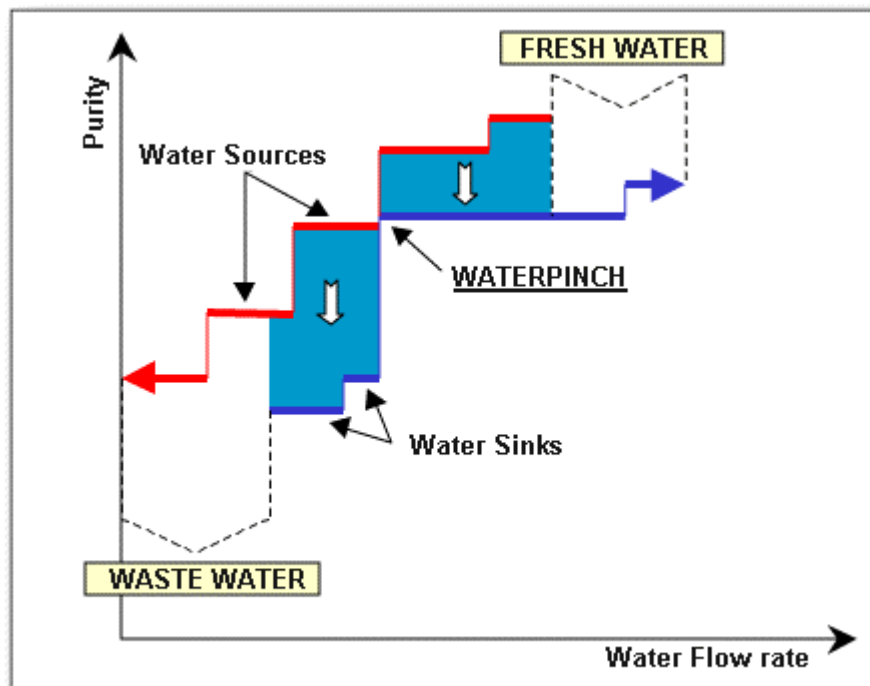
Figure 7.3: Pinch Technology – Analysis, Source and Sink Curves

Step 2:
- Selecting key contaminants or properties that prevent the direct re-use of the respective waste water stream
- Choosing design concentrations – maximum allowable for sinks, and minimum practical for sources.

Step 3:
- Developing the multi-dimensional pinch analysis to determine optimum matches between sources and sinks. Appropriate software is available for this. The procedure includes identification of pinches and a consideration of process modifications and regeneration options resulting in lower targets.

Step 4:
- Repetition of step 3 until a practical design has evolved.

The application of Pinch Technology has succeeded in waste water savings of up to 60 % [cww/tm/86]. Performance examples for waste water flow reduction are:

- Chemicals and Fibres   25 %
- Chemicals   40 %
- Oil Refining   20–30 %
- Coal Chemicals   50 %
- Polymers   60 %

An example of water conservation strategy is given in Figure 7.4 [cww/tm/86]
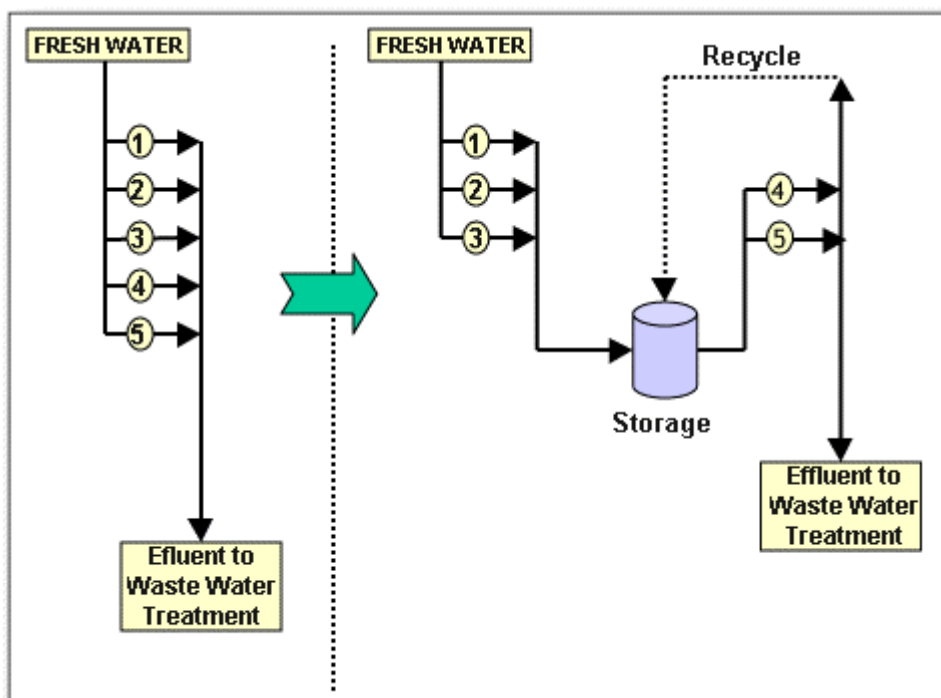
Figure 7.4: Example of Water Conservation Strategy before and after Pinch Analysis

Cost savings are not normally restricted to the water saving costs. They can be significant if waste water reduction leads to the construction of a smaller central WWTP, makes expansion of the existing waste water treatment facilities unnecessary or allows the expansion of production unit capacity without hydraulically overloading the existing central WWTP. Process modification and selective water regeneration can result in product recovery, which can be economically profitable as well.

The major applications for Pinch Technology [cww/tm/86] are:

- to avoid production cutbacks under limited water supply conditios
- to reduce water supply costs
- to reduce capital costs of new water supply facilities (e.g. new wells or pipelines)
- to reduce capital costs of water treatment facilities
- to reduce waste water treatment costs
- to reduce sewage charges
- to reduce capital costs of expanding on-site waste water treatment facilities to meet increased production loads or more stringent emission regulations
- to help comply with environmental regulations.

7.3   Annex III. Monitoring of a Central Biological WWTP

Proper operation of a biological WWTP requires constant surveillance and the targeted adjustment of various process parameters. Monitoring of the relevant parameters can be accomplished by on-line measurements that facilitate direct intervention and control, or analytical results derived from waste water samples, which reflect longer-term trends and are also essential for monitoring and documentation purposes. Both the needs with respect to on-line measurements and analyses applicable to the various process stages associated with a WWTP are provided in Table 7.1. Specific requirements may vary in individual cases [cww/tm/132].

Parameter	Influent	Neutrali-sation	Preclari-fication	Buffer influent to biology	Biology	Effluent	Sludge treat-ment
Analyses from on-line measurements							
waste water flow	c					c	
pH	c	c	c	c	c	c	c
temperature	c					c	
bacteria toxicity	c						
TOC				c	c	c	
nitrogen				c	c	c	
phosphorous				c	c	c	
total solids [g/l]					c		
dissolved oxygen					c	c	
Analyses from random samples							
total solids [g/l]			i		i		i
settling volume			i		i	i	
Analyses from average samples							
TOC	i			i		i	
COD	i			i		i	
BOD	i			i		i	
AOX / EOX	i			i		i	
total nitrogen	i			i		i	
NH$_4$-N	i			i		i	
NO$_3$-N	i			i		i	
total phosphorus	i			i		i	
PO$_4$-P	i			i		i	
individual substances	i			i		i	
c: continuously online i: inhalatory samples							

Table 7.1: Monitoring of a WWTP

7.4   Annex IV. Monitoring Standards

The followings lists (version July 1999) give the available CEN standards of analytical parameters for emission monitoring in the domains air, water, sludge and sediment. CEN standards are adopted in all EU Member States [cww/tm/167].

The table lists either the standards ratified by CEN (EN number and date of ratification) or the drafts under public enquiry or vote (ISO or prEN number). When neither is given it signifies that work is still in progress.

Standards for water, sludge and sediment

Parameter	Domain	Standards ratified by CEN	Drafts under public enquiry or vote
Surrogate, sum and group parameters			
AOX	water	EN 1485: 1996	
BOD	water	EN 1899: 1998	
Suspended solids	water	EN 872: 1996	
TOC	water	EN 1484: 1997	
Complexing agents	water		
Hydrocarbon oil index	water		ISO DIS
Oxygen consumption	water, sludge	EN ISO 8192: 1995	
PAH	water		
Phenol index by flow analysis	water, sludge		prEN 14402
Permanganate value	water	EN ISO 8467: 1995	
Anionic surfactants	water	EN 903: 1993	
Activated sludge simulation test	water	EN ISO 11733: 1998	
Inherent biodegradability	water	EN ISO 9887: 1994	
Methylene blue index by flow analysis	water		
Inhibition of nitrification	water	EN ISO 9509: 1995	
Sulphite reducing Clostridia	water	EN 26461: 1993	
Ultimate biodegradability (released CO_2)	water	EN 29439: 1993	
Ultimate biodegradability (Zahn Wellens)	water	EN 29888: 1993	
Ultimate biodegradability (closed respirometer)	water	EN 29408: 1993	
Ultimate biodegradability (DOC measurement)	water	EN ISO 7827: 1995	
Ultimate biodegradability (low soluble substances)	water	EN ISO 10634: 1995	
Ultimate biodegradability (biogas production)	water	EN ISO 11734: 1998	
Ultimate biodegradability (BOD measurement)	water	EN ISO 10707: 1997	
Alkalinity	water	EN ISO 9963: 1995	
Colour	water	EN ISO 7887: 1994	
Electrical conductivity	water	EN ISO 7888: 1993	
Odour, flavour	water	EN 1622: 1997	
Turbidity	water	EN 27027: 1999	

Parameter	Domain	Standards ratified by CEN	Drafts under public enquiry or vote
Toxicity parameters			
Algal growth inhibition test	water	EN 28692: 1993	
Bacteria toxicitiy (pseudomonas)	water	EN ISO 10712: 1995	
Fish toxicity	water	EN ISO 7346: 1998	
Inhibition of mobility of daphnia magna	water	EN 6341: 1996	
Luminescent bacteria test	water	EN ISO 11348: 1998	
Marine algal growth inhibition test	water	EN ISO 10253: 1998	
Single organic substances			
Benzene and homologues	water		
Carbontetrachloride (tetrachloromethane)	water	EN 10301: 1997	
Chloroform (trichloromethane), dichloroethane, trichloroethene, tetrachloroethene	water	see EN 10301	
Chlorophenols, polychlorinated phenols	water	EN 12673: 1997	
Epichlorohydrine	water		
Hexachlorobenzene, trichlorobenzene	water	see EN 6468	
Hexachlorocyclohexane and isomers	water	EN 6468: 1996	
Organotin	water		
Pesticides			
Aldrin, dieldrin, endrin	water	see EN 6468	
Atrazine, simazine by HPLC	water	EN 11369: 1997	
Atrazine, simazine by GC	water		ISO/DIS 10695-1
DDT, DDD, DDE	water	see EN 6468	
Endosulfane	water	see EN 6468	
Parathione, parathione methyl and related compounds	water		prEN 12918
Parathione and related compounds by solid-liquid extraction	water		
Inorganic parameters			
Aluminium	water		
Arsenic	water	EN 11969: 1996 EN 6595: 1992	
Arsenic,l selenium, antimony by atomic fluorescence	water		
Cadmium	water, sludge, sediment	EN 5961: 1995	
Calcium and magnesium	water		
Chlorine	water		
Chromium	water, sludge, sediment	EN 1233: 1996	
Kjeldahl nitrogen	water	EN 25663: 1993	
Mercury	water, sludge, sediment	EN 1483: 1997	
Mercury – enrichment method	water, sludge, sediment	EN 12338: 1998	
Mercury by atomic fluorescence	water, sludge, sediment		
Metals by flameless AAS	water		

Parameter	Domain	Standards ratified by CEN	Drafts under public enquiry or vote
Thallium by AAS	water		
Total nitrogen, instrumental method	water	ENV 12260: 1996	
33 elements by ICP-OES	water, sludge, sediment	EN ISO 11885: 1997	
Inorganic parameters, cationic			
Ammonium by flow analysis	water	EN ISO 11732: 1997	
Cations by IC	water, sludge	UAP 1998	
Inorganic parameters, anionic			
Bromate by IC	water		
Chloride by flow analysis	water		
Cyanide by flow analysis	water, sludge		prEN 14403
Dissolved anions by IC	water	EN ISO 10304-1: 1995 EN ISO 10304-2: 1996 EN ISO 10304-3: 1997	prEN 10304-4
Nitrite	water	EN 26777: 1993	
Nitrite and nitrate by flow analysis	water	EN ISO 13395: 1996	
Phosphate by flow analysis	water		
Phosphorous	water	EN 1189: 1996	
Silicate by flow analysis	water		
Water quality parameters			
Dissolved oxygen	water	EN 25813: 1992 EN 25814: 1992	

Standards for emission to the atmosphere and ambient air

Parameter	Domain	Standards ratified by CEN	Drafts under public enquiry or vote
Air from soil	air emission		
Benzene	ambient air		
Carbon monoxide (CO)	ambient air		
Carbon monoxide (CO) Concentration in stack	air emission		
Diffusive samplers Requirements and test methods	ambient air		prEN 13538-1
Diffusive samplers Specific requirements test methods	ambient air		prEN 13538-2
Diffusive samplers Guide for selection, use, maintenance	ambient air		
Dioxins and furans Sampling	air emission	EN 1948-1: 1996	
Dioxins and furans Extraction and clean-up	air emission	EN 1948-2: 1996	
Dioxins and furans Identification and quantification	air emission	EN 1948-3: 1996	
Dust, total, at low concentration Reference method	air emission		prEN 13284-1
Dust, total, at low concentration Validation of AMS	air emission		
HCl, gaseous Sampling and gas pretreatment	air emission	EN 1911-1: 1997	

Parameter	Domain	Standards ratified by CEN	Drafts under public enquiry or vote
HCl, gaseous Gaseous compound absorption	air emission	EN 1911-2: 1997	
HCl, gaseous Solution analysis and calculation	air emission	EN 1911-3: 1997	
Fugitive/diffuse emissions	air emission		
Mercury	ambient air		
Mercury, total Reference method	air emission		prEN 13211-1
Mercury, total Validation of AMS	air emission		
Metals – metaloids (except Hg – Sn)	air emission		
Metals – metaloids Pb – Cd – As – Ni	ambient air		
Nitrogen oxide (NO_2)	ambient air		
Nitrogen oxides (NO-NO_2) Concentration in stack	air emission		
Odour by dynamic olfactometry	air emission		
Organic carbon, gaseous, total (FID) – low concentration	air emission		prEN 12619
Organic carbon, gaseous, total (FID) – high concentration	air emission		prEN 13526
Organic carbon, gaseous Individual compounds	air emission		
Oxygen (O_2) concentration in stack	air emission		
Ozone (O_3)	ambient air		
Particulate matter (<PM_{10})	ambient air		prEN 12341
Particulate matter (<$PM_{2.5}$)	ambient air		
Quality assurance of AMS Performance and requirements	air emission		
Quality assurance of AMS Periodic validations	air emission		
Quality assurance of AMS Operation monitoring	air emission		
Certification systems for AMS	air emission and ambient air		
Strategy/Quality of emission measurement	air emission		
Sulphur dioxide (SO_2)	ambient air		
Sulphur dioxide (SO_2) Concentration in stack	air emission		
Water vapour (H_2O vapour) Concentration in stack	air emission		

7.5   Annex V. Pollution Incident Response Plan

An example of a Pollution Incident Response Plan [cww/tm/148], as mentioned in Section 2.2.4.2, is detailed here. The information asked for is general, applicable to all sites. Special productions or site-specific features might require further information.

	NAME AND ADDRESS OF COMPANY
	NATURE OF BUSINESS

DATE OF PLAN	REVIEW DATE
APPROVED BY	DATE

COPIES TO	ENVIRONMENTAL AUTHORITY FIRE AUTHORITY POLICE SEWAGE UNDERTAKING WATER SUPPLIER LOCAL AUTHORITY OTHER
CONTACT PHONE NUMBERS DURING OFFICE AND OUT OF OFFICE HOURS	EMERGENCY SERVICES LOCAL POLICE MEDICAL SERVICE ENVIRONMENTAL HOTLINE ENVIRONMENTAL REGULATOR LOCAL AUTHORITY SEWAGE UNDERTAKING WATER SUPPLIER GAS SUPPLIER ELECTRICITY SUPPLIER WASTE DISPOSAL CONTRACTOR SPECIALIST ADVICE SPECIALIST CLEAN-UP CONTRACTORS
COMPANY CONTACTS (OUT OF HOURS)	MANAGING DIRECTOR SITE MANAGER ENVIRONMENTAL MANAGER FOREMAN HEAD OFFICE CONTACT

SITE DRAINAGE PLAN

OIL, CHEMICAL AND PRODUCT INVENTORY

MAXIMUM QUANTITIES AT PEAK TIMES

TRADE NAME	CHEMICAL	LIQUID/GAS/POWDER	CONTAINER SIZE	MAXIMUM QUANTITY

7.6 Annex VI. Examples of Waste Water and Waste Gas Treatment

The following examples give data from effluent treatment plants currently operated in different EU Member States. Their inclusion, however, does not automatically imply that all these plants and their equipment are BAT. The BAT conclusions are detailed in Chapter 4.

7.6.1 Technical Information on Waste Water Treatment Plants (Examples)

[cww/tm/105]

	Example I	Example II
Production	production mix, mainly organic	production mix
Year of construction	1988	1978
Function	tower biology plant with separate final clarification for chemical waste water treatment	tower biology with final clarification
Process steps	neutralisation biological treatment final clarification	equalisation neutralisation biological treatment sedimentation
Plant characteristics	- buffer tank: V = 300 m^3 - neutralisation tank: V = 3.0 m^3 - 2 aeration tanks: V = 3000 m^3 each - bottom hopper, diameter 14 m	- 2 buffer tanks: V = 1500 m^3 - 1 buffer tank: V = 1700 m^3 - 3 neutralisation vessels: V = 25 m^3 each - 6 biological treatment towers: V = 1600 m^3 each, diameter 11 m - 6 bottom hoppers: V = 112 m^3 each as final clarification
Sludge treatment	dewatering before off-site incineration	centrifuge evaporation combustion
Process data		
Waste water flow [m^3/d]	5280	3840
COD load [tonnes/d]	4.2	3
NH$_4$-N load	0.2	0.3
BOD$_5$ [tonnes/d]	1.75	1
organic N [tonnes/d]	0.15	
NO$_3$-N [tonnes/d]		0.5
PO$_4$-P [tonnes/d]	0.005	
Consumables		
O$_2$ input [tonnes/d]	12.0	6.8
Flocculants [tonnes/yr]	6	1.57
Nutrients [tonnes/yr]	1.18	
Electricity WWTP [MWh/yr]	885	2581
Electricity sludge treatment [MWh/yr]	38	105
Steam WWTP [tonnes/yr]	-	1200
Steam sludge treatment [tonnes/yr]	-	50718
Compressed air WWTP [1000 Nm^3/yr]	1700	4750
Compressed air sludge treatment [Nm^3/yr]	-	17.6
Cross-media effect		
Sludge [tonnes dry solids/d]	0.11	0.13
Sludge [kg dry solids per tonne eliminated COD]	34	118
Performance data [a]		
waste water amount [m^3/d]	4704	1882
COD elimination [%]	53	81
COD emission [mg/l]	616	132
[a] daily mean average		

	Example III	Example IV
Production	production mix: large volume and fine chemicals, organic and inorganic	
Year of construction	1972-74, expansions 1979, 1981, 1985-6	1978, expansion 1994, 1999
Function	tower biology as high load and tank biology as low load treatment	tower biology with final clarification
Process steps	rake screen neutralisation pre-clarification buffering, equalisation part denitrification biological stage 1 with intermediate clarification biological stage 2 with final clarification flotation off-gas treatment sludge treatment	rake screen neutralisation pre-clarification buffering, equalisation biological stage 1 biological stage 2 final clarification sludge treatment
Plant characteristics	- neutralisation: V = 628 m^3 - 8 pre-clarifiers industrial: V = 480 m^3 each - 2 pre-clarifiers municipal: V = 1950 m^3 each - 3 buffer tanks: V = 10000 m^3 each - 2 buffer tanks: V = 25000 m^3 each - 1 buffer tank: V = 15000 m^3 - 1 denitrification tank: V = 10000 m^3 - 4 tower biology: V = 13000 m^3 each - 4 intermediate clarifiers: V = 1000 m^3 each - aeration basin 1: V = 11000 m^3 - aeration basin 2: V = 25000 m^3 - 6 bottom hoppers: each V = 1520 m^3, diameter 18 m - 4 bottom hoppers: each V = 1520 m^3, diameter 20 m - 3 secondary clarifiers - 2 flotation tanks: diameter 12 m	- neutralisation: V = 600 m^3 - 1 buffer tank: V = 15600 m^3 - 1 aeration tank: V = 5000 m^3 - 1 aeration basin: V = 5500 m^3 - 4 aeration basins: V = 2000 m^3 each - 3 clarification basins: V = 3500 m^3, diameter 40 m each
Sludge treatment	thickener lime- and iron conditioning mechanical dewatering with membrane filter presses sludge combustion	sludge thickener 2 filter presses
Process data (industrial / municipal part)		
Waste water flow [m^3/d]	65000 / 65000 (dry weather)	18000
	65000 / 180000 (rainy weather)	
COD load [tonnes/d]	150 / 40	26
NH_4-N load	3 / 2.5	0.6
BOD_5 [tonnes/d]	80 / 20	8
organic N [tonnes/d]	5 / 1	
NO_3-N [tonnes/d]	3 / -	2.1
PO_4-P [tonnes/d]	1.6 / 0.8	0.07
Consumables		
O_2 input [tonnes/d]	180 (tower biology) / 30 (tank)	20
Flocculants [tonnes/yr]	50	360
Nutrients [tonnes/yr]		10.6
Electricity WWTP [MWh/yr]	39558	4320
Electricity sludge treatment [MWh/yr]	3644	145
Electricity exhaust air treatment [MWh/yr] [a]	2812	
Steam WWTP [tonnes/yr]	4241	
Steam sludge treatment [tonnes/yr]	3	
Compressed air WWTP [1000 Nm^3/yr]	199459	
Compressed air sludge treatment [Nm^3/yr]	3220	
Cross-media effect		
Sludge [tonnes dry solids/d]	77.25	7.9
Sludge [kg dry solids per tonne eliminated COD]	720	620

	Example III	Example IV
Performance data [b]		
waste water amount [m³/d]	148615	12269
COD elimination [%]	87	91
COD emission [mg/l]	107	106
[a] off-gas thermal treatment [b] daily mean average		

	Example V	Example VI
Production	production mix, mainly organic	production mix, mainly organic
Year of construction	1977	1974-76
Function	waste water treatment for chemical production plants	denitrification and biological treatment
Process steps	neutralisation pre-clarification denitrification biological treatment final clarification flotation cooling sludge treatment	neutralisation pre-clarification denitrification final clarification biology

Plant characteristics	- neutralisation: V = 220 m³ /
	  V = 110 m³
	- pre-clarification: V = 1000 m³
	- 2 denitrification basins:
	  V = 1500 m³ each
	- 2 aeration basins: V = 2500 m³ each
	- 2 bottom hoppers, diameter 14 m
	  each
		- neutralisation: V = 380 m³
		- 4 pre-clarification tanks:
		  V = 750 m³ each
		- 3 buffer basins: V = 9100 m³
		- aeration basin/denitrification:
		  V = 28000 m³ each
		- 16 clarification tanks, diameter 15 m

Sludge treatment	thickener polyelectrolyte conditioning centrifuge sludge drying	pre-thickening by separators dewatering of excess and other sludge landfilling
Process data		
Waste water flow [m³/d]	8500	60000
COD load [tonnes/d]	17.5	60
NH_4-N load	0.96	
BOD_5 [tonnes/d]	9.55	
organic N [tonnes/d]	0.45	
NO_3-N [tonnes/d]	1.9	
PO_4-P [tonnes/d]		
Consumables		
O_2 input [tonnes/d]	16	15-20
Flocculants [tonnes/yr]	196.2	17
Nutrients [tonnes/yr]	7.71	91
Electricity WWTP [MWh/yr]	4204	1163
Electricity sludge treatment [MWh/yr]	625	3882
Steam WWTP [tonnes/yr]	36	641
Steam sludge treatment [tonnes/yr]	2380	120
Compressed air WWTP [1000 Nm³/yr]	356	337
Compressed air sludge treatment [Nm³/yr]	39.5	166
Cross-media effect		
Sludge [tonnes dry solids/d]	1.83	103
Sludge [kg dry solids per tonne eliminated COD]	150	2000
Performance data [a]		
waste water amount [m³/d]	8616	61359
COD elimination [%]	84	87
COD emission [mg/l]	255	120
[a] daily mean average		

	Example VII	Example VIII
Production	production mix, mainly organic	production mix, organic
Year of construction	1977	1977/78
Function	waste water pretreatment of central WWTP, 2-stage waste water treatment existing of biological treatment with simultaneous precipitation of phosphate and nitrification in a closed plant	waste water treatment for chemical and pharmaceutical production plants
Process steps	rake screen neutralisation pre-clarification biological treatment intermediate clarification nitrification final clarification	rake screen buffering, equalisation neutralisation biological stage 1 (with pure oxygen) intermediate clarification biological stage 2 final clarification
Plant characteristics	- 2 neutralisation tanks: V = 380 m^3 - 4 pre-clarification: V = 750 m^3 each - 3 buffer basins: V = 9000 m^3 each - 2 aeration basins: V = 5600 m^3 each - 1 intermediate clarifiers: diameter 20 m, surface area 300 m^2 - 2 final clarifiers: diameter 20 m, surface area 300 m^2	- neutralisation: V = 50 m^3 - 2 buffer tanks: V = 4000 m^3 each - 2 aeration basins: V = 3100 m^3 each - 1 intermediate clarifier: V = 4400 m^3 - 2 aeration basins: V = 1600 m^3 each - 2 final clarifiers: V = 2400 m3
Sludge treatment	excess sludge pumped to sludge dewatering	excess sludge treated externally
Process data		
Waste water flow [m^3/d]	8000	20000
COD load [tonnes/d]	15	60
NH$_4$-N load	1.5	0.1
BOD$_5$ [tonnes/d]		34
organic N [tonnes/d]		
NO$_3$-N [tonnes/d]	1.5	
PO$_4$-P [tonnes/d]	0.2	
Consumables		
O$_2$ input [tonnes/d]	30	60
Flocculants [tonnes/yr]	2.1	
Nutrients [tonnes/yr]	37.5	12
Electricity WWTP [MWh/yr]	6200	5155
Electricity sludge treatment [MWh/yr]		
Electricity exhaust air treatment [MWh/yr] [a]	675	
Steam WWTP [tonnes/yr]	2323	
Steam sludge treatment [tonnes/yr]		
Compressed air WWTP [1000 Nm^3/yr]	3261	
Compressed air sludge treatment [Nm^3/yr]		
Cross-media effect		
Sludge [tonnes dry solids/d]	3.75	3.08
Sludge [kg dry solids per tonne eliminated COD]	340	300
Performance data [b]		
waste water amount [m^3/d]	5344	3549
COD elimination [%]	83	98
COD emission [mg/l]	411	56

[a] off-gas thermal treatment
[b] daily mean average

	Example IX	
Production	production mix, organic and inorganic	
Year of construction	1974/75, expansion 1980/81	
Function	waste water treatment for chemical production plants	
Process steps	rake screen neutralisation buffering, equalisation pre-clarification biological stage 1 intermediate clarification biological stage 2 final clarification flotation off-gas treatment	
Plant characteristics	- neutralisation tank: V = 240 m^3 - 2 buffer tanks: V = 5000 m^3 each - 2 pre-clarifiers: V = 3000 m^3 - aeration basin 1: V = 6000 m^3 - 2 intermediate clarifiers: surface area 500 m^2 - aeration basin 2: V = 8000 m^3 - 6 bottom hoppers: diameter 15 m - 2 flotation cells: diameter 10 m	
Sludge treatment	excess sludge pumped to external treatment	
Process data		
Waste water flow [m^3/d]	36000	
COD load [tonnes/d]	35	
NH$_4$-N load	1	
BOD$_5$ [tonnes/d]	20	
organic N [tonnes/d]		
NO$_3$-N [tonnes/d]	1	
PO$_4$-P [tonnes/d]		
Consumables		
O$_2$ input [tonnes/d]	35	
Flocculants [tonnes/yr]	12.87	
Nutrients [tonnes/yr]	30	
Electricity WWTP [MWh/yr]	11107	
Electricity sludge treatment [MWh/yr]	219	
Electricity exhaust air treatment [MWh/yr] [a]	788	
Steam WWTP [tonnes/yr]	1615	
Steam sludge treatment [tonnes/yr]		
Compressed air WWTP [1000 Nm^3/yr]	1183	
Compressed air sludge treatment [Nm^3/yr]		
Cross-media effect		
Sludge [tonnes dry solids/d]	4.73	
Sludge [kg dry solids per tonne eliminated COD]	250	
Performance data [b]		
waste water amount [m^3/d]	22700	
COD elimination [%]	95	
COD emission [mg/l]	44	

[a] off-gas treatment with activated carbon
[b] daily mean average

7.6.2 Information on Waste Water Discharges (Examples)

[cww/tm/160]

	Example X			Example XI		
Production	active pharmaceutical ingredients and intermediates			inorganic fine chemicals, pharmaceuticals		
Process steps	rake screen neutralisation buffering, equalisation denitrification biological treatment, 2 stages microscreening			waste water with mainly inorganic load: - neutralisation - precipitation, flocculation, sedimentation waste water with relevant organic load treated off-site		
Pretreatment facilities				wet oxidation (H_2O_2/Fe salt) for tributary stream (COD reduction)		
Facilities for emergency situations	additional biological treatment facility $V = 13500 \ m^3$ (covering 3 days)			additional retention and treatment facilities $V = 3800 \ m^3$ and $V = 1800 \ m^3$		
Exhaust air treatment	closed facilities, except biological stages					
Waste water amount [m^3/d]	3800			3500		
Performance data [a]	input [mg/l]	output [mg/l]	performance [%]	input [mg/l]	output [mg/l]	performance [%]
COD	1600	100	94	150	40	
BOD$_5$	1100	7	>99	49	20	
NH$_4$-N	30	2	93			
total inorganic N		20				
total N	40	25	37.5	15	15	
total P	4.2	0.5	88	3,8	0.3	
T$_F$		2				
T$_D$		1				
T$_A$		1-8				
T$_L$		1-8				
T$_M$		1.5				
[a] daily mean average						

	Example XII			Example XIII		
Production	large volume organic and inorganic chemicals, polymers, dyes, pharmaceutical ingredients and intermediates, municipal waste water (13 %)			pharmaceutical ingredients, pesticides, dyes		
Process steps	neutralisation sedimentation biological treatment final clarification (sedimentation)			neutralisation sedimentation tower biology with final clarification		
Pretreatment facilities	stripping (ammonia from tributary streams) extraction (tributary streams for pesticide production precipitation of heavy metals			central GAC adsorption (tributary streams from production of chlorinated nitroaromatics with high AOX load), on-site regenration		
Facilities for emergency situations	possibility to isolate 2 aeration tanks retention volume 60000 m^3			retention facility $V = 12000 \ m^3$		
Exhaust air treatment	closed biological stages			closed biological facilities waste gas combustion		
Waste water amount [m^3/d]	430000			11000		
Performance data [a]	input [mg/l]	output [mg/l]	performance [%]	input [mg/l]	output [mg/l]	performance [%]
COD	1050	112	91	160	18	89 [b]
BOD$_5$	500	7	98.6		1	
NH$_4$-N	27	22	19.5	4.2	0.9	78
total inorganic N		22		50	28	44
total N						
total P	9	0.5	94		0.13	
AOX				1.1	0.16	85 [c]
T$_F$		2			2	
T$_D$		2			1	
T$_A$		2			3	
T$_L$		8				
T$_M$		1.5				
[a] daily mean average [b] 96 % when considering pretreatment [c] 99 % when considering pretreatment						

	Example XIV			Example XV		
Production	polymers, fibres, optical brighteners, detergents, pharmaceutical ingredients			light stabilisers, antioxidants, corrosion inhibitors, additives, stabilisers		
Process steps	neutralisation preliminary clarification biology: trickling filters, activated sludge tank final clarification			neutralisation oil-water separation flocculation, clarification denitrification 2-stage biology final clarification flotation		
Pretreatment facilities	sedimentation of natural resins in tributary streams distillation of tributary streams from pharmaceutical productions with recycling of solvent			precipitation-flocculation-sedimentation-filtration (tributary stream from organo tin production) distillation (tributary stream from amine production)		
Facilities for emergency situations	retention tank(s) V = 9500 m^3			2 buffer tanks V = 250 m^3		
Exhaust air treatment	combustion of waste gas from trickling filters and sludge thickeners			biofilter combustion of waste gas from sludge thickener		
Waste water amount [m^3/d]	14700			1300		
Performance data [a]	**input [mg/l]**	**output [mg/l]**	**performance [%]**	**input [mg/l]**	**output [mg/l]**	**performance [%]**
COD	2300	350	85	4750	220	95.4
BOD$_5$	920	18	98	2430	18	99.3
NH$_4$-N						
total inorganic N	65	7	89	88	14.7	83.3
total N						
total P	4.4	0.5	88.4	16	1.5	90.6
AOX	0.4	0.16	60	1.5	0.25	83.3
T$_F$		2			3	
T$_D$		2			5	
T$_A$		8			12	
T$_L$		2			8	
T$_M$						
[a] daily mean average						

	Example XVI			Example XVII		
Production	organic and inorganic speciality chemicals			pharmaceutical ingredients, vitamins, organic fine chemicals		
Process steps	neutralisation preliminary clarification denitrification biological treatment with integrated final clarification			neutralisation preliminary clarification biological treatment with denitrification final clarification		
Pretreatment facilities	wet oxidation with H$_2$O$_2$ of tributary streams from production of fungicides oxidation of tributary streams containing Na$_2$S concentrating tributary streams containing sulphuric acid precipitation of tributary stream containing Ni and recycling Ni			precipitation of Hg and Ni from tributary streams stripping of tributary streams containing high concentrations of AOX and solvents		
Facilities for emergency situations	retention facilities V = 18000 m^3			retention facilities V = 23000 m^3 facilities for treatment with activated carbon		
Exhaust air treatment	biofilter for waste gas from buffer tanks, preliminary clarification and sludge thickener			closed biology and buffer tanks bioscrubber		
Waste water amount [m^3/d]	4300			5750		
Performance data [a]	**input [mg/l]**	**output [mg/l]**	**performance [%]**	**input [mg/l]**	**output [mg/l]**	**performance [%]**
COD	1750	68	96	1740	98	94.4
BOD$_5$	820	9	99	890	5	99.4
NH$_4$-N						
total inorganic N	35	3.7	89.5	45	2.7	94
total N						
total P	5	0.7	86	7	0.9	87
AOX		0.3			0.4	
T$_F$		2				
[a] daily mean average						

	Example XVIII			Example XIX		
Production	textile dyes, intermediates, plastics, resins			organic dyes and intermediates, optical brighteners, antimicrobica, municipal waste water (50 %)		
Process steps	neutralisation sedimentation tower biology with integrated final clarification			2-stage neutralisation preliminary clarification 2-step biology with denitrification / nitrification final clarification		
Pretreatment facilities	recycling of nitric acid from tributary streams filtration-extraction-stripping			central high pressure wet oxidation for tributary streams with recalcitrant TOC load stripping of ammonia precipitation of Cu of effluent of wet oxidation precipitation of heavy metals from several tributary streams adsorption of special tributary streams extraction of special tributary streams, concentrate to wet oxidation NF of tributary streams from dye production (concentrate to wet oxidation, raffinate to WWTP)		
Facilities for emergency situations	retention tanks $V = 10000$ m^3 and $V = 7500$ m^3			retention tanks $V = 6000$ m^3		
Exhaust air treatment	closed facilities			closed facilities, except biology and final clarification off-gas with plasmacat (ozone, ionisation)		
Waste water amount [m^3/d]	16000			11000		
Performance data [a]	input [mg/l]	output [mg/l]	performance [%]	input [mg/l]	output [mg/l]	performance [%]
COD	620	107	83	1000	250	75 [b]
BOD$_5$	280	7	97.5	370	6	98.4
NH$_4$-N				152	13	91.5
total inorganic N	42	24	43	153	18	88
total N						
total P		1.6		7	1.1	84
AOX		1.2		8.5	1.7	80
T$_F$		2			2	
T$_D$		2			1-4	
T$_A$		1			1-32	
T$_L$		19			4-32	
T$_M$					1.5	

[a] daily mean average
[b] 89 % when considering wet oxidation

	Example XX
Production	vitamins, intermediates
Process steps	neutralisation primary clarification, essentially activated carbon trickling filters activated sludge plant, nitrification, denitrification final clarification
Pretreatment facilities	low pressure wet oxidation for tributary stream containing recalcitrant TOC evaporation of highly loaded organic waste water streams and subsequent incineration of residue distillation of solvent, recycling extraction of recalcitrant TOC from tributary streams hydrolysis of tributary streams containing recalcitrant TOC
Facilities for emergency situations	retention tank $V = 10000$ m^3 possibility to isolate and circumvent one basin
Exhaust air treatment	off-gas treatment with GAC adsorption closed facilities
Waste water amount [m^3/d]	8000

Performance data [a]	Example XX		
	input [mg/l]	output [mg/l]	performance [%]
COD	3300	167	95
BOD$_5$	1400	7	99.5
NH$_4$-N	100	5	95
total inorganic N	100	7	93
total N	155 [b]	23 [b]	85
total P	5	0.9	82
AOX	1.1	0.13	88
T$_F$		2	
T$_D$		1-2	
T$_A$		1	
T$_L$		1	
T$_M$		1.5	
[a] daily mean average [b] Kjeldahl-N			

7.6.3 Information on Complete-Site Waste Water Treatment Systems (Examples)

Example XXI

Example XXI describes a chemical industry site in Finland which is shared by five chemical companies (A – E), their production characteristics being:

Company	Main production	Capacity [tonnes/yr]
A	oil products and lubricants	
B	plastics and petrochemicals	
C	polyesters	max. 20000
	plasticizing agents	max. 30000
	PVC	70000-90000
D	EPS (encapsulated polystyrene	40000
E	SB-latex	17000

All companies have established or are establishing ISO 14001 standardised environmental management systems.

The situation is illustrated in Figure 7.5.

Information on waste water flows and treatment techniques and efficiency is detailed in Table 7.2.

Waste water stream	Treatment techniques	Waste water amount [m^3/h]	Input concentration [mg/l]	Output concentration [mg/l]	Performance rate [%]
WW-1 + WW-4	GAC treatment, regeneration; pretreatment by API, sandfilter	10000	COD: 300-400 phenols: 5	COD: <100 phenols: 1-2	COD: 67-75 phenols: 60-80
WW-2 + WW-3	biochemical treatment, subsequent sludge treatment, incineration; pretreatment by stripping, several APIs, flocculation, flotation	2000	COD: 500-900 phenols: 30	COD: <100 phenols: 0.02-0.04	COD: 80-89 phenols: >99.8
D-1		12000		COD: <100 phenols: 1-2	

Waste water stream	Treatment techniques	Waste water amount [m³/h]	Input concentration [mg/l]	Output concentration [mg/l]	Performance rate [%]
WW-6 (D-3)	biochemical treatment	88	COD: 870	COD: 118	COD: 86.5
WW-7 (D-4)	stripping	16-20	VCM: 100-200	VCM: 0.20	VCM: >98
WW-8 (D-5)	sedimentation, flocculation, precipitation, biological aerobic treatment, sedimentation as final clarification	240			COD: 99.1 BOD$_7$: 98.8 TSS: 99.7 Styrene: 99.3 Phosphorus: 98.4

Table 7.2: Waste Water Flows and Treatment Details on Complex Chemical Site (Example XXI)
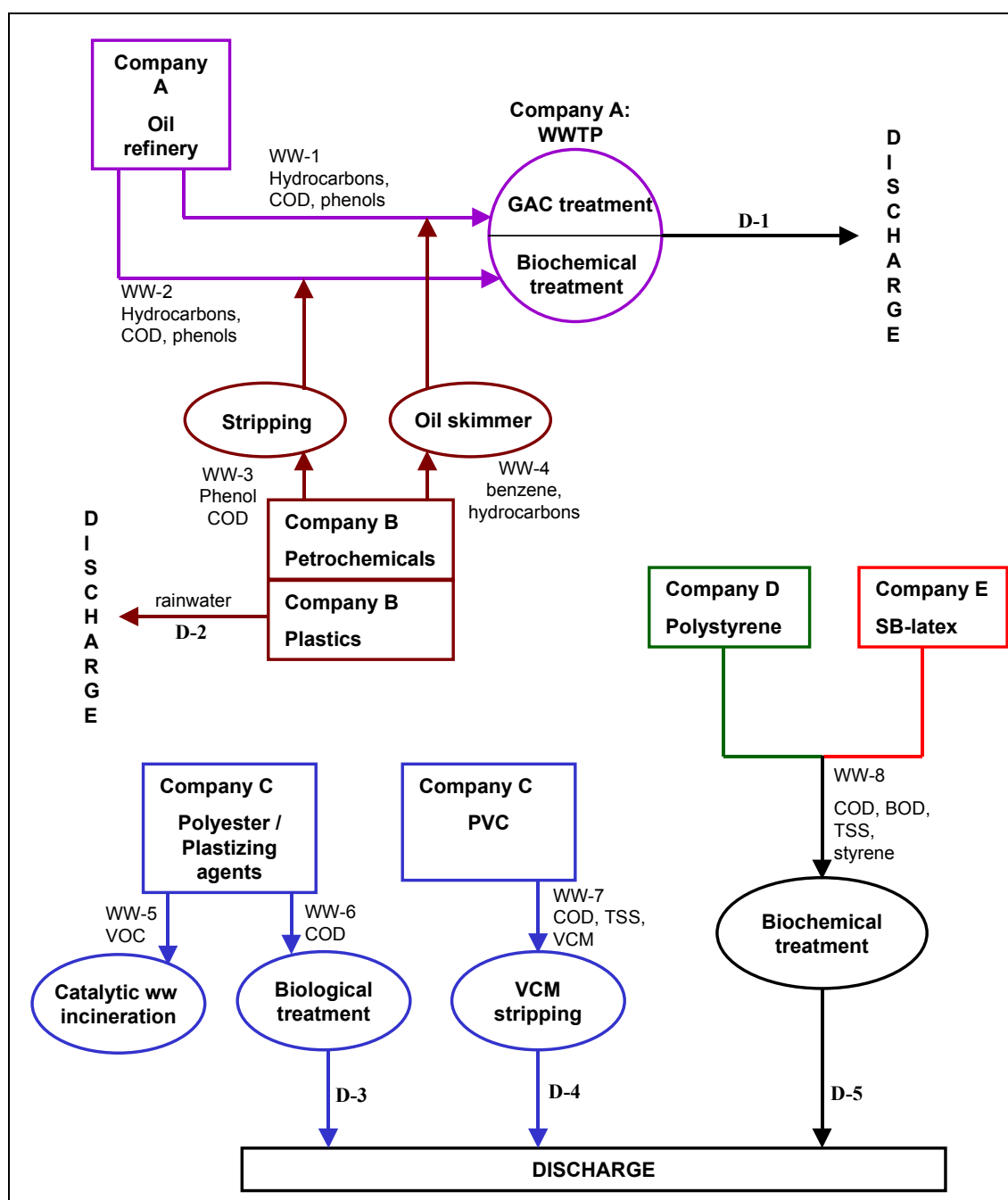
Figure 7.5: Situation of Complex-site Chemical Production (Example XXI)

Example XXII

Central waste water treatment of a chemical site producing organic and inorganic fine chemicals, such as pharmaceuticals, pesticides and hydrogen fluoride.

Amount of waste water: about 300 m^3/h

Waste water treatment consists of:

- stepwise neutralisation with lime to pH 9.5 to precipitate fluoride, sulphate and heavy metals, flocculation and sedimentation
- high-load activated sludge aeration with clarifier
- low-load activated sludge aeration with clarifier
- third-stage biology, biocarb carrier biology to remove refractory COD, phenols and AOX
- exhaust air purification with GAC adsorption, further treatment by incineration
- sludge dewatering, sludge sent to cement industry or landfill.

Emissions:

COD: 123 mg/l
BOD$_5$:   13 mg/l
phenols: 0.5 mg/l
AOX: 1.1 mg/l
total-N: 16 mg/l

The central WWTP is illustrated in Figure 7.6.
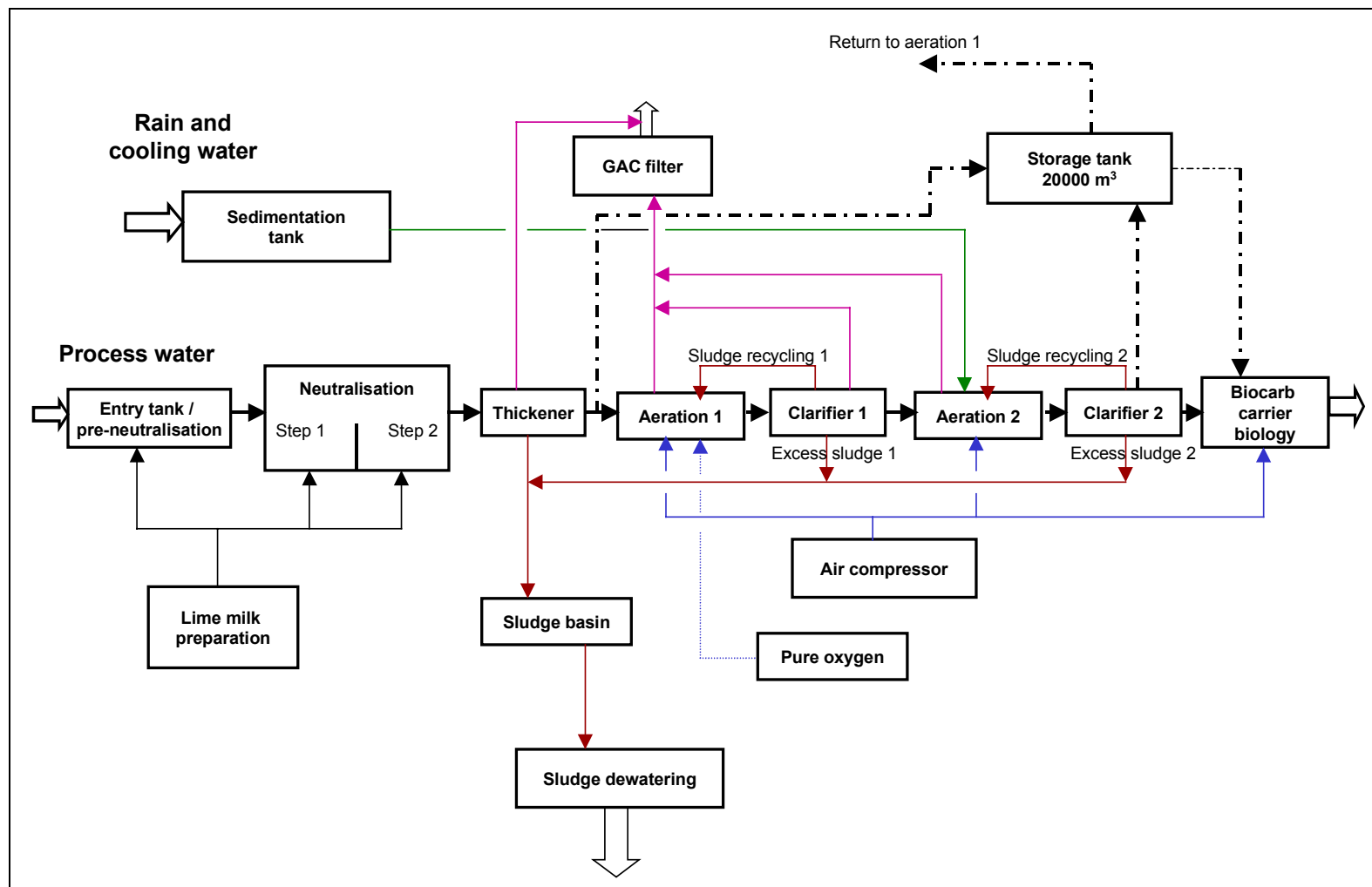
Figure 7.6: Central Waste Water Treatment for a Chemical Site Producing Pharmaceuticals, Pesticides

7.6.4 Examples of Heavy Metal Discharges

[cww/tm/160]

The following Table 7.3 contains the concentrations of heavy metals from 23 waste water discharges. The values given are yearly averages of 24 hours mixed samples; the ones in brackets are the highest values found. The concentrations are achieved at the final discharge point, after treatment at source, without dilution with rainwater or cooling water. They depend on the share of heavy metals in the total waste water mix.

(Plant Nr.) Characterisation	Hg [µg/l] [maximum]	Cr [µg/l] [maximum]	Ni [µg/l] [maximum]	Zn [µg/l] [maximum]	Cu [µg/l] [maximum]	Cd [µg/l] [maximum]	Pb [µg/l] [maximum]	As [µg/l] [maximum]
(1) no central biology	0.32 [1.96]	-	- [20]	4 [27]	-	0.057 [0.4]	- [7]	- [1]
(2) no central biology	1.01 [2.82]	- [10]	30 [180]	54 [230]	50 [100]	0.395 [1.2]	- [32]	4 [28]
(3) no central biology	0.23 [0.7]	- [40]	60 [180]	145 [470]	20 [180]	0.276 [3.8]	-	-
(4) no central biology	0.50 [3.6]	- [60]	-	158 [540]	-	-	100 [100]	-
(5) no central biology	0.84 [2.95]	- [20]	10 [20]	-	-	-	-	-
(6) no central biology	0.10 [0.3]	-	40 [60]	-	-	0.2 [0.6]	- [6]	-
(7) no central biology	-	-	- [20]	74 [380]	30 [180]	0.083 [1.0]	10 [36]	-
(8) no central biology	-	30 [120]	80 [190]	174 [490]	60 [280]	0.833 [8.2]	10 [16]	-
(9) central biology	0.01 [0.2]	-	-	5 [70]	-	-	- [7]	-
(10) central biology	- [0.2]	- [20]	10 [40]	61 [190]	20 [50]	0.023 [1.0]	- [12]	-
(11) central biology	-	- [20]	- [10]	30 [70]	- [20]	-	- [38]	-
(12) no central biology	0.02 [0.35]	10 [60]	10 [90]	111 [230]	20 [90]	0.031 [0.8]	20 [110]	-
(13) central biology	0.11 [2.3]	- [10]	20 [95]	18 [40]	10 [20]	0.042 [0.3]	- [18]	3 [9]
(14) central biology	- [0.1]	-	- [8]	4 [20]	- [50]	0.012 [0.1]	- [10]	-
(15) central biology	0.01 [0.1]	20 [50]	50 [85]	117 [360]	30 [70]	0.212 [1.3]	- [16]	-
(16) central biology	- [0.1]	- [5]	- [13]	13 [390]	- [30]	0.006 [0.1]	- [10]	- [1]
(17) central biology	0.09 [1.3]	-	- [13]	-	20 [70]	0.018 [0.3]	- [7]	-
(18) central biology	0.01 [0.1]	-	-	-	-	0.16 [0.8]	-	-

(Plant Nr.) Characterisation	Hg [µg/l] [maximum]	Cr [µg/l] [maximum]	Ni [µg/l] [maximum]	Zn [µg/l] [maximum]	Cu [µg/l] [maximum]	Cd [µg/l] [maximum]	Pb [µg/l] [maximum]	As [µg/l] [maximum]
(19) central biology	0.45 [1.2]	-	-	64 [150]	-	-	-	-
(20) central biology	0.49 [1.6]	-	-	4 [29]	-	0.064 [1.61]	- [7]	-
(21) central biology	0.05 [0.3]	-	50 [130]	23 [60]	- [20]	0.017 [0.4]	-	-
(22) central biology	-	-	10 [30]	613 [1350]	- [50]	0.106 [0.6]	10 [34]	-
(23) central biology	<0.17	2.7	34	39	38	<0.3	<2.6	

Table 7.3: Emission Levels of Heavy Metals at the Final Discharge Point
[cww/tm/160]

7.6.5 Examples of Waste Gas Treatment Plants

Example 1

Process waste gas from a chemical site, several companies sharing joint equipment.

Waste gas	Treatment method	Discharge [mg/Nm³]	Reduction [%]
Incineration of sludge from biological WWTP	ESP and wet gas scrubber	SO_2: 500 CO: 250 HCl: 1	
Process gas from phenol production	Incineration	Hydrocarbons: 14-15	Hydrocarbons: 99.5
Fugitive emissions from production of aromatic hydrocarbons	Incineration	Hydrocarbons: 5-6	Hydrocarbons: about 99
Process gas from PVC production	GAC adsorption	VC monomer: 0-5	
Company X (latex production)	Thermal destruction		95
Process gas from polystyrene production	Thermal destruction	VOC: 25	VOC about 95

Production:

- plastics and petrochemicals
- oil products and lubricants
- polyester
- plasticizing agents
- PVC
- SB-latex
- encapsulated polystyrene.

Example 2

Treatment of waste gas from incineration.

The treatment system consists of:

- venturi scrubber with alkali solution to remove HCl, some gaseous compounds and part of the solids. The acidic solution from the scrubber is neutralised with lime, the solids are removed from the solution with additives and landfilled
- radial flow scrubber to remove SO_2 with alkali or lime solution / suspension
- wet ESP, solid residues are landfilled.

Emission levels are:

PM: 2-12 mg/Nm³
SO_2:   58-84 mg/Nm³
CO: 2-55 mg/Nm³
HCl: 7-22 mg/Nm³
dioxines: 0.007-0.02 ng/Nm³ TEQ

Example 3

Highly effective SCR to control high initial NO$_x$ content.
[Comments from France to Draft 2]

Production	high performance abrasive grit for the manufacture of grinding wheels and sand paper
Production process	Norton SG process using nitric acid and emitting highly concentrated nitrous waste gas
Conditions:	waste gas stream 800 Nm^3/h, NOx concentration 10000 ppm
NOx abatement chosen	SCR process
Alternative abatement process	Scrubbing with peroxide / water, conversion of NOx to nitric acid
Rationale of decision in favour of SCR	• investment and operating costs of SCR seem to be reasonable • no more polluting effluents • operation and maintenance of SCR are easy
Abatement process	The gas (70-90 °C) is first diluted to reduce the NOx concentration to less than 5000 ppm. The mixture is heated to about 240 °C, the stoichiometric amount of NH$_3$ (NH$_3$/NO$_x$ up to 1.24) sprayed as 25 % ammonia solution into it. The mixture is immediately led across the catalyst bed of granules. Finally, the waste gas is again diluted with air by a factor >10 (reduction of NOx concentration from 200 mg/Nm3 to 20 mg/Nm3) to eliminate any rust that colours the flue gas.

Performance data	
Catalyst temperature upstream:	215-225 °C
NO$_x$ concentration downstream catalyst:	1240-1450 ppm
NO$_x$ concentration after dilution:	50-100 ppm
ratio NH$_3$/NO$_x$ (mol/mol):	1.17-1.24
NH$_3$ leakage:	up to 15 mg/Nm^3
NO$_x$ conversion:	93.1-96.2 %

Costs	
Investment costs	2.4 million FFR
equipment and civil engineering	1.755 million FFR
design	0.645 million FFR]
Annual operating costs	2176 FFR/t converted NOx
Overall cost	5182 FFR/t abated NOx

7.7 Annex VII. Member States' Legislation on Waste Water and Waste Gas in the Chemical Sector

Annex VII surveys the chemical sector emission limits for waste water and waste gas in Member States. Note that there may be different criteria behind the figures, concerning such items as averaging time, reference conditions, sampling techniques, measurement and analysis and method of compliance testing.

1. AUSTRIA

Emissions to Air

No special legislation exists in Austria on emission standards for air emissions from the chemical industry. In general the "Gewerbeordnung" (BGBl. 194/1994) regulates the licensing of chemical plants and means that plants have to be "state-of-the-art" in their performance. Emission standards for air emissions from chemical plants are usually based on the German "Technical Instructions on Air Quality" (TA – Luft).

Combustion plants are regulated with the "Feuerungsanlagenverordnung" (BGBl. II 1997/331), except for steam boilers including waste heat boilers, afterburners of exhaust gases, gas turbines and combustion engines.

Emission standards for boiler plants are regulated by the "Luftreinhaltegesetz für Kesselanlagen" (BGBl. 1988/380 i.d.F. BGBl. 1993/185, BGBl. I 1997/115, BGBl. I 1998/158) and the "Luftreinhalteverordnung für Kesselanlagen" (BGBl. 1989/19 i.d.F. BGBl. 1990/134, BGBl. 1994/785, BGBl. II 1997/324).

- Feuerungsanlagenverordnung (Ordinance for Firing Installations) (BGBl. II 1997/331)
  The "Feuerungsanlagenverordnung" regulates emissions of combustion plants with a nominal thermal output of 50 kW or more. This ordinance is based on § 82 Abs. 1 of the Gewerbeordnung. As mentioned above, steam boilers including waste heat boilers, afterburners of exhaust gases, gas turbines, combustion engines and plants using waste as fuel are not regulated by this ordinance.

  The "Feuerungsanlagenverordnung" provides different emission standards, depending on the fuel used and the thermal output. The emission standards for coal- and coke-firing plants, oil-fired furnaces and combustion plants for gaseous fuels are presented in the following section.

a) Coal- and coke-fired plants

Emission standards for furnaces using coal or coke							
Pollutants		**Capacity [a] [MW]**					
		≤0.35	>0.35-1	>1–2	>2–10	>10-50	>50
Dust	[mg/m³]	150	150	150	50	50	50
SO₂	[mg/m³]	-	-	-	-	400	200
CO	[mg/m³]	1000	1000	150	150	150	150
NOₓ	[mg/m³]	-	400	400	400	350	100
[a] The capacity is defined as the average of the hourly added amount of heat related to the calorific value of the fuel The emission standards are related to dry exhaust gas at 0 °C, a pressure of 101.3 kPa and oxygen content of 6 % in the exhaust gas.							

b) <u>Oil-fired plants</u>

There are four different kinds of heating oils in Austria. The sulphur content in the different kinds of heating oil is laid down in the 'Verordnung über den Schwefelgehalt von Heizölen' (BGBl. 1989/94 i.d.F. BGBl. 1994/545). The following table presents the maximum sulphur content in different kinds of heating oil in Austria.

Maximum sulphur content of different kinds of heating oil	
Type of heating oil	**Maximum sulphur content**
Heating oil extra light	0.10 wt.-%
Heating oil light	0.20 wt.-%
Heating oil medium	0.60 wt.-%
Heavy fuel	1.00 wt.-%

For the lowest capacities of firing installations, the quality of heating oils to be used is restricted. Heating oils with a higher sulphur content may be used in an installation with a lower power capacity if the SO_2 emission levels in the following table are guaranteed by other measures.

Power capacities for the use of different kinds of heating oils	
Capacity [a]	**Heating oil**
≤0.07 MW	extra light
>0.07–5 MW	extra light light
5–10 MW	extra light light medium
>10 MW	all kinds of heating oils
[a] The capacity is defined as the average of the hourly added amount of heat related to the calorific value of the fuel	

Some of the emission standards are different for the different kinds of heating oil. The following four tables present the emission standards for dust, SO_2, CO and NO_x in oil-firing plants.

Dust emission standards [mg/Nm³] when using heating oils as fuel			
Fuel	**Capacity [a] [MW]**		
	>2–30 MW	**>30–50 MW**	**>50 MW**
Heating oil extra light	30	30	30
Heating oil light	50	35	35
Heating oil medium	60	50	35
Heavy fuel	60	50	35
[a] The capacity is defined as the average of the hourly added amount of heat related to the calorific value of the fuel The emission standards for liquid fuels are related to dry exhaust gas at 0 °C, a pressure of 101.3 kPa and an oxygen content of 3 % in the exhaust gas			

The emission standards for SO_2 and CO are related to the thermal output of the firing plants.

SO₂ emission standards [mg/Nm³] when using heating oils as fuel		
Pollutant	**Capacity [a] [MW]**	
	>50–300 MW	**>300 MW**
SO_2	350	200
[a] The capacity is defined as the average of the hourly added amount of heat related to the calorific value of the fuel The emission standards for liquid fuels are related to dry exhaust gas at 0 °C, a pressure of 101.3 kPa and an oxygen content of 3 % in the exhaust gas		

CO emission standards [mg/Nm^3] when using heating oils as fuel		
Pollutant	Capacity ^{a} [MW]	
	≤1 MW	**>1 MW**
CO	100	80
^{a} The capacity is defined as the average of the hourly added amount of heat related to the calorific value of the fuel The emission standards for liquid fuels are related to dry exhaust gas at 0 °C, a pressure of 101.3 kPa and an oxygen content of 3 % in the exhaust gas		

For NO$_x$, different emission standards for different kinds of heating oils are distinguished. Again the thermal output is a further criterion for the emission standard. The next table shows the different NO$_x$ emission standards.

NO$_x$ emission standards [mg/Nm^3] when using heating oils as fuel				
Fuel	Capacity ^{a} [MW]			
	≤3 MW	**>3–10 MW**	**>10–50 MW**	**>50 MW**
Heating oil extra light	150	150	150	100
Heating oil light	450	400	350	100
Heating oil medium	450	450	350	100
Heavy fuel	450	450	350	100
^{a} The capacity is defined as the average of the hourly added amount of heat related to the calorific value of the fuel The emission standards for liquid fuels are related to dry exhaust gas at 0 °C, a pressure of 101.3 kPa and an oxygen content of 3 % in the exhaust gas				

c) Gas-fired plants

For plants using gaseous fuels (natural gas or liquefied petroleum gas) the "Feuerungsanlagenverordnung" only provides emission standards for NO$_x$ and CO.

Emissions standards for gaseous fuels			
Pollutant	**Fuel**	Capacity ^{a} [MW]	
		≤3 MW	**>3 MW**
CO [mg/Nm^3]	Natural gas	80	80
	Liquefied petroleum gas	80	80
NO$_x$ [mg/Nm^3]	Natural gas	120	100
	Liquefied petroleum gas	160	130
^{a} The capacity is defined as the average of the hourly added amount of heat related to the calorific value of the fuel The emission standards for liquid fuels are related to dry exhaust gas at 0 °C, a pressure of 101.3 kPa and an oxygen content of 3 % in the exhaust gas			

For combustion plants with high temperature processes, higher NO$_x$ emissions are allowed. Using natural gas, 200 mg/Nm³ NO$_x$ and using liquefied petroleum gas, at maximum 260 mg/Nm³ NO$_x$ are allowed.

The requirement for continuous measurements of different pollutants depends on the fuel type and on plant capacity.

Thresholds above which continuous measurement is required				
Fuel	Pollutant			
	Dust	**CO**	**SO$_2$**	**NO$_x$**
Solid	>10 MW	>10 MW	>30 MW	>30 MW
Liquid	>10 MW	>10 MW	>50 MW	>30 MW
Gaseous	-	>10 MW	-	>30 MW

This ordinance came into force on 1.6.1998. Combustion plants which were improved before this date have to comply with the emission values of this ordinance within five years, or if they do exceed these values for not more than 50 % they have to keep the emission limits eight years later.

- Luftreinhaltegesetz and Luftreinhalteverordnung für Kesselanlage (Clean Air Act and Clean Air Ordinance for Steam Boilers) (LRG-K and LRV-K)

  In Austria emissions from steam boiler plants and waste heat boilers are regulated by the "Luftreinhaltegesetz für Kesselanlagen" (BGBl. 1988/380 i.d.F. BGBl. 1993/185, BGBl. I 1997/115, BGBl. I 1998/158) and the ordinance "Luftreinhalteverordnung für Kesselanlagen" (BGBl. 1989/19 i.d.F. BGBl. 1990/134, BGBl. 1994/785, BGBl. II 1997/324). The emission standards for dust, SO_2, CO and NO_x due to the Luftreinhalteverordnung für Kesselanlagen depend on the kind of fuel and on the thermal output of the plants.

Dust emission standards [mg/Nm³]			
	Capacity [a] [MW]		
Fuel	**<2 MW**	**2–30 MW**	**30–50 MW**	**>50 MW**
Solid fuels [b]	150	50		
Gaseous fuels	-	5	5	5
Heating oil extra light	-	30	30	30
Heating oil light	-	50	35	35
Heating oil medium	-	60	50	35
Heavy fuel	-	60	50	35

[a] The capacity is defined as the average of the hourly added amount of heat related to the calorific value of the fuel
[b] Wood is excluded

SO₂ emission standards [mg/Nm³]		
	Capacity [a] [MW]		
Fuel	**10–50 MW**	**50–300 MW**	**>300 MW**
Lignite coal	400	400	400
Other solid fuels	400	200	200
Liquid fuels	1700	350	200

[a] The capacity is defined as the average of the hourly added amount of heat related to the calorific value of the fuel

CO emission standards [mg/Nm³]		
	Capacity [a] [MW]	
Fuel	**≤1MW**	**>1MW**
Solid fuels	1000	150
Liquid fuels	100	80
Liquefied petroleum gas	100	
Natural gas	80	

[a] The capacity is defined as the average of the hourly added amount of heat related to the calorific value of the fuel

NOₓ emission standards [mg/Nm³]			
	Capacity [a] [MW]			
Fuel	**0.35–3 MW**	**3–10 MW**	**10–50 MW**	**>50 MW**
Solid fuels	400		350	200
Gaseous fuels	125	100		
Heating oil extra light	150			
Heating oil light	400	400	350	100
Heating oil medium	450		350	100
Heavy fuel	450		350	100

[a] The capacity is defined as the average of the hourly added amount of heat related to the calorific value of the fuel
The emission standards for solid fuels are related to 6 % oxygen in the exhaust gas. For liquid and gaseous fuels they are related to 3 % oxygen. All emission values are related to dry exhaust gas at 0 °C and a pressure of 101.3 kPa.

Emissions to Water

The discharge of waste water into surface water or the public sewerage system in Austria is regulated by the ordinance "Allgemeine Abwasseremissionsverordnung" (General Waste Water Emission Ordinance) (BGBl. 1996/186) and special ordinances for different industrial sectors.

These ordinances are based on the Austrian "Wasserrechtsgesetz" (Water Right Act) (BGBl. I 155/1999). Special ordinances that are of interest for plants producing organic chemicals are:

- Verordnung über die Begrenzung von Abwasseremissionen aus der Herstellung von Kohlenwasserstoffen und organischen Grundchemikalien BGBl. II 1999/7 (Ordinance for the limitation of waste water emissions from the production of hydrocarbons and basic organic chemicals)
- Verordnung über die Begrenzung von Abwasseremissionen aus der Erdölverarbeitung BGBl. II 1997/344 (Ordinance for the limitation of waste water emissions from oil refining)
- Verordnung über die Begrenzung von Abwasseremissionen aus der Herstellung von technischen Gasen BGBl. 1996/670 (Ordinance for the limitation of waste water emissions from the production of industrial gases)
- Verordnung über die Begrenzung von Abwasseremissionen aus der Herstellung von anorganischen Düngemitteln sowie von Phosphorsäure und deren Salzen BGBl. 1996/669 (Ordinance for the limitation of waste water emissions from the production of inorganic fertilizers or phosphoric acid and its salts).

- Hydrocarbons and basic organic chemicals
  The ordinance for the limitation of waste water emissions from the production of hydrocarbons and basic organic chemicals regulates the emission standards for the production of hydrocarbons and basic organic chemicals. This ordinance entered into force at the 13.1.2000. Plants, which have been approved before this date have to fulfil these requirements within the next six years. This ordinance regulates:

  i. storage of products from the processing of crude oil or crude oil fractions, which are used in the production processes of item ii to vi
  ii. production of alkenes, alkines or aromatics from processing products of crude oil or crude oil fractions with cracking, using additional steam (steam cracking)
  iii. production of chemically pure hydrocarbons or their mixtures from cracking products of item ii by using physical separation processes
  iv. production of basic organic chemicals from products of item ii or iii using alkylation, desalkylation, dehydrogenation, disproportionation, hydration, hydroxylation, hydrodesalkylation, hydrogenation, isomerization, oxidation or etherification
  v. production of nitrogen containing basic organic chemicals from hydrocarbons of item ii or iii or from substances of item iv (e. g. amides, amines, cyanates, isocyanates, lactams, nitriles, nitro-, nitroso or nitrate compounds, nitrogen containing aromatics)
  vi. production of sulphur or phosphorus containing basic organic chemicals from hydrocarbons of item ii or iii or from substances of item iv
  vii. production of halogenated basic organic chemicals from hydrocarbons of item ii or iii or from substances of item iv
  viii. storage of products from item ii to vii
  ix. cleaning of drawing-off air and aqueous condensates from actions according to item to viii
  x. cleaning of combustion gases from actions according to item i to viii with the use of aqueous substances if simultaneously physical or chemical reactions with the aim of a synthesis or production are made or if the exhaust gas of the combustion is mixed with an other waste gas and the composition of the residual exhaust gas is significantly different compared to the composition of the combustion gas.

Emission standards for the production of hydrocarbons		
General parameters	**Standards for the discharge into surface waters**	**Standards for the discharge into the public sewerage system**
Temperature	30 °C	40 °C
T_A	8	no impairment of the public waste water treatment plant
T_L	4	no impairment of the public waste water treatment plant
T_D	4	No impairment of the public waste water treatment plant
T_F	2	No impairment of the public waste water treatment plant
TSS	30 mg/l	150 mg/l
pH	6.5 – 8.5	6.5 – 10
Inorganic parameters	**Standards for the discharge in surface waters**	**Standards for the discharge in the public sewerage system**
Aluminium (calculated as Al)	2 mg/l	Limited with the standard for TSS
Lead (calculated as Pb)	0.5 mg/l	0.5 mg/l
Iron (calculated as Fe)	3.0 mg/l	Limited with the standard for TSS
Copper (calculated as Cu)	0.5 mg/l	0.5 mg/l
Nickel (calculated as Ni)	0.5 mg/l	0.5 mg/l
Mercury (calculated as Hg)	0.01 mg/l	0.01 mg/l
Zinc (calculated as Zn)	1 mg/l	1 mg/l
Tin (calculated as Sn)	1 mg/l	1 mg/l
Ammonium (calculated as N)	5 mg/l	
Chloride (calculated as Cl)	limited with standards for toxicity	
Cyanide (easily released and calculated as CN)	0.1 mg/l	0.5 mg/l
Fluoride (calculated as F)	30 mg/l	30 mg/l
Total bound nitrogen (including ammonium, nitrite and nitrate nitrogen)	40 mg/l	-
Total phosphorus (calculated as P)	2 mg/l	-
Sulphate (calculated as SO_4)	-	200 mg/l
Sulphide (easily released and calculated as S)	0.5 mg/l	1 mg/l
Organic parameters	**Standards for the discharge in surface waters**	**Standards for the discharge in the public sewerage system**
TOC (calculated as C)	25 mg/l	-
COD (calculated as O_2)	75 mg/l	-
BOD_5 (calculated as O_2)	20 mg/l	-
AOX (calculated as Cl)	0.5 mg/l	0.5 mg/l
Sum of hydrocarbons	5 mg/l	20 mg/l
POX (calculated as Cl)	0.1 mg/l	0.1 mg/l
Phenolindex (calculated as phenol)	0.2 mg/l	20 mg/l
Sum of anionic and non-ionic tensides	2 mg/l	No impairment of the public waste water treatment plant
Sum of volatile aromatics (BTXE)	0.1 mg/l	1 mg/l
To meet the emission limits, four out of five successively measured values have to be lower than the emission limit value and only one measured value may exceed the emission limit (maximum 50 % of the emission limit). The majority of the parameters have to be determined with mass proportional homogeneous daily average samples. The parameters temperature, TSS, pH, cyanide, sulphide, POX and sum of volatile aromatics (BTXE) are determined with random samples.		

Waste water from the production of the following substances has to observe the following special emission limits. The production specific emission limits are related to the installed production capacity in tonnes.

Emission limits for the production of several organic substances		
Substance	**Emission standard**	
	[mg/l]	**[g/tonne installed production capacity]**
1. Ethylbenzene, cumene	1.0	20
2. Acetaldehyde, vinyl acetate	1.0	30
3. Vinyl chloride (VC)	1.0	2
4. Trichlorophenols (TCP, all isomers)	1.0	20
5. Trichlorobenzenes (TCB, all isomers)	0.2	2
6. Tetrachloromethane	1.5	3
7. Hexachlorobutadiene (HCBD)	1.5	2
8. Ethane-1,2-dichloride (EDC)	1.0	2
9. Trichloroethene (TRI)	1.0	3
10. Perchloroethene (PER)	1.0	3
11. Halogenated organic solvents except: 1,2,4-trichlorobenzene and items 6 – 11	1.0	10
To meet the emission limits, four out of five successively measured values have to be lower than the emission limit value and only one measured value may exceed the emission limit (maximum 50 % of the emission limit). The majority of the parameters have to be determined with mass proportional homogeneous daily average samples. The parameters temperature, TSS, pH, cyanide, sulphide, POX and sum of volatile aromatics (BTXE) are determined with random samples.		

For the production of acetylene with calcium carbide as raw material emission limits are set in the ordinance "Verordnung über die Begrenzung von Abwasseremissionen aus der Herstellung von technischen Gasen" (BGBl. 1996/670). All acetylene plants in Austria use calcium carbide processes for acetylene production

Emission standards for the production of acetylene from calcium carbide		
General parameters	**Standards for the discharge in surface water**	**Standards for the discharge in the public sewerage system**
Temperature	35 °C	40 °C
T_L	4	No impairment of the public waste water treatment plant
T_F	2	No impairment of the public waste water treatment plant
TSS	50 mg/l	No impairment of the operation of the public sewage system or wastewater treatment plant
pH	6.5 – 9	6.5 – 10
Inorganic parameters	**Standards for the discharge in running waters**	**Standards for the discharge in the public sewerage system**
Iron (calculated as Fe)	2 mg/l	Limited with the standard for TSS
Ammonium (calculated as N)	10 mg/l	-
Cyanide (easy to release and calculated as CN)	0.1 mg/l	0.1 mg/l
Total phosphorus (calculated as P)	1 mg/l	-
Sulphate (calculated as SO_4)	-	200 mg/l
Sulphide (calculated as S)	0.1 mg/l	1 mg/l
Sulphite (calculated as SO_3)	1 mg/l	10 mg/l
Organic parameters	**Standards for the discharge in running waters**	**Standards for the discharge in the public sewerage system**
COD (calculated as O_2)	50 mg/l	-
Sum of hydrocarbons	10 mg/l	20 mg/l
Phenolindex (calculated as phenol)	0.1 mg/l	10 mg/l
To meet the emission limits, four out of five successively measured values have to be lower than the emission limit value and only one measured value may exceed the emission limit (maximum 50 % of the emission limit). The majority of the parameters have to be determined with mass proportional homogeneous daily average samples. The parameters temperature, TSS, pH, cyanide, sulphide are determined with random samples.		

The ordinance "Verordnung über die Begrenzung von Abwasseremissionen aus der Herstellung von anorganischen Düngemitteln sowie von Phosphorsäure und deren Salzen " (BGBl. 1996/669) regulates the emission standards for the discharge of waste water from melamine and urea production.

Emission standards for waste water from urea and melamine production		
General parameters	**Standards for the discharge into surface water**	**Standards for the discharge into the public sewerage system**
Temperature	30 °C	35 °C
T_F	4	No impairment of the public waste water treatment plant
TSS	30 mg/l	150 mg/l
pH	6.5–8.5	6.5–9.5
Inorganic parameters	**Standards for the discharge into surface water**	**Standards for the discharge into the public sewerage system**
Ammonium (calculated as N)	0.5 kg/t	0.5 kg/t
Nitrate (calculated as N)	0.5 kg/t	0.5 kg/t
Nitrite (calculated as N)	0.02 kg/t	0.02 kg/t
Organic parameters	**Standards for the discharge into surface water**	**Standards for the discharge into the public sewerage system**
COD (calculated as O_2)	0.5 kg/t	-
The emission standards are related to the installed production capacity of the plant (related to the tonne nitrogen in the final product). To meet the emission limits, four out of five successively measured values have to be lower than the emission limit and only one measured value may exceed the emission limit (maximum 50 % of the emission limit). Most of the parameters have to be determined with mass proportional homogeneous daily average samples. The parameters temperature, filter out matter, pH and nitrite have to be determined with random samples.		

2. BELGIUM

Flemish Legislation on Waste Water and Waste Gas in the Chemical Sector

In the Flemish environmental legislation, **VLAREM**, the chemical sector is classified under different subsections:

- classification number 7 'Chemicals'
  (see Annex 1)
- classification number 17 'Hazardous Substances'
  (see Annex 2)
- classification number 20.4 'Chemical Industry, Industrial activities subject to 84/360/EEG'
  (see Annex 3)

Chemical plants are subject to some sector-specific legislation that may differ from the general environmental legislation specified in VLAREM:

- Vlarem II, Hoofdstuk 5.7 'Chemicals' (classification number 7)
  (see Annex 4)
- Vlarem II, Hoofdstuk 5.17 'Hazardous Substances' (classification number 17)
  (see Annex 5)
- Vlarem II, Hoofdstuk 5.20 'Industrial activities that can give rise to air pollution'
  (classification number 20)
  (see Annex 6)

Annex 1

7.	CHEMICALS (see also sections 17 and 20.4)					
7.1	Establishments which are not classified elsewhere for the production or treatment of organic or inorganic chemicals involving: - alkylation - amination with ammonia - carbonylation - condensation - dehydrogenation - esterification - halogenation and halogen manufacture - hydrogenation - hydrolysis - oxidation - polymerisation - desulphurisation, synthesis and conversion sulphur-containing compounds - nitration and synthesis of nitrogen-containing compounds - synthesis of phosphorus-containing compounds - distillation - extraction - solvatation - mixing with an annual capacity of:					
	1. up to and including 1000 tonnes	3				
	2. between 1000 up to and including 10000 tonnes	2	A,G			
	3. over 10000 tonnes	1	G,M	A	P	J
7.2	Integrated chemical installations, i.e. for the manufacture on an industrial scale of substances by chemical conversion, in which different units co-exist and are functionally interconnected, intended for the manufacture of: 1. basic organic chemicals 2. basic inorganic chemicals 3. phosphate, nitrogen or potassium-containing fertilizers (simple or composite fertilizers) 4. basic products for crop protection and biocides 5. basic pharmaceutical products with a chemical or biological process 6. explosives	1	G,M	A	P	J
7.3	Petrochemical plants or factories based on these for the cracking or vaporisation of naphtha, gas oil, LPG or other petroleum derivatives, as well as organic chemistry based thereon which is not classified elsewhere, with a processing capacity of:					
	1. up to and including 500000 tonnes per year	2	A			
	2. over 500000 tonnes per year	1	M	A	P	J
7.4	Establishments for the preparation of one of the following products: a) phenols, carbon disulphides and mercaptans, with an annual capacity of:					
	1. up to and including 10 tonnes	2				
	2. 10 tonnes and over	1	G,M	A	P	J
	b) amines and halogenated organic compounds with an annual capacity of:					
	1. up to and including 10 tonnes	2				
	2. 10 tonnes and over	1	G,M	A	P	J
7.5	Production of chlorine by electrolysis and/or by the mercury or diaphragm process with an annual capacity of:					
	1. up to and including 10 tonnes	2				
	2. 10 tonnes and over	1	G,M	A	P	J
7.6	Manufacture of organic and inorganic peroxides with an annual capacity of:					
	1. up to and including 10 tonnes	2				
	2. 10 tonnes and over	1	G,M	A	P	J

7.	CHEMICALS (see also sections 17 and 20.4)					
7.7	Production of hydrogen chloride and derivatives, as well as its polymers, other than those referred to in section 5, with an annual capacity of:					
	1. up to and including 10 tonnes	2				
	2. 10 tonnes and over	1	G,M	A	P	J
7.8	Production of sodium pentachlorophenol by electrolysis or hexachlorobenzene, with an annual capacity of:					
	1. up to and including 10 tonnes	2				
	2. 10 tonnes and over	1	G,M	A	P	J
7.9	Production of soda (sodium carbonate) as end product and/or of calcium and sodium chloride as by-product, with an annual capacity of end product or by-product of:					
	1. up to and including 10 tonnes	2				
	2. 10 tonnes and over	1	G,M	A	P	J
7.10	Production of methyl cellulose by action of methyl chloride on cellulose, with an annual capacity of:					
	1. up to and including 10 tonnes	2				
	2. 10 tonnes and over	1	G,M	A	P	J
7.11	Chemical installations for the manufacture of [1,2]:		G,M,X	A	P	J
	1. basic organic-chemical products, such as: a) simple hydrocarbons (linear or cyclic, saturated or unsaturated, aliphatic or aromatic) b) oxygen-containing hydrocarbons, such as alcohols, aldehydes, ketones, carboxylic acids, esters, acetates, ethers, peroxides, epoxy resins c) sulphur-containing hydrocarbons d) nitrogen-containing hydrocarbons, such as amines, amides, nitroso, nitro and nitrate compounds, nitriles, cyanates, isocyanates e) phosphor-containing hydrocarbons f) halogen–containing hydrocarbons g) organo-metallic compounds h) plastic-based products (polymers, artificial fibres, cellulose fibres) i) synthetic rubber j) dyes and pigments k) surfactants and tensides	1	G,M,X	A	P	J
	2. basic inorganic-chemical products, such as: a) gases, such as ammonia, chlorine or hydrogen chloride, fluoride or hydrogen fluoride, carbon oxides, sulphur compounds, nitrogen oxides, hydrogen, sulphur dioxide, carbonyl dichloride b) acids, such as chromic acid, hydrogen fluoride, phosphoric acid, nitric acid, hydrogen chloride, sulphuric acid, oleum, sulphurous acid c) bases, such as ammonium hydroxide, potassium hydroxide, sodium hydroxide d) salts, such as ammonium chloride, potassium chlorate, potassium carbonate, sodium carbonate, perborate, silver nitrate e) non-metals, metal oxides or other inorganic compounds, such as calcium carbide, silicon, silicon carbide	1	G,M,X	A	P	J
	3. phosphate-, nitrogen- or potassium-containing fertilizers (simple or composite fertilizers)	1	G,M,X	A	P	J
	4. basic pharmaceutical products which use a chemical or biological process	1	G,M,X	A	P	J
	5. explosives	1	G,M,X	A	P	J

[1] There may be overlapping with other subsections of sections 7, 13 and 38
[2] Manufacture in the meaning of this section is understood to mean the manufacture of the substances or groups of substances referred to in this section on an industrial scale by chemical conversion

Annex 2

17	**Hazardous Products** [1] (discharge of waste water which contains one or more of the hazardous substances referred to in list 2C of Appendix 2 to title I of the Vlarem: see section 3.5)					
17.2	Industrial activities and storage depots with risks of major accidents (EU Directive 96/82/EC of 9 December 1996 concerning the control of the hazards of major accidents involving hazardous substances)					
17.2.1	establishment in which hazardous products are present in quantities equal to or greater than the amount specified in Appendix 6, parts 1 and 2, column 2 appended to title I of the VLAREM (see also Article 7 of title I of the VLAREM)	1	G	A	P	J
17.2.2	VR-obliged establishment in which hazardous products are present in quantities equal to or greater than the amount specified in Appendix 6, parts 1 and 2, column 3 appended to title I of the VLAREM (see also Article 7 of title I of the VLAREM)	1	G	A	P	J
17.3	Establishments or storage depots for hazardous products not classified under 17.2 or 17.4 [2,3]					
17.3.1	Establishments for the industrial production of very toxic, toxic, extremely flammable, highly flammable, explosive or environmentally dangerous substances with an annual capacity of:					
	1. up to and including 10 tonnes	2			P	J
	2. 10 tonnes and over	1	G	A	P	J
17.3.2	Establishments for the storage of very toxic, toxic and explosive substances with the exception of those referred to under section 48, with a storage capacity of:					
	1. over 10 kg up to and including 100 kg	3				
	2. over 100 kg up to and including 1 tonne	2				
	3. over 1 tonne	1	G	B	P	J
17.3.3	Storage depots for oxidizing, harmful, corrosive and irritating substances, with the exception of those referred to under section 48, with a total capacity of:					
	1. 200 kg up to and including 1000 kg	3				
	2. over 1000 kg up to and including 50000 kg	2				
	3. over 50000 kg	1	G	B	P	J
17.3.4	Storage depots for extremely flammable and highly flammable liquids with the exception of those referred to under section 48, with a total capacity of:					
	1. 50 l up to and including 500 l	3				
	2. over 500 l up to and including 30000 l	2				
	3. over 30000 l	1		B		
17.3.5	Storage depots for flammable liquids with the exception of those referred to under section 48, with a total capacity of:					
	1. 100 l up to and including 5000 l	3				
	2. over 5000 l up to and including 100000 l	2				
	3. over 100000 l	1		B		
17.3.6	Storage depots for liquids with a flame point higher than 55°C but not exceeding 100°C, with the exception of those referred to under section 48, with a total capacity of:					
	1a) 5000 l up to and including 20000 l if the establishment is connected with the residential function of a property that is used mainly for residential purposes.	3				
	1b) 100 l up to and including 20000 l for establishments other than those referred to in a)	3				
	2. over 20000 l up to and including 500000 l	2				
	3. over 500000 l	1		B		
17.3.7	Storage depots for liquids with a flame point higher than 100°C, with the exception of those referred to under section 48, with a total capacity of:					
	1. 200 l up to and including 50000 l	3				
	2. over 50000 l up to and including 5000000 l	2				
	3. over 5000000 l	1		B		

17	**Hazardous Products** [1] (discharge of waste water which contains one or more of the hazardous substances referred to in list 2C of Appendix 2 to title I of the Vlarem: see section 3.5)					
17.3.8	Storage depots for environmentally dangerous substances, with the exception of those referred to in section 48, with a storage capacity of:					
	1. over 100 kg up to and including 1 tonne	3				
	2. over 1 tonne up to and including 100 tonnes	2	G			
	3. over 100 tonnes	1	G	A	E	J
17.3.9	Fuel distribution installations for motor vehicles, i.e. installations for the filling of fuel tanks of motor vehicles with liquid hydrocarbons intended to power the engine(s) fitted therein.					
	1. establishments for the distribution of the liquids referred to in section 17.3.6.1° with a maximum of 1 distribution pipe	3				
	2. establishments for the distribution of: a) the fuels referred to in section 17.3.6.2 with a maximum of 1 distribution hose and/or b) fuels referred to in section 17.3.4.1 and 2 with a maximum of 1 distribution hose	2				
	in which only the company's own vehicles are supplied	2				
	3. other establishments	1		B		
17.4	Storage depots, with the exception of those referred to under section 48, and/or points of sale of the hazardous substances referred to in Appendix 7 to title I of the VLAREM in packagings with a maximum capacity of 25 litres or 25 kilograms, provided the maximum storage is between 50 kg or 50 l and 5000 kg or 5000 l (EC directive 67/548/EEC of 27 June 1967 concerning the application of the legal and administrative provisions on the classification, packaging and marking of hazardous substances).	3				
17.5	Devices that contain over 5 dm³ of PCBs and devices of which it can be reasonably assumed that the fluids therein contain between 0.05 and 0.005% by weight of PCBs (EC directive 96/59/EC of 16 September 1996) [4]	3				

[1] This section concerns solid and liquid substances. Gases are classified in section 16.
[2] For the application of this section, "hazardous products" are considered as the substances referred to in Appendix 7 to title I of the VLAREM.
3 For the application of the classification criteria of this subsection, the main property and the flame point must be taken into account. For liquid fuels, however, only the flame point needs to be taken into account.
In this context, the "main property" is understood to mean the cataloguing according to EC directive 67/548/EEC of 27 June 1967 concerning the classification, packaging and marking of hazardous substances and EC directive 88/379/EEC of 7 June 1988 concerning the classification, packaging and marking of hazardous preparations. If a product is marked with two or more hazard symbols, the most relevant risk must be taken into account. If this is not specified in the above mentioned EC directive, the classification of the ADR regulations must be followed as laid down by the Royal Decree of 16 September 1991 concerning the transport of hazardous goods by road with the exception of explosive and radioactive substances as identified in the Belgian State Gazette of 18 June 1997.
[4] for power current condensors, the threshold applies to the total of the separate components of a combined device.

Annex 3

20.4	**Chemical industry (also see section 7):**					
20.4.1	Chemical establishments for the production of olefins, olefin derivatives, monomers and polymers not classified in section 7.3					
	1. with a production capacity of up to and including 10 tonnes per year;	2				
	2. with a production capacity of over 10 tonnes per year	1	G,M	A	P	J
20.4.2	Chemical establishments for the manufacture of organic intermediate products, not classified in section 7:					
	1. with a production capacity of up to 10 tonnes per year	2				
	2. with a production capacity of over 10 tonnes per year	1	G,M	A	P	J
20.4.3	Establishments for the manufacture of basic inorganic chemical products not classified in section 7:					
	1. with a production capacity of up to and including 10 tonnes per year	2				
	2. with a production capacity of over 10 tonnes per year	1	G,M	A	P	J
	(Establishments for the disposal of toxic and dangerous waste by incineration: see sections 2.3.4) (Establishments for the treatment of other solid and liquid waste by incineration: see section 2.3.4)					

Annex 4

CHAPTER 5.7: CHEMICALS

Section 5.7.1. General provisions

Art. 5.7.1.1

§ 1. The provisions of this chapter are applicable to the establishments specified in section 7 of the classification list.

§ 2. The substances falling within the scope of the regulations relating to hazardous substances, in particular the provisions of chapter 5.17, may only be brought into, stored at, used at and removed from the establishment on condition that the provisions of the aforementioned regulations are strictly adhered to.

§ 3. For the application of these provisions, "production capacity" means: the total capacity for an uninterrupted working period of 24 hours, multiplied by the average number of days per year during which the installations can operate, under normal conditions as regards maintenance and safety. This capacity is expressed in tonnes.

Art. 5.7.1.2

§ 1. The operator is responsible for the acceptance, manufacture, production, preparation, processing, handling, formulation, packaging and/or removal of the substances and products.

§ 2. Production of polychlorinated biphenyls (PCBs) and polychlorinated terphenyls (PCTs) is prohibited.

§ 3. Production of the chlorofluorocarbons (CFCs), bromofluorocarbons (BFCs or halons), or mixtures of them, specified in appendix 5.7, is prohibited.

§ 4. In accordance with article 11 of the EU Council regulation no. 3322/88 of 14 October 1988, operators of establishments where the CFCs and BFCs referred to in § 3 are manufactured, must provide the following information to the Commission of the European Community as well as to the Environmental Licence Department, and this for each of the CFCs and BFCs referred to in § 3:

1. at the latest two months after the date of the coming into force of the present order, with respect to the year 1986, and for the whole of the period concerned:
    a) the produced quantities
    b) the commercialised quantities
    c) the quantities used for their own account
    d) the imported quantities
    e) the exported quantities
    f) the quantities removed;
finally also the quantities in stock on 31 December of the year concerned must be indicated;

2. with respect to the CFCs, not later than 31 August of each year, for the preceding period of 1 July to 30 June:
    a) the produced quantities
    b) the commercialised quantities
    c) the quantities used for their own account
    d) the imported quantities
    e) the exported quantities
    f) the quantities removed;
finally also the quantities in stock on 30 June of the year concerned must be indicated;

3. with respect to BFCs, not later than 28 February of each year, for the preceding calendar year:

     a) the produced quantities

     b) the commercialised quantities

     c) the quantities used for their own account

     d) the imported quantities

     e) the exported quantities

     f) the quantities removed;

finally also the quantities in stock on 31 December of the preceding calendar year must be indicated.

§ 5. The production of the following substances is prohibited except when the production of one or several of them is explicitly permitted in the environmental licence:

     1. bromomethane;

     2. cyanogen, hydrocyanic (prussic acid) and its salts (cyanides);

     3. organic cyanides (nitriles).

Art. 5.7.1.3

§ 1. If an establishment is subject to a licence requirement because of its classification in section 7 of the classification list, any storage of dangerous substances must also meet the conditions of chapter 5.17 "Hazardous substances" of this order, providing that the storage quantities concerned fall within the scope of said chapter.

However, in the environmental licence exceptions can be indicated with respect to the separation distances between two groups and/or sub-groups with non-classified storage quantities. In such cases, the grounds for the exception must also be indicated.

§ 2. Unless specified otherwise in the environmental licence, bromomethane must be stored in pressure vessels with a contents of at most 100 kg of bromomethane per drum; the drums of bromomethane must be placed vertically, with the closing device of the drum at the top; drums of bromomethane must be protected against weather influences such as sunshine and rain and may not be stacked; during storage, the closing devices of the drums of bromomethane must be protected against mechanical damage by closing caps; empty drums must be stored as full drums;

§ 3. The construction of all spaces for the processing of hazardous products is provided in such a way that accidentally spilt substances or leaked liquids can be collected.

To prevent the spreading of fire, all spaces for the handling of extremely flammable and highly flammable liquids must be constructed in such a way that accidentally spilt substances and leaked liquids end up in a collection device and are taken to one or more collection wells by means of collection channels.

This collecting device may in no way be connected indirectly or directly to a public sewer, a surface water, a collecting basin for surface water, a ditch or a groundwater layer.

The collection device and the collection wells must be regularly emptied, and at least after each incident. The resulting waste flows must be disposed of in an appropriate manner.

§ 4. Without prejudice to any other relevant legal or regulatory provisions, the operator takes all measures required to sufficiently protect the surrounding area against the risks of fire and explosion. This includes the mandatory availability of the necessary firefighting equipment. The type of firefighting equipment required and where it should be kept is determined after consultation with the authorised fire brigade. This matter is completely unrelated to the environmental licence.

The firefighting equipment must be kept in a properly maintained condition, protected against frost, appropriately marked, easily accessible and placed in appropriate locations. It must immediately be able to be brought into operation.

§ 5. At the establishment, the necessary provisions must be present to prevent fire extinguishing water contaminated with chemicals from draining into the ground, public sewers, surface or groundwater. The collected contaminated fire extinguishing water must be disposed of in an appropriate fashion. The collection capacity for contaminated fire extinguishing water must be determined in consultation with the authorised fire brigade.

§ 6. All persons and staff working at the establishment must be fully aware of the nature of the substances and products manufactured and the dangers involved. Personnel must be well informed about the measures to be taken when irregularities occur. The operator is to provide up-to-date instructions as required. These instructions must be evaluated by the operator at least once per year.

Art. 5.7.1.4

§ 1. Unless specified otherwise in the environmental licence and as a derogation from the general emission limit values specified in chapter 4.4, the emission limit values given below - expressed in mg/Nm^3 and relating to the following circumstances: temperature 0 °C, pressure 101.3 kPa, dry gas, or wet gas if steam ejectors are used - apply to the waste gases discharged: The quantities of air supplied to a part of the installation for the dilution or cooling of the waste gas are not taken into account with the calculation of the emission values.

1. propenenitrile:
   - in the gaseous effluent of the combustion plants for the production of propenenitrile, irrespective of the mass flow: 0.2 mg/Nm^3
   - remaining, with a mass flow of 25 g/h or more: 5.0 mg/Nm^3

2. the following organic substance, at a mass flow per substance of 100 g/h or more:
   1,2-dichloroethane:
   - with the production of this compound: 5.0 mg/Nm^3
   - in other cases: 20.0 mg/Nm^3

3. total dust:
   plants for the production of biocides or active ingredients thereof, at a mass flow of 25 g/h or more:
   - for highly toxic or highly bioaccumulative and persistent biocides: 5.0 mg/Nm³
   - for highly toxic, harmful or corrosive biocides: 20.0 mg/Nm³
   - for non-harmful biocides: 100.0 mg/Nm³

§ 2. Gaseous effluents are to be collected at the place they originate and, after any necessary purification for compliance with the prevailing emission and immission conditions, discharged into the ambient air through a chimney stack. This chimney stack must be sufficiently tall to, from an environmental perspective, adequately disperse the discharged substances and not affect public health. The minimum height must be determined in accordance with the chimney stack height calculation system as specified in art. 4.4.2.3.

Section 5.7.2 The production of titanium dioxide

Art. 5.7.2.1

The provisions of this section are applicable to the establishments referred to in subsection 7.1 of the classification list, as far as these establishments belong to the sector of titanium dioxide production.

Art. 5.7.2.2

§ 1. The dumping of all solid wastes, strongly acid wastes, purifying waste materials, weakly acid wastes or neutralised wastes is prohibited.

§ 2. For existing establishments the following transitional provisions apply:

1. for existing plants making use of the sulphate process:
   the discharge of weakly acid and neutralised wastes in all waters is restricted to a value of no more than 800 kg total quantity of sulphate – i.e. corresponding to the SO_4-ions in the free sulphuric acid and in the metal sulphates – per produced tonne of titanium dioxide.
2. for existing plants making use of the chloride process:
   the discharging of weakly acid wastes, purifying waste materials and neutralised wastes in all waters is restricted to the following values for the total quantity of chloride – i.e. corresponding to the Cl-ions in the free hydrochloric acid and in the metal chlorides – per produced tonne of titanium dioxide:
   - 130 kg when use is made of natural rutile
   - 228 kg when use is made of synthetic rutile
   - 450 kg when use is made of slag;
   in the case of an establishment that makes use of more than one kind of ore, the values apply in proportion to the quantities of the ores used.

Art. 5.7.2.3

For emissions into the atmosphere the following emission limitations apply:

1. for existing plants making use of the sulphate process:
   - emission limit value for dust: $\qquad$ 50 mg/Nm^3
   - provisions must be made to prevent the emission of acid droplets
   - the emissions of SO_x originating from the dissolution and roasting phases of titanium dioxide production are restricted to a maximum of 10 kg SO_2-equivalent per tonne of titanium dioxide produced
   - plants where the waste acids are concentrated may not discharge more than 500 mg/Nm^3 of SO_x, calculated as SO_2-equivalent
   - plants where the salts originating from the purification of wastes are roasted, are to be equipped with the best available techniques to reduce the SO_x-emissions;

2. for existing plants making use of the chloride process:
   - emission limit value for dust: $\qquad$ 50 mg/Nm^3
   - chlorine: - daily average of: $\qquad$ 5 mg/Nm^3
   - instantaneous value of $\qquad$ 40 mg/Nm^3.

Art. 5.7.2.4

Regarding wastes from the titanium dioxide industry - and in particular wastes of which the discharge or dumping into water or emission into the atmosphere is prohibited - the necessary measures must be taken in order to ensure that:

1. as far as possible they are not created, or that they are reused, insofar as this is possible technically and economically;
2. they are reused or disposed of without endangering human health and without adverse effects on the environment.
The same applies to wastes generated during the recycling or purification of the aforementioned wastes.

Art. 5.7.2.5

§ 1. The quantities of SO_2, SO_3 and acid droplets - expressed in SO_2-equivalent - emitted by certain plants, must be calculated taking account of the volume of gases emitted during the specific activities concerned and the average SO_2/SO_3-content measured during the same period. The determination of the flow rate and of the SO_2/SO_3-content must be performed under the same conditions of temperature and humidity.

§ 2. Without prejudice to the provisions of article 5.7.1.4 and of chapters 2.5 and 4.4, at one or several measurement stations located near the establishment in a location which is representative for the pollution originating from the plant, the following must be monitored:

1. sulphur dioxide immissions, if use is made of the sulphate process for the production of titanium dioxide;
2. chlorine immissions, if use is made of the chlorination process for the production of titanium dioxide.

If no immission measuring station as referred to in the first paragraph is provided, measurements must be made at least 12 times per year of the total quantity of gaseous emissions of sulphur dioxide and chlorine, respectively, from the production site.

§ 3. From 1 January 1995, unless specified otherwise in the environmental licence and as a derogation from the provisions of chapter 4.4, the SO_x-emissions originating from the dissolution and roasting phases of the titanium dioxide production must be restricted to a value of no more than 10 kg of SO_2-equivalent per tonne of titanium dioxide produced.

Section 5.7.3. The production of sulphur dioxide, sulphur trioxide, sulphuric acid or oleum (fuming sulphuric acid)

Art. 5.7.3.1

§ 1. The provisions of this section are applicable to the sulphur dioxide, sulphur trioxide, sulphuric acid or oleum producing plants referred to in subsection 7.1 of the classification list.

§ 2. For the implementation of these provisions, the "conversion efficiency of SO_2 to SO_3" is defined as follows:

$$\text{conversion efficiency} = \frac{SO_2(\text{in}) - SO_2(\text{out})}{SO_2(\text{in})} \times 100 \ (\%)$$

Art. 5.7.3.2

§ 1. If - in view of the gases used as raw material - it is technically possible from the viewpoint of the best available techniques, the double-contact process must be used for the conversion of SO_2 to SO_3. If it proves indispensable, in order to achieve the emission limitations corresponding to the conversion efficiency values prescribed in § 4 of this article, the emissions of SO_2 and SO_3 can be further reduced by making use of a fifth contact bed, or by means of equivalent measures. The use of any alternative process is allowed, providing that such process is at least equivalent from the perspective of pollution control and in particular providing that it guarantees the same or higher conversion rates.

§ 2. The single-contact process (without intermediary absorption) is permitted only if gases with SO_2-contents lower than 10 % are processed, or gases of which the SO_2-contents are widely varying. If it proves indispensable, in order to achieve the emission limitations corresponding to

the conversion efficiency values prescribed in § 4 of this article, the emissions of SO_2 and SO_3 must be further reduced by alkaline scrubbing, or by means of equivalent measures.

§ 3. The wet catalytic process is allowed only with molybdenum sulphide roasting and for flue gas desulphurisation.

§ 4. The daily average conversion rate must be at least:

1. when use is made of the single-contact process:
    a) with a feed gas containing less than 6 % SO_2, a conversion rate of at least 97.5 % must be achieved
    b) with a feed gas containing 6 % SO_2 or more, a conversion rate of at least 98.5 % must be achieved;
2. when use is made of the double-contact process:
    a) with a feed gas containing less than 8 % SO_2, a conversion rate of at least 99 % must be achieved
    b) with a feed gas containing 8 % SO_2 or more, a conversion rate must be achieved of at least:
        • 99.5 % with varying gas conditions
        • 99.6 % with constant gas conditions;
3. when use is made of the wet catalytic process, a conversion rate of at least 97.5 % must be achieved;
4. when any other process is used, a conversion rate must be achieved of at least 99 %.

§ 5. As a derogation from the provisions of chapter 4.4, the following emission limit values apply for:

1. sulphur dioxide: 1700 mg/Nm^3, without prejudice to the conversion rate prescribed in article 5.7.5.1;

2. sulphur trioxide:
    • with constant gas conditions: 60 mg/Nm^3;
    • in the other cases: 120 mg/Nm^3.

§ 6. In addition, in the environmental licence limit values may be imposed for the mass flow of the SO_3 and H_2SO_4 emissions (expressed in SO_3) in the emitted waste gases.

§ 7. The conversion efficiency values indicated in § 4 of this article do not apply for SO_3-generators of category 3 which are used to stimulate the emission of fly ash by the injection of SO_3 in the flue gases of heating installations. For the flue gases treated in this way, the SO_3 emission standards of the corresponding heating installation apply.

Section 5.7.4 The production of nitric acid

Art. 5.7.4.1

§ 1. The provisions of this section are applicable to the nitric acid producing plants referred to in subsection 7.1 of the classification list.

§ 2. As a derogation from the provisions of chapter 4.4, for nitrogen oxides in emitted gaseous effluents - expressed in NO_2 - an emission limit value applies of: 450 mg/Nm^3.
In addition, the gaseous effluents may only be emitted colourless into the ambient air. In order to achieve this, and without prejudice to the limit value prescribed in the first paragraph, the NO_2 emission may not exceed the value resulting from the calculation of the formula below:

$$NO_2 \text{ concentration} = \frac{1200}{\text{open width of the chimney mouth in dm}}$$

Section 5.7.5 The production of chlorine

Art. 5.7.5.1

§ 1. The provisions of this section are applicable to the establishments referred to in subsection 7.5 of the classification list.

§ 2. As a derogation from and supplementing the provisions of section 4.4.3, the following emission limit values apply for:

1. chlorine:
   a) with plants for the production of chlorine with complete liquefaction: 6 mg/Nm^3;
   b) in the other cases: 1 mg/Nm^3;
2. mercury and its compounds:
   a) with a mass flow of 1 g/h or more: 0.2 mg/Nm^3
   b) with chlorine-alkali-electrolysis according to the amalgam process, the annual average emissions of mercury in the air removed form the cell hall may not exceed:
    i. 1.5 g per tonne of chlorine produced, for new plants
    ii. 2 g per tonne of chlorine produced, for existing plants
    iii. the mercury in the hydrogen compounds emitted into the atmosphere or burned, is included in this limit value.

§ 3. The construction of new plants for the production of chlorine according to the mercury cathode process will no longer be licensed. After the year 2010, the mercury cathode process may no longer be applied.

Section 5.7.6 The production of sulphur

Art. 5.7.6.1

§ 1. The provisions of this section are applicable to the sulphur producing plants referred to in subsection 7.1 of the classification list.

§ 2. With Claus-process plants, the following sulphur conversion efficiencies must be achieved:

1. with a production capacity of up to 20 tonnes of sulphur per day: 97 %;
2. with a production capacity of between 20 and 50 tonnes of sulphur per day: 98 %;
3. with a production capacity of over 50 tonnes of sulphur per day: 99 %.

Here, sulphur conversion efficiency must be understood as the proportion between the sulphur produced and the sulphur in the feed gas.

§ 3. As a derogation from the provisions of section 4.4.3, the emissions of hydrogen sulphide in the gaseous effluents may not exceed 10 mg/Nm^3. To this end, the waste gases must be passed through an incinerator.

§ 4. The SO_2-emission concentrations of Claus-process installations that form part of oil refineries are regulated by article 5.20.2.2 ("Oil refineries") of chapter 5.20.

Section 5.7.7 The production of organic chemicals or solvents

Art. 5.7.7.1

§ 1. The provisions of this section are applicable to the establishments producing organic chemicals or solvents, referred to in section 7 of the classification list.

§ 2. The waste gases of plants for the production of 1,2-dichloroethane and of vinyl chloride must be ducted to an air emission abatement installation for gaseous effluent. As a derogation from the provisions of section 4.4.3, for 1,2-dichloroethane in the emitted waste gases an emission limit value applies of 5 mg/Nm^3.

§ 3. The waste gases from the reactor system and the absorber of an installation for the production of propenenitrile must be ducted to an incinerator. As a derogation from the provisions of section 4.4.3, for propenenitrile in the emitted waste gases an emission limit value applies of 0.2 mg/Nm^3. The waste gasses resulting from the purification of the reaction products (distillation) as well as the waste gases generated during the filling, must be ducted to a scrubber.

Section 5.7.8 The production of hydrocarbons in petrochemical plants not belonging to an oil refinery

Art. 5.7.8.1

§ 1. The provisions of this section are applicable to the establishments producing hydrocarbons, referred to in section 7.3 of the classification list.

§ 2. Waste gases discontinuously released by process plants such as gaseous effluents resulting from the regeneration of catalytic agents or with inspection and cleaning activities must be ducted to a combustion facility, or equivalent abatement measures should be taken.

§ 3.Gaseous effluents released with the starting up or shutdown of an installation must, to the extent possible, be transported to a collection system for gaseous effluent or incinerated in process heating installations. If this is not possible the gases must be transported to a flare in which an emission level for organic substances of 1 % with respect to the total carbon content may not be exceeded.

§4. Gaseous effluents from desulphurisation installations or other sources with a volume level of hydrogen sulphide of over 0.4 % and a mass flow of hydrogen sulphide of over 2 tonnes/day must be further processed.
Gaseous effluents which are not further processed must be ducted to an incinerator.
As a derogation from the provisions of chapter 4.4, emissions of hydrogen sulphide in the discharged gaseous effluent may not exceed 10 mg/Nm^3.
Hydrogen sulphide-containing water may only be processed in such a way that the release of gaseous effluent into the atmosphere is avoided.

§ 5. With the transfer of base, intermediary and final products the emissions of organic substances with a vapour pressure of over 13.3 kPa at a temperature of 35 °C must be reduced by means of appropriate measures, such as by gas displacement systems, extraction and transfer to an effluent gas purification installation.

§ 7. Process water may only be discharged into an open system after degassing. The gaseous effluents collected here must be cleaned by washing or incineration.

Section 5.7.9 The production of carbon

Art. 5.7.9.1

§ 1. The provisions of this section are applicable to the plants producing carbon (hard lignite) or electrographitic carbon (e.g. used in electrodes, current collectors or parts for appliances) referred to in subsection 7.1 of the classification list.

§ 2. As a derogation from the provisions of chapter 4.4, the emission limit values for organic substances in the gaseous effluent are as follows:

1. with mixing and moulding, from mixing and moulding installations where pitch, tar or other volatile binders and liquefiers are processed at increased temperatures, expressed in total carbon: 100 mg/Nm^3
2. with combustion, from furnaces with one chamber, furnaces with combined chambers and tunnel kilns, expressed in total carbon: 500 mg/Nm^3
3. with combustion, from annular kilns for graphite electrodes and carbon blocks, expressed in total carbon,: 200 mg/Nm^3
4. with impregnation, from impregnating installations where tar-based impregnating agents are used, expressed in total carbon: 50 mg/Nm^3.

Section 5.7.10 The manufacture of peroxides

Art. 5.7.10.1

§ 1. The provisions of this section are applicable to the establishments referred to in subsection 7.6 of the classification list.

§ 2. Organic peroxides may only be manufactured if this is explicitly permitted in the environmental licence.
The organic peroxides, which may explode or detonate in a violent thermal reaction, at the establishment must be retained at a temperature lower than the temperature which from the point of view of safety is the permissible maximum temperature according to the nature of the substance concerned; for the substances indicated below, this maximum temperature is:

- acetyl cyclohexane sulphonyl peroxide: −10 °C
- amber acid peroxide: +10 °C
- tert.-butyl peroxyisopropylcarbonate (BPIC): room temperature
- tert.-butyl peroxypivalate: −10 °C
- dibenzoyl peroxide: room temperature
- dicyclohexyl peroxydicarbonate: +5 °C
- diisopropyl peroxydicarbonate: −15 °C.

§ 3. The peroxides referred to in § 2 which must be kept at the establishment at a temperature lower than room temperature, must be stored:

1. either in refrigerators or freezers located in the production building, in which case each refrigerator or freezer may contain a quantity of at most 30 kg non-refrigerated organic peroxides;
2. or in refrigerators or freezers, located in a detached storage building in which only the said peroxides are stored. In this case each refrigerator or freezer may contain a quantity of at most 150 kg non-refrigerated organic peroxides;
3. or in a detached cold store that is solely intended for this purpose. In this case, unless specified otherwise in the environmental licence, per cold store a quantity of at most 500 kg non-refrigerated organic peroxides may be stored.

Section 5.7.11 The production of polyvinyl chloride

Art. 5.7.11.1

§ 1. The provisions of this section are applicable to the establishments producing polyvinyl chloride referred to in section 7 of the classification list.

§ 2. At the transition from the closed system for polymerisation or drying to the open system, the residues of vinyl chloride (VC) in the polymerisate must be kept as low as possible. With this, the following maximum monthly average values may not be exceeded:
- mass-PVC: 10 mg VC / kg PVC
- suspension-homopolymerisates: 0.10 g VC / kg PVC
- suspension-copolymerisates: 0.40 g VC / kg PVC
- micro-suspension-PVC and emulsion-PVC: 1.5 g VC / kg PVC.

§ 3. To further reduce the mass concentration of vinyl chloride in the gaseous effluent, insofar as possible the spent gas of the drying plant must be used as combustion gas in heating installations.

Section 5.7.12 The production of caprolactam

Art. 5.7.12.1

§ 1. The provisions of this section are applicable to the establishments producing caprolactam, referred to in section 7 of the classification list.

§ 2. With the production of caprolactam according to the Raschig-process, NO_2-emissions may not exceed 15 kg NO_x/tonne of caprolactam produced.

Section 5.7.13 The production of polyacrylonitrile-based synthetic materials

Art. 5.7.13.1

§ 1. The provisions of this section are applicable to the establishments producing polyacrylonitrile-based synthetic materials, referred to in section 7 of the classification list.

§ 2. The production and processing of propenenitrile-polymerisates for fibres.

1. For the emissions of propenenitrile in the gaseous effluent of the drying plants, an emission limit value of 20 mg/Nm^3 applies.
2. The propenenitrile-containing spent gases originating from the reaction vessels, from the intensive waste gas purging, from the suspension tank and from the washing filter, must be ducted to a spent gas scrubber or an adsorber. For the emissions of propenenitrile in the gaseous effluent of the adsorber, an emission limit value of 10 mg/Nm^3 applies.
3. With the spinning into fibres of the polymer, the waste gas flows with an propenenitrile-content of over 5 mg/Nm^3 must be ducted to an air emission abatement installation for spent gas.

§ 3. The production of ABS-resins

1. Emulsion polymerisation:
   the propenenitrile-containing gaseous effluents released during polymerisation, during precipitation or with the cleaning of the reactor, must be ducted to an incinerator; for the emissions of propenenitrile in the gaseous effluent of the drying plant an emission limit value of 25 mg/Nm^3 applies as monthly average;

2. Combined solution/emulsion polymerisation:

the propenenitrile-containing gaseous effluents released from the reactors, during intermediary storage, during precipitation, during dehydration, with the recycling of solvents and at the mixers, must be ducted to an incinerator; for the propenenitrile emissions released near the mixer exhaust, an emission limit value of 10 mg/Nm^3 applies as monthly average.

§ 4. The production of nitrile rubber (NBR)
The propenenitrile-containing spent gases released from the butadiene recycling, during the intermediary storage of the latex and with the washing of the solid rubber, must be ducted to an incinerator.
The spent gases released during the recycling of the propenenitrile must be ducted to a spent gas scrubber.
For the emissions of propenenitrile in the gaseous effluent of the drying plant an emission limit value of 15 mg/Nm^3 applies.

§ 5. The production of dispersions by emulsion polymerisation of propenenitrile
The propenenitrile-containing gaseous effluents released from the monomer receiving vessels, the reactors, the intermediary storage tanks and from the condensers, must be ducted to a waste gas purification plant if the propenenitrile-content exceeds 5 mg/Nm^3.

Section 5.7.14 The production and processing of viscose

Art. 5.7.14.1

§ 1. The provisions of this section are applicable to the establishments producing viscose, referred to in section 7 of the classification list.

§ 2. The spent gases from the viscose production, from the reprocessing of the spinning bath and from the post-treatment to produce textile rayon must be ducted to an air emission abatement installation.
As a derogation from the provisions of chapter 4.4, the emission limit values for the waste gases are:

1. for hydrogen sulphide: 5 mg/Nm^3 as daily average value
2. for carbon disulphide: 0.10 g/Nm^3 as daily average value.

§ 3. With the production of cellulose wool and cellophane, the gaseous effluents from the spinning machines and from the post-treatment must be ducted to an air emission abatement installation.
As a derogation from the provisions of chapter 4.4, the emission limit values for the waste gases are:

1. for hydrogen sulphide: 5 mg/Nm^3 as daily average value
2. for carbon disulphide: 0.15 g/Nm^3 as daily average value.

§ 4. With the manufacture of viscose products for all gaseous effluents – including the air extracted from the various rooms and near the machines – the following emission limit values apply until 31 December 2001:

1. for hydrogen sulphide: 100 mg/Nm^3 as daily average value
2. for carbon disulphide: 600 mg/Nm^3
3. for the sum of hydrogen sulphide and carbon disulphide: 650 mg/Nm^3.

The best available techniques must be applied to maximally reduce and if possible prevent the emissions of hydrogen sulphide and carbon disulphide.

From 1 January 2002, and as a derogation from the provisions of chapter 4.4, the following emission limit values apply for the gaseous effluent:

1. for hydrogen sulphide: 50 mg/Nm^3 as daily average value
2. for carbon disulphide different values apply according to the viscose product concerned:
   a) cellulose wool: 150 mg/Nm^3
   b) cellophane: 150 mg/Nm^3
   c) rayon (textile):   150 mg/Nm^3
   d) synthetic casings: 400 mg/Nm^3
   e) synthetic chamois: 400 mg/Nm^3
   f) rayon (technical):   600 mg/Nm^3.

Section 5.7.15 The production of enamel

<u>Art. 5.7.15.1</u>

The provisions of this section are applicable to the establishments producing enamel, referred to in section 7 of the classification list.

<u>Art. 5.7.15.2</u>

§ 1. As a derogation from the provisions of chapter 4.4, the emission limit values for gaseous effluents from enamel production are:

1. for gaseous inorganic fluorides, expressed in hydrogen fluoride: 15 mg/Nm^3, with 5 mg/Nm^3 as guiding value;
2. for nitrogen oxides (NO$_x$), expressed in NO$_2$: 15 kg per tonne of enamel produced as monthly average, with a maximum concentration of 2200 mg/Nm^3 and with 500 mg/Nm^3 as guiding value.

§ 2. As a derogation from article 1.1.2, the concentrations indicated in § 1 are related to the actual oxygen content of the emitted gaseous effluents.

§ 3. Unless specified otherwise in the environmental licence, the emission values of the substances above must be measured continually using measuring equipment installed at the operator's expense that is built and operated according to a code of good practice and which has been approved by an environmental expert accredited in the discipline air.

Section 5.7.16 Batch processes in the production of fine chemicals and pharmaceuticals

<u>Art. 5.7.16.1</u>

For processes in the production of fine chemicals and pharmaceuticals the conditions for the emission limit value in mg/Nm^3 for batch processes not exceeding 500 kg of pure final product per batch, are replaced by the following regulation:

the process must comply with a maximum total emission of at most 15 % of the solvents input.

Annex 5

CHAPTER 5.17 THE STORAGE OF HAZARDOUS PRODUCTS

Section 5.17.1 General provisions

Art. 5.17.1.1

§ 1. The regulations in this chapter are applicable to the establishments specified in section 17 of the classification list. For the application of the provisions in this chapter, both the main property and the flashpoint must be taken into account. For liquid fuels only the flashpoint must be taken into account.

§ 2. Short-term storage in connection with transport by road, rail, inland waterways, by sea or by air, including the loading and unloading and the transfer to or from another form of transport in ports, on quays or in railway yards is not subject to the conditions of these regulations.
However, if the hazardous products referred to in these regulations are stored in storage facilities located in ports, along quays or on railway yards and if these storage facilities are intended for the regular short-term storage of such hazardous products, then these storage facilities are subject to the conditions of these regulations.

Art. 5.17.1.2

§ 1. Unless specified otherwise in the environmental licence, the operation of a category 1 establishment for the storage of other than P1, P2, P3 or P4 products is prohibited:

1. in a water abstraction area or a type I, II or III protected zone
2. in an area other than an industrial zone
3. at a distance of less than 100 metres from:
    a) a residential area
    b) parkland
    c) a recreation area.

§ 2. The prohibitory rules of § 1 do not apply:

1. for existing plants or parts of them, as specified in article 3.2.1.1
2. for hazardous products which are in a physico-chemical state such that they do not have any properties that might result in a serious accident, insofar as this has been confirmed by an expert accredited for the discipline external safety and risks for serious accidents
3. for hazardous products belonging to the actual operation of a public water abstraction.

§ 3. Unless specified otherwise in the environmental licence, the operation of a tank farm for the storage of other than P1, P2, P3 or P4 products is prohibited in a water abstraction area or a type I, II or III protected zone:

§ 4. Unless specified otherwise in the environmental licence, the storage of the following substances is prohibited :
1. bromomethane
2. cyanogen, hydrogen cyanide (prussic acid) and its salts (cyanides)
3. organic cyanides (nitriles).

Art. 5.17.1.3

§ 1. Unless specified otherwise in the environmental licence, at the entrance to category 1 establishments for which article 7 of title I of Vlarem is applicable, an identification and information sign of at least 1 m^2 must be placed, indicating at least the information below in a clearly readable way:

1. "VR-PLICHTIG BEDRIJF" (enterprise required to submit a safety report) if in accordance with article 7 § 3 of title I of VLAREM it concerns an enterprise for which a safety report is required, or
   "GEVAARLIJKE STOFFEN" (hazardous substances), at establishments for which article 7 § 1 and § 2, of title I of VLAREM is applicable
2. the operator's name, address and phone number
3. the contact and emergency (fire brigade) phone numbers.

§ 2. At the entrance to establishments for which article 7 of title I of VLAREM is applicable, an up-to-date site plan of the establishment must be kept inside a fireproof cabinet that is easily accessible to the emergency services. For all storage facilities for hazardous products at the establishment, the following information must be clearly
marked on this site plan:

1. the exact location
2. the chemical and/or technical names of the hazardous product, with the specification of the classification according to EC directives 67/548/EEC of 27 June 1967 or 88/379/EEC of 7 June 1988 and of the UN number
3. the specification whether it concerns storage in:
   a) mobile receptacles
   b) fixed aboveground containers
   c) buried containers
   d) containers placed in a trench;
4. the maximum storage capacity in tonnes or m^3
5. the normal storage temperature in °C and the storage pressure in Pa.

§ 3. The cabinet referred to in § 2 bears the notice "GS-SITUATIEPLAN" ("hazardous materials site plan"), in black letters with a height of at least 8 centimetres on a yellow background. If this cabinet is kept locked, either:

1. the key to the lock in question must be kept next to the cabinet, behind a protective glass cover that can be broken with a little hammer in an emergency
2. or the cabinet itself must be closed with a protective glass front that can be broken with a little hammer in an emergency.

§ 4. The conditions specified in § 2 and § 3 may be derogated from if an alternative system is used that is accepted by the Environmental Licence Department and which offers at least the same guarantees as regards information.

§ 5. The necessary provisions must be put in place to make the installation inaccessible to unauthorised persons.

§ 6. The provisions of § 5 are not applicable to storage facilities for liquid fuels which form part of a fuel distribution installation for motor vehicles.

Art. 5.17.1.4

§ 1. The leak-tightness of the piping, the couplings, the valves and all accessories must be ensured. They must be protected against corrosion in an effective way.

§ 2. The non-accessible pipes must be fitted in a ditch that must be filled in with a fine-grained inert material. This ditch must be impervious and must slope down to an impervious collection well.

This system may be replaced by an alternative system which offers the same guarantees as regards the prevention of ground and/or groundwater pollution. The alternative system must be accepted by an environmental expert accredited in the discipline containers for gases or hazardous substances. A certificate of this acceptance is drawn up and signed by the aforementioned environmental expert. This certificate is kept available for the perusal of the supervisory official. A copy of the certificate will be forwarded by the operator to the Environmental Licence Department.

§ 3.The fitting of piping for the transport of P1 and/or P2 products inside spaces is prohibited, except if such piping is made of a single tube (no couplings with seals), or if the spaces have been laid out and zoned in accordance with the requirements referred to in the general regulations for electrical installations, in particular the articles dealing with spaces in which an explosive atmosphere can originate.

Art. 5.17.1.5

§ 1. Without prejudice to further provisions, the necessary precautionary measures must be taken to prevent products from coming into contact with each other if:

1. this could result in dangerous chemical reactions
2. such products could react with each other to form harmful or dangerous gases and vapours
3. contact between such products could result in explosions and/or fire.

§ 2. If at the establishment products with different main properties are stored, the storage facility must be subdivided into different compartments, with in each compartment only products being stored with the same main properties.
These compartments must be delimited by means of walls, safety screens, markings on the ground, chains or fixed demarcations at a height of 1 metre.
However, products with different main properties may be stored together in a single compartment if according to appendix 5.17.1 the minimum separation distance between the products is 0 metres.

§ 3. Any manufacturing operation or other treatment not concerned with the storage or transfer of the products is prohibited inside the storage facilities and the zones delimited by the separation distances and/or screens prescribed in appendix 5.17.1

§ 4. The products may not be stored outside the storage spaces intended for this purpose. Contaminated empty mobile receptacles that have contained hazardous products must be stored in a dedicated place that must be clearly indicated.

Art. 5.17.1.6

§ 1. With respect to aboveground compartments for products with a specific main property, minimum separation distances as indicated in appendix 5.17.1 are to be observed.

§ 2. The distances specified in § 1 may be reduced by the construction of a safety screen, on the condition that the distance measured horizontally around this screen between the compartment concerned and the elements indicated in appendix 5.17.1 is equal to or larger than the minimum safety distances prescribed in § 1.
The safety screen must be made either of brickwork with a thickness of at least 18 cm, or of concrete with a thickness of at least 10 cm, or of any other material with a thickness providing

an equivalent fire-resistance coefficient. The screen has a height of at least 2 m and must exceed the maximum height of the receptacles or containers stored by at least 0.5 m.

§ 3. The aforementioned minimum separation distances may be diverted from in the environmental licence, if necessary and in particular on the basis of the results specified in the safety report or on the basis of a risk analysis drawn up by an expert accredited for the discipline external safety and risks for serious accidents.

§ 4. Unless specified otherwise in the environmental licence, the stipulations of distances to be observed do not apply to:

1. products stored in laboratories
2. products for which the total storage capacity for a specific main property per storage facility is less than the lower limit indicated in category 3 of the corresponding classification section
3. storage facilities as referred to in section 17.4.

<u>Art. 5.17.1.7</u>

§ 1. The necessary measures (e.g. earthing) must be taken to prevent the formation of hazardous electrostatic charges with the storage and handling of explosive, extremely flammable, highly flammable and flammable products.

§ 2. The spaces where hazardous products are stored may only be heated by means of appliances of which the location and use offer sufficient guarantees against any fire hazard or danger of explosion.

§ 3. In the spaces where hazardous products are stored:

1. no work may be carried out for which the use is required of an appliance that works with naked flame or which may generate sparks, with the exception of maintenance and/or repair work, on the condition that the necessary precautions have been taken and subject to instructions in writing being drawn up and/or initialled by the head of the Prevention and Protection Department or by the operator
2. a smoking ban applies; this smoking ban must be indicated in clearly readable letters or with the regulatory signs on the outside of the entrance doors and inside the spaces in question; the obligation to post the prescribed "no smoking" pictogram does not apply if this pictogram is posted at the entrance to the enterprise and if the ban on smoking and on open fire applies for the whole of the enterprise
3. the chimney stacks and the discharge ducts for the extracted vapours and emanations must be made of non-combustible or self-extinguishing materials.

§ 4. It is forbidden:

1. to smoke, light a fire or store combustible substances above or near the containers, near the pumps, the piping, the dispensing units, the filling areas and the unloading site for road tankers, within the bounds of the zoned locations as shown in the zoning plan, and demarcated according to the general regulations for electrical installations
2. to wear shoes or clothing that may cause sparkover in the places that are not accessible to the public.
3. to store flammable products in any location within the establishment where temperatures may exceed 40 °C as a result of heat generated by technological means.

§ 5. The prohibitory rules indicated in § 4 must be made clear using safety pictograms in keeping with the Labour Welfare Code, to the extent that such pictograms are available.

Art. 5.17.1.8

§ 1. Without prejudice to any other relevant legal or regulatory provisions, the operator takes all measures required to sufficiently protect the surrounding area against the risks of fire and explosion.
One of the implications of this is that the necessary firefighting equipment must be provided. The type of firefighting equipment required and where it should be kept is determined after consultation with the authorised fire brigade. This matter is completely unrelated to the environmental licence.
The firefighting equipment must be kept in a properly maintained condition, protected against frost, appropriately marked, easily accessible and placed in appropriate locations. The firefighting equipment must be able to be deployed immediately.

§ 2. At the establishment, in consultation with the authorised fire brigade the necessary provisions must be present to prevent fire extinguishing water contaminated with dangerous products from draining into the ground, public sewers, surface or groundwater. The collected contaminated fire extinguishing water must be disposed of in an appropriate fashion. The collection capacity for contaminated fire extinguishing water must be determined in consultation with the authorised fire brigade.

Art. 5.17.1.9

§ 1. The electrical installations, appliances and lighting appliances must meet the requirements of the General Regulations for Labour Safety or of the general regulations for electrical installations, in particular the articles dealing with spaces in which an explosive atmosphere can originate.

§ 2. Without prejudice to the regulatory provisions, in zones where there is danger of fire and explosion because of the possible accidental presence of an explosive mixture, electrical installations must be designed and installed according to the conditions of a zoning plan.

§ 3. With respect to installations for which the general regulations for electrical installations are not as yet applicable, the zoning is to take place in accordance with the provisions of article 105 of the said general regulations.

Art. 5.17.1.10

§ 1. Containers intended for the storage of extremely toxic, toxic, harmful or corrosive liquids with a vapour pressure of over 13.3 kPa at a temperature of 35 °C, must be equipped with an effective system to restrict to a minimum the air pollution during storage and handling, such as a vapour recovery system, a floating roof, or another equivalent system.

§ 2. With the loading and unloading of storage containers and/or supplying road tankers, rail tankers or tanker vessels containing the liquids referred to in § 1, air pollution must be restricted to a minimum.

Art. 5.17.1.11

§ 1. Without prejudice to the obligations from article 7 of title I of VLAREM, the operator of a category 1 establishment must keep a register or alternative data carrier in which, per main property, at least the nature and quantities of the stored hazardous products are specified.
This information must be stored in such a way that it is possible at all times to determine the quantities of hazardous products present at the establishment.

§ 2. The register or alternative data carrier referred to in § 1 is to be kept available on site for the supervisory official for a period of at least 1 month.

Art. 5.17.1.12

All personnel at the establishment must be fully aware of the nature of the hazardous products stored and the dangers involved. Personnel must be well informed about the measures to be taken when irregularities occur.
The operator must be able to prove that he has provided up-to-date instructions as required to this end.
These instructions must be evaluated by the operator at least once per year.

Art. 5.17.1.13

Unless specified otherwise in the environmental licence, solid products that are hazardous because of the concentration of leachable substances as specified in appendix 2B and/or in appendix 7 of title I of VLAREM, must be stored op an impervious base equipped with a collection system for possibly contaminated rainwater.
Extremely toxic and toxic products, products susceptible to spontaneous ignition, products reacting with water to form combustible gases and explosive products must be stored inside or under a shelter on an impervious floor.
In any event the necessary measures must be taken to prevent the product from infiltrating or being released into the public sewers, a groundwater layer or a surface water.

Art. 5.17.1.14

§ 1. Measures must be taken to ensure an effective supervision of the different spaces and storage facilities at the establishment.
If the total storage capacity at the establishment is 1 million litres of P1 and P2 products or more, the supervision must be continuous - by dedicated security personnel or by means of a permanent surveillance system equipped with effective smoke, gas or fire detection and which raises the alarm with a permanently manned security service. All this in consultation with the authorised fire brigade and an expert accredited for the discipline external safety and risk's for serious accidents.

§ 2. The buildings, containers, bunds, embankments, appliances, etc., must be kept in perfectly maintained condition. Any fault or defect that may jeopardise the protection of man and the environment must be remedied forthwith.

Art. 5.17.1.15

§ 1. Before repairs to or internal inspections of containers having contained P1 and/or P2 products may be carried out, the establishment must dispose of a procedure for such activities that has been initialled either by the operator or by the head of the Prevention and Protection Department. One of the elements of such procedure must be the cleaning of the container, proceeding according to a method that offers sufficient guarantees as regards both fire and explosion safety as well as environmental protection.

§ 2. At the workshop for the repair of containers for P1 and/or P2 products, no P1 and/or P2 products may be stored.

Art. 5.17.1.16

§ 1. The drawing off of P1 and/or P2 products into mobile receptacles must be performed either in the open air or in a well-ventilated space constructed with non-flammable materials. The necessary measures must be taken to prevent dangerous electrostatic charges from being generated during the drawing off. This place or space must be provided with signs according to the General Regulations for Labour Safety indicating a fire hazard.

§ 2. The floor of the space referred to in § 1 must be impervious and made of non-flammable materials. It must be constructed in such a way that accidentally spilt substances and leaked liquids are drained into a collection device and subsequently are taken to one or more collection wells by means of collection channels. This collecting device may in no way be connected indirectly or directly to a public sewer, a surface water, a collecting basin for surface water, a ditch or a groundwater layer.

§ 3. If P1 and/or P2 products are stored in aboveground containers, the filling of the mobile receptacles must be performed in a suitable filling area located at least 10 metres from the containers or completely outside the bund.

§ 4. P1 and/or P2 products must be handled in such a way that spillage of the liquids on the floor is avoided.

§ 5. P1 and/or P2 products must be stored in closed receptacles offering all guarantees of sealing. In addition, the sealing must be checked immediately after the filling. Receptacles found to be defective in this respect must immediately be emptied and removed from the space where the filling takes place.

§ 6. The maximum quantities of P1 and/or P2 products (number of mobile receptacles, etc.) that may be present in the spaces where the filling of the mobile receptacles takes place, may be restricted in the environmental licence.

Art. 5.17.1.17

With respect to the filling of fixed containers and road tankers the following regulations apply:

1. the necessary measures must be taken to prevent spillages of liquids and pollution of the ground, groundwater and surface water
2. the flexible hose used for the filling must be connected to the opening of the container or the conduit by means of a device with screw coupling or an equivalent system
3. each filling operation must be performed under the supervision of the operator or his appointee; said supervision must be organised in such a way that the filling operation can be monitored and that immediate action can be taken in the event of an incident
4. to prevent overfilling all fixed containers must be equipped with an overfilling protection, which may be:
   a) either a warning system, giving an acoustic signal which the supplier must always be able to hear in the filling area and which informs the supplier that the container to be filled is 95 % full; this system may be mechanical or electronic
   b) or a safety system, which automatically shuts off product flow as soon as the container to be filled is at most 98% full; this system may be mechanical or electronic
   c) at storage facilities forming part of a fuel distribution installation for motor vehicles, a safety system of the type indicated in b) must be used
5. all containers must be equipped with the possibility to measure the level
7. the filling position for the road tanker, the zones where the nozzles of the filling pipes are grouped and the filling zones at the distribution installation must always be located on the premises of the establishment and must:

a) provide sufficient strength of ground and be impervious;

b) be equipped with the necessary gradients and possibly also with upright edges, to ensure that all spilt liquids drain to a collection system; the elimination of collected liquids is effected in accordance with regulatory provisions, in particular those relating to the disposal of waste materials;

for P1 and/or P2 products this filling position and these zones must always be located in the open air or under a shelter;

no trenches, crawl spaces or rooms may be present under the aforementioned filling position and zones; in the case of weighbridges, effective arrangements must be made to limit the spreading of leaks and to preclude any danger of explosion;

the provisions of this paragraph are not applicable to storage sites for products only intended for the heating of buildings.

7. during filling with P1 or P2 products, measures must be taken to divert static electricity; the electrical connection between the road tanker and the container must be made before the filling operation is commenced and may only be broken after the filling hose has been uncoupled when the filling is completed;

8. adequate measures must be taken to maintain the storage at atmospheric pressure;
the underground ventilation and vapour recovery piping must fulfil the same requirements as the rest of the piping; in addition, the aboveground ventilation piping must have sufficient mechanical strength

9. it is forbidden to fill a container with another liquid than the one for which the container has been designed, unless after an inspection by an environmental expert accredited in the discipline containers for gases or hazardous substances or by an authorised expert, proving that the container in question is suitable for such other liquid.

Art. 5.17.1.18

The overfilling protection described in appendix 5.17.7 must be manufactured in accordance with a code of good practice accepted by an environmental expert accredited in the discipline containers for gases or hazardous substances.

The control of the construction must be performed in accordance with the selected code of good practice by an environmental expert accredited in the discipline containers for gases or hazardous substances.

The control of the construction for overfilling protection devices manufactured in series may be limited to a single approval of the prototype. The approval of the prototype must be performed by one of the aforementioned environmental experts and in accordance with the procedure of appendix 5.17.7.

The report on the approval mentions the controls carried out and must be signed by the aforementioned expert.

For each overfilling protection device the operator must dispose of a certificate signed by the constructor. This certificate must mention the number of the prototype approval certificate and the name of the environmental expert who issued the test certificate (and his accreditation number). The constructor also confirms in the certificate that the overfilling protection has been built and controlled in accordance with the provisions of title II of VLAREM.

Art. 5.17.1.19

§ 1. Organic peroxides which may explode or detonate in a violent thermal reaction must be retained at the establishment at a temperature lower than the temperature which from the point of view of safety is the permissible maximum temperature according to the nature of the substance concerned. For the substances indicated below, this maximum temperature is:

1. acetyl cyclohexane sulphonyl peroxide:	–10° C
2. succinic acid peroxide:	+10° C
3. tert-butyl peroxyisopropylcarbonate (BPIC):	room temperature
4. tert.-butyl peroxypivalate:	–10° C
5. dibenzoyl peroxide:	room temperature
6. dicyclohexyl peroxydicarbonate:	+5° C
7. diisopropyl peroxydicarbonate:	–15° C.

§ 2. Peroxides which for reasons of safety must be kept at the establishment at a temperature lower than room temperature, must be stored:

1. either in refrigerators or freezers located in the production building, in which case each refrigerator or freezer may contain a quantity of at most 30 kg non-refrigerated organic peroxides
2. or in refrigerators or freezers located in a detached storage building in which only the said peroxides are stored. In this case each refrigerator or freezer may contain a quantity of at most 150 kg non-refrigerated organic peroxides
3. or in a detached cold store that is solely intended for this purpose. In this case, unless specified otherwise in the environmental licence, per cold store a quantity of at most 500 kg non-refrigerated organic peroxides may be stored.

Art. 5.17.1.20

As regards the construction certificates, inspections and tests prescribed in this chapter, the operator must dispose of certificates in which the codes of good practice applied, the controls carried out and the relevant observations are clearly indicated. He must at all times keep the certificates concerned at the disposal of the supervisory official.

Art. 5.17.1.21

Without prejudice to the provisions of this chapter, the transport, the installation and connection of containers must be performed according to the prevailing Belgian or European standards.

Section 5.17.2 Storage of hazardous liquids in underground containers

Art. 5.17.2.1

§ 1. The necessary measures must be taken to give maximum protection to the containers against mechanical damage and corrosion.

§ 2. It is forbidden to place containers intended for the storage of P1 and/or P2 products directly under a building or under a vertical projection of a building. A lean-to is not considered as a building.

§ 3. The distance between the container and the boundaries of the parcels of third parties must be at least 3 metres. The distance between the container and the basement space of the company's own buildings must be at least 2 m. The distance between the container and the wall of the establishment's own buildings must amount to at least 0.75 m. The distance between the containers themselves must amount to at least 0.5 m.
The distance between containers for P3 and/or P4 products which do not form part of a distribution installation and the boundaries of the parcels of third parties must amount to at least 1 m.

§ 4. In the event of possible flooding or high water levels, the necessary provisions must be installed to prevent empty containers from being floated upwards.

§ 5. Without prejudice to the requirements referred to in this section, storage sites for petrol and their associated installations must comply with the provisions of section 5.17.4.

Art. 5.17.2.2

§ 1. A notice is to be provided in a clearly visible place by the container in accordance with the provisions of appendix 5.17.2.

§ 2. The following information is to be shown near the filling opening and near the manhole:

1. the number of the container
2. the name or the code numbers or letters of the stored liquid
3. the danger symbols
4. the water content capacity of the container.

The information must be clearly readable.
The provisions of this paragraph do not apply to storage sites for P3 and/or P4 products which are only intended for the heating of buildings.

Art. 5.17.2.3

§ 1. The venting pipe must open into the open air at least 3 metres above ground level and at least 3 metres from each opening in a space and the boundaries of the parcels of third parties.
Outlets of venting pipes may not be located under construction parts such as, e.g. roof overhangs.

§ 2. The provisions of § 1 are not applicable to venting pipes belonging to storage sites for P3 and/or P4 products which do not form part of a fuel distribution installation for motor vehicles. For these storage sites it is to be ensured that the place and the height of the outlet of the venting pipe does not excessively cause nuisance to the vicinity, particularly as a result of the filling of the containers

§ 3. For the storage of P1 and/or P2 products the air supply and discharge system must be shut off by an appliance that prevents the spreading of fire.

Art. 5.17.2.4

§ 1. Storage in containers directly buried in the ground is only permitted in:

1. double-walled metal containers which have been manufactured according to the provisions of appendix 5.17.2
2. containers of reinforced thermoset synthetics which have been manufactured according to the provisions of appendix 5.17.2
3. stainless steel containers which have been manufactured in accordance with a code of good practice accepted by an environmental expert, accredited in the discipline containers for gases or hazardous substances, or accepted by an authorised expert
4. a storage system which provides the same guarantees of the prevention of soil and/or groundwater pollution as the aforementioned containers

this storage system must be accepted by an environmental expert accredited in the discipline of containers for gases or hazardous substances; a certificate of this acceptance is drawn up and

signed by the aforementioned environmental expert; this certificate is kept available for the perusal of the supervisory official; a copy of the certificate will be forwarded by the operator to the Environmental Licence Department.

§ 2. All containers must be provided with a permanent leak detection system. This obligation does not apply for containers of reinforced thermoset synthetics or stainless steel located outside a water abstraction area or a protected zone, and of which the individual water content capacity amounts to less than 5000 l, or less than 10000 l if these containers are for the storage of P3 and/or P4 products.

The leak detection system must detect a leak inside an interstitial space formed either by an additional, solid or flexible impervious inside or outside casing, or by an impervious coat on the walls and the bottom of the excavation, and must meet the corresponding provisions of appendix 5.17.3.

§ 3. For the installation of a metal container with an individual water content capacity from 5000 l, or for the storage of P3 and/or P4 products from 10000 l and the associated ducts:

1. in a water abstraction area or a protected zone type I or II, or
2. in an area surrounding electrical conductors where major stray currents can be present, the corrosiveness of the soil and of the filling-in soil must be specified and categorised by an environmental expert accredited in the discipline soil corrosion according to the method mentioned in appendix 5.17.5.

Here the corrosiveness of the soil at the deepest point in the place where the metal container is to be installed, or the filling-in soil is to be categorised as 'barely corrosive', 'moderately corrosive', 'corrosive' or 'highly corrosive'.

The determining of the corrosiveness may not take place under extreme circumstances of drought or frost.

The provisions of this paragraph may be departed from if the corrosiveness of the soil and filling-in soil has already been determined during the last five years or when without a prior soil corrosiveness investigation cathodic protection is applied. The application of this cathodic protection must take place under the supervision of an environmental expert accredited in the discipline soil corrosion.

§ 4. Cathodic protection:

1. if the result of the inspection mentioned in § 3 is 'corrosive' or 'highly corrosive', cathodic protection must be applied
2. if the result of the examination mentioned in § 3 is 'moderately corrosive', it may initially be decided to not install cathodic protection. In this case, corrosion monitoring on the basis of permanent or periodic potential measurements must be provided for; with a potential measurement more positive than -500 mV compared to a $Cu/CuSO_4$ reference electrode, indicating possible corrosion or stray currents, cathodic protection must be applied
3. if the result of the inspection specified in § 3 is 'barely corrosive' and the container is adequately cladded, cathodic protection is not required.

The cathodic protection must bring the whole surface of the container, including the metal ducts (if this proves necessary), to a potential of -850 mV or a greater negative value measured with respect to a $Cu/CuSO_4$ reference electrode. In anaerobic soils his potential must amount to at least -950 mV.

§ 5. The containers must be covered by a layer of earth, sand or another adapted inert material at least 50 cm thick.

Measures must be taken to prevent the passage of vehicles or the storage of goods above the containers, unless these are protected by a non-flammable and sufficiently resistant floor.

Art. 5.17.2.5

§ 1. Storage in containers placed in a trench is only allowed in:

1. single- or double-walled metal containers which have been manufactured according to the provisions of appendix 5.17.2
2. containers of reinforced thermoset synthetics which have been manufactured according to the provisions of appendix 5.17.2
3. containers of stainless steel manufactured according to a code of good practice which has been approved by an environmental expert accredited in the discipline containers for gases or hazardous substances, or by an authorised expert
4. a storage system which provides the same guarantees of the prevention of soil and/or groundwater pollution as the aforementioned containers; this storage system must be accepted by an environmental expert accredited in the discipline of containers for gases or hazardous substances; a certificate of this acceptance is drawn up and signed by the aforementioned environmental expert; this certificate is to be kept available for the perusal of the supervisory official; a copy of the certificate will be forwarded by the operator to the Environmental Licence Department.

§ 2. All containers must be provided with a permanent leak detection system. This obligation does not apply for containers of reinforced thermoset synthetics or stainless steel which are located outside a water abstraction area or a protected zone, and of which the individual water content capacity is less than 5000 l, or less than 10000 l if these containers are for the storage of P3 and/or P4 products.
The leak detection system must meet the provisions of appendix 5.17.3.

§ 3. The trench must be built according to the provisions of appendix 5.17.6. The walls may not meet any property boundaries.

§ 4. At the lowest point of the trench the necessary provisions must be installed to be able to register and remove any leaked liquid or water.

§ 5. It is forbidden to give the trench any other purpose than that of storage space for the containers. Only the ducts required for the operation of the containers placed therein may be brought through the trench.

§ 6. If the container has a content greater than 2000 l, there is to be a free space around the container at least 50 cm wide to make possible the inspection of the container.

§ 7. Unless specified otherwise in the environmental licence, the filling in of the trench is compulsory for the storage of P1 and/or P2 products.
If the trench is filled up, between the container and the wall of the trench there must be a distance of at least 30 cm, and account is to be taken of the provisions of appendix 5.17.6 to this order.

§ 8. Measures must be taken to prevent the passage of vehicles or the storage of goods above the trench, unless these are protected by a non-flammable and sufficiently resistant floor.

§ 9. A prefab construction, consisting of a concrete cylindrical container in which a single-walled metal container is placed, is only allowed for the storage of P3 and/or P4 products intended for the heating of buildings with a water content capacity of max. 5300 l and if the metal container and the prefab concrete cylindrical container has been built as a prototype accepted by an environmental expert accredited in the discipline containers for gases or hazardous substances or by an authorised expert.

Art.5.17.2.6

§ 1. The monitoring of the construction must take place in accordance with the provisions of appendix 5.17.2.
The monitoring of separately constructed containers is done by an environmental expert accredited in the discipline containers for gases or hazardous substances, or by an authorised expert.
The control of containers installed in series may be limited to one prototype. The approval of the prototype is given by an environmental expert accredited in the discipline containers for gases or hazardous substances, of which the accreditation allows the approval of prototypes.
The report on this approval mentions the controls carried out and must be signed by the aforementioned expert.

§ 2. For each container the operator must dispose of a "declaration of conformity of the container" signed by the constructor, drawn up according to the specimen form in appendix 5.17.2.
The containers must be provided with the identification plate applied by the constructor.

Art. 5.17.2.7

Before the installation of the container, either directly in the ground or in a trench, it must be checked whether the container and where appropriate also the trench meet the conditions of these regulations.
After installation but before the bringing into use of the container, it must be checked whether the container, the ducts and the accessories, overfilling warning or safety system, the leak detection system and, where appropriate, the cathodic protection and the provisions for vapour recovery comply with the conditions of these regulations.
The specified controls must be carried out under the supervision of an environmental expert accredited in the discipline containers for gases or hazardous substances or an authorised expert, or with a technician accredited for the storage of P3 and/or P4 products intended for the heating of buildings.
The monitoring of any cathodic protection must take place in collaboration with an environmental expert accredited in the discipline soil corrosion.

Art. 5.17.2.8

§ 1. At least once a year for containers located in water abstraction areas and protected zones and every two years for containers located in the other areas, the installation must be subjected to a limited examination, comprising if relevant:

1. perusal of the previous report or certificate
2. the checking of the good state of the overfilling protection
3. checking for the presence of water and sludge in single-walled containers for liquid fuels (appendix 5.17.4)
4. an inspection for any visible or organoleptically observable pollution on the surface outside the container (appendix 5.17.4)
5. an examination of the state of the external visible parts of the container, the valves, ducts, pumps, etc.
6. the checking of the effectiveness of any cathodic protection or corrosion monitoring
7. the checking of the effectiveness of the leak detection system
8. the checking of the effectiveness of the provisions for vapour recovery.

§ 2. Except for containers of reinforced thermoset synthetics, at least every 10 years for containers located in a water abstraction areas and protected zones, and every 15 years for containers located in other areas, the installation must be subjected to a general inspection, comprising:

1. the limited examination as specified in § 1
2. the state of the inner wall with an observed major presence of water or sludge; if an internal inspection is required the container must be internally cleaned; to the extent technically possible, the inner wall and the internal parts of the container must be investigated, and where appropriate a non-destructive inspection will be carried out to determine the wall thickness of the container
3. the state of the outer cladding, to the extent technically possible and without the container having to be exposed for this
4. where appropriate, in particular in the situation described in article 5.17.2.4, § 3, the detection of possible corrosion on the basis of a potential measurement and a measurement of the corrosiveness of the adjacent soil
5. a seal test on directly buried in the ground single-walled containers at an overpressure of at least 30 kPa for a period of minimum 1 hour or at an underpressure of a maximum of 30 kPa; testing at an overpressure of more than 30 kPa may only be carried out if the containers are completely filled with water for this;
   non-accessible single-walled ducts must be tested at an overpressure of at least 30 kPa for a period of 1 hour;
   an equivalent seal test, carried out according to a code of good practice accepted by the Environmental Licence Department, is also allowed.

§ 3. The periodic examinations, as referred to in § 1 and § 2, must be carried out by an environmental expert accredited in the discipline containers for gases or hazardous substances, by an authorised expert, or by a technician accredited for storage sites for P3 and/or P4 products intended for the heating of buildings.
The inspection with respect to corrosion and cathodic protection must take place in collaboration with an environmental expert accredited in the discipline soil corrosion.

Art. 5.17.2.9

Following the inspections described in article 5.17.2.7 with the installation and/or the periodic investigations referred to in article 5.17.2.8, the experts or the accredited technician will draw up a certificate from which it unambiguously appears whether or not the installation complies with the conditions of these regulations. The aforementioned conformity certificate also mentions the name and the accreditation number of the expert or accredited technician who has conducted the inspection.
He then applies a clearly legible sticker or plate to the filling pipe, on which his/her accreditation number, the year and the month of the inspection on installation and the last inspection conducted are mentioned.
The sticker or plate must have the following colour:

1. green, when the container and the installation comply with the provisions of these regulations
2. orange, when the container and the installation do not comply with the provisions of these regulations, but the faults established cannot cause pollution outside the container
3. red, when the container and the installation do not comply with the provisions of these regulations and the faults observed can lead or have led to pollution outside the container.

Art. 5.17.2.10

Only containers of which the filler pipe is provided with a green sticker or plate, as referred to in article 5.17.2.9, may be filled, replenished and operated.
Containers of which the filler pipe is provided with an orange sticker or plate, as referred to in article 5.17.2.9, may be filled or replenished during a transitional period of a maximum of 6 months starting on the first day of the month following the month mentioned on the orange sticker or plate. In this case a new control must take place before the expiry of the aforementioned term.
Containers of which the filler pipe is provided with a red sticker or plate, as referred to in article 5.17.2.9, may in no event be filled or replenished.

Art. 5.17.2.11

§ 1. The following are considered as existing containers for the storage of P1, P2, P3 or P4 products:

1. containers of which operation was licensed on 1 January 1993 or for which the application for the renewal of the environmental licence was being processed on the aforementioned date by the competent authority
2. containers which on 1 September 1991 had already been brought into use and without the application of title I of the General Regulations for Labour Safety were not classified as hazardous, unhealthy or nuisance-producing establishments
3. containers for which before 1 July 1993 notification took place in accordance with the provisions of Title I of VLAREM.

These containers continue to be existing containers, also with the renewal of the environmental licence.

§ 2. Existing containers for the storage of other than P1, P2, P3 or P4 products are containers of which their operation was licensed on 1 May 1999 or for which the application for the renewal of the environmental licence was being processed on the aforementioned date by the competent authority.
These containers continue to be existing containers, also with the renewal of the environmental licence.

§ 3. The distance and prohibitory rules as well as the provisions of this section concerning the method of construction and installation of the containers, the associated ducts and the filling point are not applicable to existing containers.

§ 4. The general inspection as referred to in article 5.17.2.8, § 2 must take place for a first time no later than on the dates mentioned in the table below, depending on the location, the nature of the stored liquid and the category.

		Location with respect to water abstraction areas or protected zones	
Product	**Category**	**Inside**	**Outside**
P1, P2	1, 2, 3	1 August 1997	1 August 1999
P3, P4	1, 2	1 August 1997	1 August 1999
P3, P4	3	1 August 1998	1 August 2000
Other	1, 2, 3	1 January 2002	1 January 2003

In anticipation of this general inspection the containers may continue to be used.
Before the same dates a corrosiveness inspection in accordance with article 5.17.2.4, § 3 must take place on the following buried metal containers with an individual water content capacity of 5000 l or those for the storage of P3 and/or P4 products from 10000 l as well as the associated ducts:

1. single-walled containers
2. double-walled containers inside a water abstraction area or a protected zone type I and II
3. double-walled containers inside the surrounding area of electrical conductors where major stray currents can be present.

From the date of the first general inspection, the periodic examinations must be conducted according to the provisions of article 5.17.2.8 and 5.17.2.9.

§ 5. Without prejudice to the particular conditions imposed in the environmental licence, the containers must comply with the provisions of this chapter no later than the dates mentioned in the table below related to:

1. overfilling warning or safety system
2. leak detection
3. cathodic protection.

		Location with respect to water abstraction areas or protected zones	
Product	**Category**	**Inside**	**Outside**
P1, P2	1, 2, 3	1 August 1998	1 August 2000
P3, P4	1, 2	1 August 1998	1 August 2000
P3, P4	3	1 August 1999	1 August 2001
other	1, 2, 3	1 January 2003	1 January 2005

§ 6. With the replacement of the containers referred to in § 1 or § 2, the new container must comply with all conditions of these regulations, except for that regarding the stipulations of distances to be observed.

§ 7. For storage sites which form part of a fuel distribution installation for motor vehicles, the provisions of § 5 can be departed from according to the provisions of article 5.17.5.7.

Art. 5.17.2.12

§ 1. If leaks are observed the operator will take all measures required to avoid the danger of explosion and restrict further soil and groundwater pollution to the extent possible.

§ 2. After professional repairs have taken place, the container may only be brought back into use providing it has successfully undergone a seal test as specified in article 5.17.2.8.

§ 3. With the final putting out of use of containers, whether or not due to leaks, the container must be emptied, cleaned and removed within a period of 36 months without prejudice to the provisions of the decree of 2 July 1981 concerning the prevention of waste and waste materials management and its implementing decisions.
With the material impossibility of removal, within the same term, after consultation with an environmental expert accredited in the discipline containers for gases or hazardous substances, with an authorised expert or for the storage of P3 and/or P4 products intended for the heating of buildings or with an accredited technician, the container must be emptied, cleaned and filled with sand, foam or an equivalent inert material. Here the necessary measures relating to explosion safety and the prevention of groundwater pollution must be taken.

§ 4. Liquids which have caused ground pollution or spillage into the sewer system, the surface waters, the groundwater layers or onto adjacent properties must be immediately reported by the operator to the Environmental Inspection Department, to the Governor of the Province and to the Burgomaster.

Section 5.17.3 Storage of Hazardous Liquids in aboveground containers

Art. 5.17.3.1

§ 1. The containers must be placed in or above a bund in order to prevent the spreading of fire, and to prevent soil and/or groundwater pollution. Equivalent collection systems can be permitted in the environmental licence.
Double-walled containers fitted with a permanent leak detection system do not have to be placed in or above a bund.

§ 2. Unless specified otherwise in the environmental licence, the storage of P1 and/or P2 products in fixed containers in basements or aboveground spaces is prohibited. It is forbidden to install storage sites for P1 and/or P2 products in moveable receptacles in basement floors.

Art. 5.17.3.2

§ 1. Fixed containers must be built according to the provisions of appendix 5.17.2.

§ 2. All metal parts of containers intended for the storage of P1 and/or P2 products, including the floating roof of the containers, must be equipotential.

Art. 5.17.3.3

§ 1. The control of the construction of fixed containers must take place according to the provisions of appendix 5.17.2.
The control of separately built containers must take place by an environmental expert accredited in the discipline containers for gases or hazardous substances or by an authorised expert.
The control of containers installed in series may be limited to one prototype; the approval of the prototype is given by an environmental expert accredited in the discipline containers for gases or hazardous substances, of which the accreditation allows the approval of prototypes.
The report on this approval mentions the controls carried out and must be signed by the aforementioned expert.

§ 2. For each container the operator must dispose of a "declaration of conformity of the container" signed by the constructor, drawn up according to the specimen form in appendix 5.17.2.
The containers must bear the identification plate applied by the constructor.

Art. 5.17.3.4.

Before the installation of the fixed container it must be checked that the container and/or the foundations meet the conditions of these regulations.
After installation, but before the bringing into use of the container, it must be checked whether the container, the ducts and the accessories, the overfilling warning or safety system, the bund and the firefighting resources, and where appropriate, the leak detection system and the provisions for vapour recovery comply with the conditions of these regulations.
The specified controls must be carried out under the supervision of an environmental expert accredited in the discipline containers for gases or hazardous substances or an authorised expert for the storage of P3 and/or P4 products intended for the heating of buildings, or an accredited technician.

Art. 5.17.3.5

§ 1. An identification plate must be applied to fixed containers in a visible and easily accessible place in accordance with the provisions of appendix 5.17.2.

§ 2. The following indications must be applied near the filling opening and in a clearly visible place on the fixed container:

1. the number of the container
2. the name or the code numbers or letters of the stored liquid
3. the danger symbols
4. the water content capacity of the container.

The provisions of this paragraph are not applicable to storage sites for P3 and/or P4 products which are only intended for the heating of buildings.

§ 3. On moveable receptacles the name of the product mentioning the main property must be applied.

Art. 5.17.3.6

§ 1. The bund and the foundations for fixed containers with an individual water content capacity from 10000 l must be built according to a code of good practice under the supervision of and according to the directions of an architect, a civil engineering architect, a civil structural engineer or an industrial architectural engineer.
For storage sites classified in category 1 or 2, the aforementioned expert confirms in a certificate that he accepts the code of good practice used and that this was adhered to.

§ 2. Fixed containers must be placed on a supporting block or surface of sufficient dimensions to prevent the load causing uneven slumps, from which a danger of toppling or breakage could originate. For the installation of containers with an individual water content capacity from 50000 l a stability study is conducted by the expert specified in §1.

§ 3. The bund must be resistant to the action of the stored liquids and must be impervious. The bund must be sufficiently strong to withstand the liquid mass which could escape in the event of the breakage of the largest container placed in the bund.
The floor must be provided in such a way that the spreading of the leaked liquids remains minimal and the leaked liquids can be easily removed.

§ 4. If the bund is made of earthen dams, these dams must be made of a very clayish, solid and strongly compressed earth, of which the gradients are a max. 4/4 and the thickness on the top side is to be at least 50 centimetres. The floor may be made of the same materials. The dams must be sown with grass. At the base, carefully calculated supporting walls with a maximum height of one metre may be constructed.

§ 5. The passage of ducts through the bund is only allowed if the sealing of the bund remains assured.

§ 6. If the bund is wider than 30 metres, the escape ladders or stairs must be positioned so that a person fleeing does not have to travel a distance greater than half the width of the bund plus 15 metres to reach an escape ladder or stairs.

Art. 5.17.3.7

§ 1. For storage sites in fixed containers or moveable receptacles located inside a water abstraction area and/or protected zone, the minimum capacity of the bund is to be equal to the total water content capacity of all containers and/or receptacles placed therein.

§ 2. For storage places in fixed containers located outside a water abstraction area and/or protected zone, the minimum capacity of the bund must be determined as follows (double-walled containers fitted with a permanent leak detection system not included):

1. for the storage of P1, P2, highly toxic, toxic and explosive products, the greatest of the following values:
a) the water content capacity of the largest container, increased by 25 % of the total water content capacity of the other containers in the bund
b) half of the total water content capacity of the containers placed therein;
2. for the storage of P3, harmful, irritating, oxidising, corrosive and environmentally harmful products: the water content capacity of the largest container;
3. for the storage of P4 products and extra heavy heating oil, irrespective of the flashpoint: only the presence of a upright edge is required
4. for the storage of P1 and/or P2 products in aboveground spaces and basements: the total water content capacity of all containers placed therein.

For the storage of products with various main properties the strictest of the regulations must be adhered to. Here account must also be taken of the flashpoint.

§ 3. For storage sites located outside a water abstraction area and/or protected zone for products other than P1 and/or P2 products in moveable receptacles, the capacity of the bund must be restricted to 10 % of the total water content capacity of the receptacles stored therein. In each case the capacity of the bund must be at least equal to the capacity of the largest receptacle placed in the bund.

§ 4. For storage sites located outside a water abstraction area and/or protected zone for P1 and/or P2 products in moveable receptacles, the capacity of the bund must be 25 % of the total water content capacity of the receptacles stored therein. The capacity may be reduced to 10% if, after consultation with the authorised fire brigade, a suitable fire extinguishing installation is provided. In each case the capacity of the bund must be at least equal to the capacity of the largest receptacle placed in the bund.

Art. 5.17.3.8

Unless specified otherwise in the environmental licence, the distance between the containers is to be at least 0.5 m, and between the containers and the inner walls of the bund or the bottom the dams at least half the height of the containers.
This last obligation does not apply:

1. for the storage of hazardous liquids in double-walled containers or containers with ring cladding or similar protection which ensures that any leaked liquid stays inside the bund, or
2. for the storage of P4 products or extra heavy heating oil, irrespective of the flashpoint.

Art. 5.17.3.9

Without prejudice to other provisions of these regulations, storage sites for P1 and/or P2 products in moveable receptacles must comply with the following conditions:

1. the storage must be protected against detrimental consequences of the action of the rays of the sun or the radiation of any other heat source
2. the storage of P1 and/or P2 products together with other liquids is allowed providing that these last liquids the do not increase the risk of or risks associated with an accident
3. storage sites in a building are constructed as prescribed in article 52 of the General Regulations for Labour Safety
4. storage sites outside buildings particularly built for the storage of these liquids and which do not meet the provisions of article 52 of the General Regulations for Labour Safety must be at least 10 m from each neighbouring building
5. doors in closed storage sites open outwards and are self-closing; with double doors 1 door must remain continually locked; the other door must be self-closing; the doors may remain temporarily opened if this is required for technical operating reasons. In the event of a fire they must also automatically close. The use of sliding partitions is allowed on the condition that these partitions, or the storage space, have one or more doors which meet the requirements of the aforementioned regulations
6. all storage sites must be adequately ventilated, either naturally or artificially.

Art. 5.17.3.10

§ 1. The construction of all spaces for the processing of hazardous products is provided in such a way that accidentally spilt substances or leaked liquids can be collected.
To prevent the spreading of fire, the construction of all spaces for the processing of P1 products must be provided in such a way that accidentally spilt substances and leaked liquids arrive in a collection device and are then taken by collecting channels to one or a multiple of collection drains.
This collecting device may in no way be connected indirectly or directly to a public sewer, a surface water, a reservoir for surface water, a ditch or a groundwater layer.

§ 2. The contents of a leaking container must be immediately loaded or pumped into a different suitable container. Spilt liquids must be immediately localised and placed in a drum for this purpose. At establishments the necessary emergency materials, such as absorption and neutralisation material, oversized drums, protection resources, etc., must be present to, in the event of leaks, be able to immediately respond to faulty packing, spills and other incidents and maximally restrict possible harmful consequences.

§ 3. Collection devices and collection basins must be regularly emptied, and at least after each incident. The waste material flows obtained must be disposed of in an appropriate manner.

Art. 5.17.3.11

All necessary measures must be taken to regularly remove any rainwater that may enter the bund.
Before the rainwater is removed, the operator will ensure there is none of the stored product present in the water. If the water contains stored products, he will take all the necessary measures to prevent the pollution of soil groundwater and surface water.

Art. 5.17.3.12

§ 1. In areas surrounding tank farms inside a water abstraction area and/or a protected zone, after consultation with the local water authority or an environmental expert accredited in the disciplines groundwater or soil, observation pipes (measuring wells) are to be installed in accordance with the provisions of appendix 5.17.3 concerning the detection of leaks in gas or liquid form outside the storage container.

The observation pipes (measuring wells) are to be made of a material that cannot be affected by the stored liquids.

The whole length of the piping is to be provided as filter piping; it is to have an internal diameter of at least 5 cm, reach a minimum of 1 m deeper than the lowest level of the phreatic groundwater table and be sealed above.

Unless specified otherwise in the environmental licence, at least three observation pipes must be installed.

The plans for the work and the drilling reports are to be available for inspection by the supervisory official.

§ 2. The operator will regularly check the groundwater in the measuring wells for the presence of pollution.

For tank farms, at least every 2 years a groundwater investigation must take place, either by the operator, with equipment and according to a method approved by an environmental expert accredited in the discipline groundwater, or by the aforementioned environmental expert himself.

Art. 5.17.3.13

§ 1. Minimum extinguishing and cooling provisions

A tank farm for the storage of P1 and/or P2 products must be provided with an effective, permanent foam installation and/or an extinguishing or cooling installation suitable to the circumstances, and this after consultation with the authorised fire service.

The establishment must dispose of a quantity of water to be able to spray and/or cool the containers for a sufficient period. With the failure of the normal electricity supply, the working of the extinguishing or cooling installations must be assured by emergency power units or equivalent emergency installations.

§ 2. Establishments with containers for the storage of P1 products classified in category 1 which are not manned or only manned during ordinary working hours must, after consultation with the authorised fire brigade, be equipped with an effective smoke, gas or flame detection system which gives an alarm at a manned monitoring department.

§ 3. For the storage of P1 and/or P2 products in tank farms, the firefighting resources must be examined when bringing into use by an expert accredited for the discipline external safety and risks for serious accidents or by an authorised expert, unless this inspection is wholly or partly conducted by the authorised fire brigade, by the Head of Prevention and Protection or by his appointed party after consultation with the authorised fire brigade.

Art. 5.17.3.14

The accessibility of the tank farm must be conceived in such a way that:

1. traffic in the zones where a reasonable danger of fire and explosion exists must be kept to a minimum
2. the tank farm must have easy access
3. easy access for the intervention material
4. vehicles with which products are taken away or delivered must, during loading or unloading, to the extent technically possible be located at a loading/unloading place with larger dimensions than an ordinary road lane.

Art. 5.17.3.15

§ 1. The operator of a tank farm will keep a file at appropriate places at the establishment for the authorised fire brigade, with at least the following information:

1. a map of the tank farm and the access roads
2. a description of the firefighting resources with their indication on a map
3. a description of the stored products with the main physical and chemical properties (danger cards) with the specification of the listing of EC directive 67/548/EEC of 27 June 1967 or 88/379/EEC of 7 June 1988, of the UN number and of the ADR code
4. the water content capacity of the containers
5. the composition of any establishment's own fire service.

Any other equivalent manner of providing information is allowed, providing the consent of the supervisory official and of the authorised fire brigade has been given.

Art. 5.17.3.16

§ 1. At least every 3 years, without the period between two consecutive examinations being able to exceed 40 months, the installations must be subjected to a limited inspection.
This inspection comprises, if relevant:

1. perusal of the previous report or certificate
2. the checking of the good state of the overfilling protection
3. an inspection for visible or organoleptically observable pollution of the surface outside the container according to the provisions of appendix 5.17.4
4. the inspection of the general state of the installation, comprising:
a)   the tracing of leaks and indications of leaks
b)   the inspection of the state of the plating, the connections and the butts of the container
c)   the inspection of the state of accessories such as: valves, temperature, pressure and level measurement devices and earthing
d)   the inspection of the pressure safety and alarm appliances
e)   the inspection of the state of the outer cladding, the paintwork and/or the insulation
f)   the inspection of the foundations and/or supporting blocks regarding stability and drainage
g)   the inspection of the bund for content, sealing, pollution, measuring wells
h)   the inspection of the state of the ducts and the accessories inside the bund.

    also for vertical containers:
a)   where appropriate, a non-destructive inspection must be conducted on the cladding and the roof plating of the containers to determine the plate thickness and any corrosion, both internal and external
b)   at the request of the environmental expert or the authorised expert, any settling will be determined by measuring the height at a number of points spread evenly over the periphery of the bottom edge.

§ 2. At least every 20 years the installations must be subjected to a general inspection. Prior to this inspection the container must be internally cleaned.
This inspection comprises:

1. the limited inspection, as referred to in § 1
2. the inspection of the state of the inner wall
3. for vertical containers the inspection also includes:
a)   the inspection of the state of the framework and the internal accessories such as valves, heating coils, roof and groundwater drains and seals in the floating roofs
b)   the inspection of the bottom plates for the tracing of internal and external corrosion
c)   the inspection of bottom deformation and the possible measuring of the profile

4. a pressure test on any heating pipes.

For category 3 storage of P3 and/or P4 products, only the limited inspection mentioned in § 1 has to take place.

§ 3. The periodic investigations must be carried out by an environmental expert accredited in the discipline containers for gases or hazardous substances or by an authorised expert, or for storage places for P3 and/or P4 products intended for the heating of buildings by an accredited technician.

Art. 5.17.3.17

Following the inspections described in article 5.17.3.4 with installation and/or the periodic investigations referred to in article 5.17.3.16, the experts or the accredited technician draw up a certificate from which it unambiguously appears whether or not the installation complies with the conditions of these regulations. The aforementioned certificate also mentions the name and the accreditation number of the expert or accredited technician who has conducted the inspection.

Except in the case of a tank farm, a clearly visible sticker or plate is to be applied to or near the filler pipe on which the accreditation number, the year and the month of the control with installation and the last inspection are mentioned.

The sticker or plate has the following colour:

1. green, when the container and the installation comply with the provisions of these regulations
2. orange, when the container and the installation do not comply with the provisions of these regulations, but the faults established cannot cause pollution outside the container
3. red, when the container and the installation do not comply with the provisions of these regulations and the faults observed can lead or have led to pollution outside the container.

Art. 5.17.3.18

Only containers of which the filler pipe is provided with a green sticker or plate, as referred to in article 5.17.3.17, third subsection, 1., may be filled, replenished and operated.

Containers of which the filler pipe is provided with an orange sticker or plate, as referred to in article 5.17.3.17, third paragraph, 2., may still be filled or replenished for a transitional period of a maximum of six months. This period starts on the first day of the month following the month mentioned on the relative orange sticker or plate. In this case a new control must take place before the expiry of aforementioned term.

Containers of which the filler pipe is provided with a red sticker or plate, as referred to in article 5.17.3.17, third subsection, 3., may in no event be filled or replenished.

Art. 5.17.3.19

§ 1. The following are considered as existing containers for the storage of P1, P2, P3 or P4 products:

1. containers of which operation was licensed on 1 January 1993 or for which the application for the renewal of the environmental licence was being processed on the aforementioned date by the competent authority
2. containers which on 1 September 1991 were already in use, and without the application of title I of the General Regulations for Labour Safety were not classified as hazardous, unhealthy or nuisance-producing establishments
3. containers for which before 1 July 1993 notification was provided in accordance with the provisions of Title I of VLAREM.

These containers continue to be existing containers, also with the renewal of the environmental licence.

§ 2. Considered as existing containers for the storage of other than P1, P2, P3 or P4 products are containers of which the operation is licensed on the date of the enforcement of this order, or for which the application for the renewal of the environmental licence was being processed on the aforementioned date by the competent authority. These containers continue to be existing containers, also with the renewal of the environmental licence.

§ 3. The distance and prohibitory rules as well as the provisions of this section concerning the method of construction and installation of the containers, the associated ducts and the filling point are not applicable to existing containers.

§ 4. The general inspection as referred to in article 5.17.3.16 must take place a first time no later than on the dates mentioned in the table below, depending on the location, the nature, the stored liquid and the category.

Product	Category	Location with respect to water abstraction areas or protected zones	
		Inside	Outside
P1, P2, P3, P4	1, 2, 3	1 August 1998	1 August 2000
other	1, 2, 3	1 January 2003	1 January 2005

In anticipation of this general inspection the containers may continue to be used.
From the date of the first general inspection the periodic examinations must be conducted according to the provisions of article 5.17.3.16 and 5.17.3.17.

§ 5. Without prejudice to the particular conditions imposed in the environmental licence, the containers must comply with the provisions of this chapter no later than the dates mentioned in the table below, with the exception of the regulations related to:

1. the construction and the installation of the containers and the ducts providing that these comply with the provisions of § 4
2. the construction and the liquid sealing of the bund of tank farms.

Product	Category	Location with respect to water abstraction areas or protected zones	
		Inside	Outside
P1, P2, P3, P4	1, 2, 3	1 August 1999	1 August 2001
other	1, 2, 3	1 January 2004	1 January 2006

§ 6. With the replacement of the containers, as referred to in § 1 and § 2, the new container must comply with all the regulations of this chapter, except for that regarding the stipulations of distances to be observed.

§ 7. As a derogation from the provisions of § 5, existing containers which do not form part of a tank farm must no later than 1 January 2003 comply with the provisions of article 5.17.3.6, 5.17.3.7 and 5.17.3.8.

§ 8. In existing tank farms for the storage of P1, P2, P3 or P4 products located inside a water abstraction area or a protected zone, no later than 1 August 1997 observation pipes must be installed in accordance with the provisions of article 5.17.3.12.
In existing tank farms for the storage of other than P1, P2, P3 or P4 products located inside a water abstraction area or a protected zone, no later than within a period of 24 months after the date of the coming into force of this order observation pipes must be installed in accordance with the provisions of article 5.17.3.12.
These obligations also apply within a period of 24 months after the date of the coming into force of a decision for the assignment of a water abstraction area and/or a protected zone.

§ 9. In existing tank farms which do not dispose of an impervious bund and which are located outside a water abstraction area or a protected zone, within a period of 24 months after the date of the coming into force of this order observation pipes must be installed in accordance with the provisions of article 5.17.3.12.

Art. 5.17.3.20

§ 1. If leaks are observed the operator will take all the measures required to avoid the danger of explosion and restrict further soil and groundwater pollution to the extent possible.

§ 2. After professional repairs the container may only be brought back into use if a certificate has been issued by an environmental expert accredited in the discipline containers for gases or hazardous substances or by an authorised expert or by a technician accredited for the storage of P3 and/or P4 products intended for the heating of buildings. From this certificate it must clearly appear that the container and the installation comply with the requirements referred to in this order.

§ 3. With the final putting out of use of containers, whether or not due to leaks, the container must be emptied, cleaned and removed within a period of 36 months without prejudice to the provisions of the decree of 2 July 1981 concerning the prevention of waste and waste materials management and its implementing decisions.
If it is impossible to remove the container within this period, after consultation with an environmental expert accredited in the discipline containers for gases or hazardous substances or with an authorised expert or with a technician accredited for the storage of P3 and/or P4 products intended for the heating of buildings, the container must be emptied, cleaned and filled with sand, foam or an equivalent inert material. Here the necessary measures must be taken for explosion protection and to prevent soil and groundwater pollution.

§ 4. Liquid leaks which have caused ground pollution or spillage into the sewer system, the surface waters, the groundwater layers or onto adjacent properties must be immediately reported by the operator to the Environmental Inspection Department, to the Governor of the Province and to the Burgomaster.

Section 5.17.4 Control of the emission of volatile organic compounds (VOC) with the storage and transferring of petrol

Art. 5.17.4.1

The provisions of this section are applicable to the establishments as referred to in the subsection 17.3.4 and the establishments as referred to in subsection 17.3.9 of the classification list, to the extent these establishments concern the collection, storage and transferring of petrol.

Art. 5.17.4.2

§ 1. Without prejudice to the other conditions in these regulations, the storage installations must comply with the technical regulations of appendix 5.17.9, § 2.

§ 2. As a derogation from § 1, existing storage installations must comply with the provisions of § 1:

1. from 1 January 1999 for storage installations with a turnover greater than 50000 tonnes per year, measured during the years 1996 and 1997

2. from 1 January 2002 for storage installations with a turnover greater than 25000 tonnes per year, measured during the years 1996 up to and including 2000; if, however, the turnover measured during the years 1998 up to and including 2000 exceeds the limit of 50000 tonnes per year, the provisions of §1 of this article are applicable from 1 January of the second year after the year for which the limit value was exceeded
3. from 1 January 2005 for other storage installations.

Art. 5.17.4.3

§ 1. Without prejudice to the other conditions in these regulations, transfer installations of mobile tanks at terminals must comply with the technical regulations of appendix 5.17.9, § 3.

§ 2. All terminals with transfer installations for the loading of tankers must be equipped with at least one loading gantry that meets the specifications for installations for filling on the bottom side in appendix 5.17.9, § 5.

§ 3. As a derogation from § 1 of this article, existing transfer installations for the loading of tankers, rail tankers and/or ships must comply with the provisions of § 1 and § 2:

1. from 1 January 1999 for transfer installations with a turnover greater than 150000 tonnes per year, measured during the years 1996 and 1997
2. from 1 January 2002 for transfer installations with a turnover greater than 25000 tonnes per year, measured during the years 1996 up to and including 2000; if, however, the turnover measured during the years 1998 up to and including 2000 exceeds the limit of 150000 tonnes per year, the provisions of §1 of this article are applicable from 1 January of the second year after the year for which the limit value was exceeded
3. from 1 January 2005 for other transfer installations of terminals.

§ 4. Not later than three months after the date of bringing into use, and then at least once a year, an environmental expert accredited in the discipline air must draw up a report. In this report the results of the measurements conducted to determine the average concentration of vapours in the vapour recovery unit outlet are shown, discussed and compared to the emission condition mentioned in appendix 5.17.9, § 3. The term between two control measurements may in no event exceed 15 months. This report must be sent to the Environmental Licence Department, the Environmental Inspection Department and the Flemish Environmental Agency.

Art. 5.17.4.4

§ 1. Without prejudice to the other conditions in these regulations, distribution installations for petrol must meet the technical regulations of appendix 5.17.9, § 4.

§ 2. As a derogation from § 1 of this article, existing distribution installations must comply with the provisions of § 1:

1. from 1 January 1999 for distribution installations with a turnover greater than 1000 m^3 per year, measured during the years 1996 and 1997, as well as for installations, irrespective of their turnover, which are located under permanent living spaces or working spaces
2. from 1 January 2002 for distribution installations with a turnover greater than 500 m^3 per year, measured during the years 1996 up to and including 2000; if, however, the turnover measured during the years 1998 up to and including 2000 exceeds the limit of 1000 m^3 per year, the provisions of § 1 of this article are applicable from 1 January of the second year after the year for which the limit value was exceeded
3. from 1 January 2005 for other distribution installations.

§ 3. The provisions of this article are not applicable to distribution installations with a turnover of less than 100 m^3 per year.

§ 4. Storage installations, which form part distribution installations for petrol which according to the provisions of this article must comply with the technical regulations of appendix 5.17.9, § 4, may only be filled by mobile tanks which meet the federal regulations for the execution of EC directive 94/63/EC of 20 December 1994 concerning the control of the emission of volatile organic substances (VOS) as a result of the storage of petrol and the distribution of petrol from terminals to distribution installations.

Art. 5.17.4.5

The operator must keep a register in which the turnover information is mentioned. This register is to be kept at the disposal of the supervisory officials.

Art. 5.17.4.6

The operator of a vapour recovery installation must keep a register in which each period of putting out of use of this installation is accurately recorded, as well as the reason for this and the measures taken. This register is to be available for perusal at the place of operation. § 3.

Section 5.17.5 Fuel distribution installations for motor vehicles

Art. 5.17.5.1

The provisions of this section are applicable to the establishments as referred to in subsection 17.3.9 of the classification list.

Art. 5.17.5.2

Without prejudice to the conditions in these regulations, the necessary measures must be taken to prevent the spillage of liquid fuels, the pollution of the soil and the groundwater and surface water.
In the case of an incident, effective measures must immediately be taken to prevent the spreading of liquid fuels.

Art. 5.17.5.3

Electrical installations must meet the requirements referred to in the General Regulations for electrical installations, in particular the articles dealing with spaces in which an explosive atmosphere can originate. These installations must be able to be manually stopped from a safe and always easily accessible place.

Art. 5.17.5.4

The filling of any vehicle whatsoever may only take place after the engines of this vehicle have been switched off.

Art. 5.17.5.5

Fuelling places for motor vehicles for P1 and/or P2 products are always in the open air and on the premises of the establishment. The floor of the aforementioned parking place is impervious and sufficiently supporting. The ground is to be provided with the necessary gradients and possible raised edges to ensure that any spilled flammable fuels run off to a collector and are removed in accordance with regulatory provisions.
No trenches, crawl spaces or rooms may be present under the aforementioned filling position.

Art. 5.17.5.6

Each fixed container which forms part of a distribution installation for the filling of motor vehicles must be equipped with its own filler pipe.
The filling point for P1 and/or P2 products :

1. is at a horizontal projection at least 2 m distance from the edge of the container
2. may not be in a closed or open building
3. must be located at least 3 m from any basement space and from the boundaries of the parcels of third parties.

Art. 5.17.5.7

§ 1. As regards existing fuel distribution installations for motor vehicles, the specific transitional period in article 3.2.1.2, § 3, b) for the specified construction requirements in article 5.17.5.5 and 5.17.1.17, 6. may be brought to:

1. 1 January 1999 for all distribution installations fitted with directly buried in the ground single-walled metal containers located inside water abstraction areas and protected zones
2. 1 January 2002 for all distribution installations, other than those mentioned sub 1., fitted with directly buried in the ground single-walled metal containers which were built before 1975, whereby it is assumed that the containers were built before 1975 if the age cannot be demonstrated
3. 1 January 2005 for all other distribution installations.

For existing containers or existing discharges of industrial sewage, the same derogation can apply as in article 5.17.1.4, § 2, article 5.17.2.11, § 5 and article 3.2.1.2, § 3, b, as regards the realisation of the requirements made in appendix 5.3.2, 52°, c).

§ 2. The operator can only be granted the exception as referred to in § 1 under the explicit condition that he, no later than on 1 January 1998, has bound himself to the following by registered mail to the Environmental Licence Department and the Environmental Inspection Department:

1. to ensure that the containers will meet the conditions of these regulations for new containers before the date set in § 1, except for that regarding the location regulations (in particular the prohibitory rules and stipulations of distances to be observed)
2. the further operation of the fuel distribution installation will be definitively stopped from the date in § 1 in the event of the undertaking in sub 1. not being achieved.

Annex 6

CHAPTER 5.20: INDUSTRIAL ESTABLISHMENTS WHICH CAN CAUSE AIR POLLUTION

Section 5.20.1 General provisions

Art. 5.20.1.1

§ 1. The provisions of this chapter are applicable to the establishments specified in section 20 of the classification list.

§ 2. As a derogation from the general emission limit values mentioned in chapter 4.4. the emission limit values specified in other chapters of this order for specific categories of establishments also apply for the categories of establishments covered by the specified sections in § 1 with the same industrial activity. This particularly concerns the emission limit values mentioned in chapters 5.7. "Chemicals" and 5.29. "Metal" which respectively apply for the establishments as referred to in subsections 20.4 and 20.2.

Section 5.20.2 Oil refineries.

Art. 5.20.2.1 Scope

The provisions of this section are applicable to the establishments as referred to in subsections 1.1 and 20.1.2. of the classification list.

Art. 5.20.2.2

§ 1. As a derogation from the provisions of the articles 5.7.6.1, chapters 5.31 and 5.43 and the general emission limit values specified in chapter 4.4., for oil refinery installations [¼] the following emission limit values apply concerning the sum of the emissions originating from heating installations, including STEG installations and processing installations:

1. from 1 January 1994:
   a) for sulphur dioxide:
     - until 31 December 1997:   2000 mg/Nm^3
     - from 1 January 1998:   1300 mg/Nm^3
   b) for nitrogen oxides:
     - until 31 December 1997:   900 mg/Nm^3
     - from 1 January 1998:   450 mg/Nm^3
   c) for suspended particulates:
     - until 31 December 1997:   300 mg/Nm^3
     - from 1 January 1998:   150 mg/Nm^3
2. from 1 January 1997:
   for CO:
   - until 31 December 1997:   250 mg/Nm^3
   - from 1 January 1998:   150 mg/Nm^3
3. from 1 January 1999:
   - for Ni and its compounds: 2 mg/Nm³ expressed in Ni
   - for V and its compounds: 7 mg/Nm³ expressed in V.

At processing installations referred to in the first subsection include, among others:
- sulphur recovery units
- catalytic cracking and converting installations
- incinerators
- torches as well as asphalt oxidisers and all other processing units with SO_2-, NO_x, CO and dust emissions.

For new, large heating installations the provisions of section 5.43.2 apply, except for the emission limit values included in the section. These are replaced by the emission limit values included in appendix 5.20.2.

As a derogation from article 3.2.1.2, § 3, a), for existing establishments the more stringent emission limit values apply as referred to in the third subsection, as of 1 January 2005.

§ 2. From 1 January 1994 the operating conditions in the operating licences for oil refineries with respect to SO_2-, NO_x-, CO and dust are replaced by the provisions of § 1.

§ 3. For the application of the provisions of § 1 of this article, the following specifications must be respected:

1. for the definitions of flue gases and emission limit values, for new and existing heating installations and for steam and gas turbine installations (STEG) the definitions of article 1.1.2 apply, in particular concerning industrial establishments which can cause air pollution. For processing installations the actual flow rates in m^3/hour must be converted at the normal temperature (273 °K) and pressure (101.3 kPa), but on a dry basis as specified in article 4.4.3.1. with the actual quantity of excess oxygen
2. measuring strategy for suspended particulates, SO_2 , NO_x , CO, Ni and V:
   - for heating installations, including machines with internal incineration the provisions of article 5.43.2.3. apply, §§ 1 and 2
   - for processing installations, residual gas measurements are constantly conducted or the emissions are calculated on the basis of constant or periodically measured relevant parameters according to codes of good practice as in article 5.43.2.3., §§ 1 and 2
3. assessment of measuring results:
   for the assessment of the measuring results the following applies:
   - for SO_2: the provisions of article 5.43.2.4 with continuous measurement or article 4.4.4.5 with discontinuous measurement
   - for NO_x and CO: the provisions of article 5.43.5.1, § 4 with continuous measurement or article 4.4.4.5 with discontinuous measurement
   - for suspended particulates: the provisions in article 5.43.5.1, § 4 with continuous measurement or article 4.4.4.5 with discontinuous measurement
   - for Ni and V: the provisions as mentioned for NO_x, in article 5.43.5.1, § 4 with continuous measurement or article 4.4.4.5 with discontinuous measurement.

§ 4. Gaseous effluents discontinuously released by a processing such as gaseous effluents resulting from the regeneration of catalytic agents and with inspection and cleaning activities must be transported to a combustion facility or a torch, or equivalent measures must be taken to ensure emission reduction.

Gaseous effluents released with the starting up or stoppage of an installation must, to the extent possible, be transported to a collection system for gaseous effluent or incinerated in process heating installations. When this not possible, the gases must be led to a torch, in which for organic substances an emission level of 1 % with respect to the total carbon content may not be exceeded.

Gaseous effluents from desulphurisation installations or other sources with a volume level of hydrogen sulphide of over 0.4 % and a mass flow of hydrogen sulphide of over 2 tonnes/day must be further processed.

Gaseous effluents which are not further processed must be transported to an incinerator.

As a derogation from the provisions of chapter 4.4, the emissions of hydrogen sulphide in the discharged gaseous effluent may not exceed 10 mg/Nm^3.

Hydrogen sulphide-containing water may only be processed in such a way that the release of gaseous effluent into the atmosphere is avoided.

With the transfer of base, intermediary and finished products the emissions of organic substances with a vapour pressure of over 13.3 kPa at a temperature of 35 °C must be reduced by means of appropriate measures, such as by gas pendulum, extraction and transfer to an effluent gas purification installation.

Process water may only be discharged into an open system after degassing. The gaseous effluents collected here must be cleaned by washing or incineration.

§ 5. As a derogation from § 1, the emission in the gaseous effluent of installations for the catalytic cracking according to the 'fluid bed' procedure with the regeneration of the catalyst may not exceed the following emission limit value for suspended particulates:

1. until 1 January 2005:   300 mg/Nm^3 as monthly average
2. from 1 January 2005:   50 mg/Nm^3 as monthly average.

§ 6. The concentration of polychlorinated dibenzo-p-dioxins (PCDD's) and polychlorinated dibenzo-p-furans (PCDF's), calculated according to article 5.2.3.1.5, § 6, expressed as nanograms dioxin toxic equivalent per Nm^3 (ng TEQ/Nm^3), may not exceed a limit value of 0.5 ng TEQ/Nm^3 for all average values over a sampling period of at least 6 hours and a maximum of 8 hours. The emission guide value is 0.1 ng TEQ/Nm^3.

As a derogation from the provisions of the first subsection, the following applies for existing establishments:

- an emission guide value of 0.4 ng TEQ/Nm^3;
- an emission limit value of 2.5 ng TEQ/Nm^3 as of 1 January 2002.

The aforementioned guide values must be striven for by the application of the best available techniques.

The mass concentration of PCDD's and PCDF's is to be measured according to the requirements referred to in the Belgian standard T95-R-NBN EN 1948-1, 2 or 3. This concentration is to be measured at least once a year by an environmental expert accredited for these measurements. This measurement is not compulsory for constituent flows which do not or do not significantly contribute to the emissions. Unless specified otherwise in the environmental licence, the omission of the measurements of specific constituent flows is only accepted providing that this has been approved of in advance by the supervisory authority.

Each measurement performed according to the above-mentioned method must, after the calculation of the accuracy as referred to in article 4.4.4.2, § 5, comply with the prescribed emission limit value. If the measured concentration, after the calculation of the aforementioned accuracy, exceeds the emission limit value, within three months new sampling and analysis will take place.

Art. 5.20.2.3 Immission control procedures

§ 1. Without prejudice to the provisions of chapter 4.4, each time the weather conditions appear unfavourable for the good dispersion of the combustion gases, in particular at the establishment, the operator will take all necessary steps to maximally restrict the emissions of SO_2 as well as of NO_x from this installation.

§ 2. Each change of fuel, sulphur content of the liquid fuel, as well as the times of putting out of use are recorded in a register that the operator keeps available to the official charged with supervision.

§ 3. When the total installed nominal thermal capacity at one establishment amounts to more than 300 MW, in the surrounding area of the installations appliances for the measuring of the immissions of SO_2 and NO_2 in the air at the ground will be installed and maintained at the operator's expense. The type, the place of measurement, the method of control and the other conditions for use for the appliances are determined in the environmental licence.

§ 4. Without prejudice to the provisions of § 1, each time the average immission value over 24 hours measured with the equipment specified in § 3, amounts to more than 300 mg/m^3 for SO_2 and/or 150 mg/m^3 for NO_2, the operator will take the steps prescribed in § 1, and maintain these measures for as long as the measured average immission values over 24 hours of SO_2 and of NO_2 amount to more than 300 mg/m^3 for SO_2 and/or 150 mg/m^3 for NO_2.

§ 5. To guarantee compliance with the emission limit values for nitrogen oxides of art. 5.20.2.2, more appropriate technical construction conditions can be imposed in the environmental licences.

If from control measurements it appears that the emission limit value is not being complied with due to unforeseen circumstances, the operator must take all suitable primary measures to ensure compliance with the emission limit values as soon as possible. The operator must report this to the Environmental Inspection Department together with the mentioning of measures taken for improvement. The European Commission is to be immediately informed through the usual channels of such events, as well as of the work carried out for improvement.

Section 5.20.3 Installations for the dry distillation of coal (coke ovens)

Art. 5.20.3.1 Underfiring, coke oven gas and heating installations

§ 1. Reference value
The emission values for waste gases from heating concern a volume level of oxygen in the spent gas of 5 %.

§ 2. Coke oven gas and fuel
As a derogation from the general emission limit value for SO_2 as specified in article 4.4.3.1, the weighed average of the mass concentration of sulphur compounds in the gas from the underfiring, as well as in the gases originating from the coke ovens used as fuel, may over a calendar year not exceed 0.80 g/m^3 expressed in sulphur.

§ 3. Nitrogen oxides
With the first time of measuring, the emissions of nitrogen monoxide and nitrogen dioxide in the gaseous effluent from the underfiring may not exceed 0.50 g/m^3 expressed in nitrogen dioxide. The best available techniques to reduce the increase of emissions due to ageing must be applied.

The measurements to be conducted for the first time after foundation or significant modification must be carried out after the installation has reached uninterrupted operation, but at the earliest after three months in operation and at the latest twelve months after being in operation.

Art. 5.20.3.2 Filling the coke ovens

With the unloading of the coal from the coal bunker in the larry car, dust emissions must be avoided.

The filling gases must be collected.

When dumping, the filling gases must be transferred to the raw gas or an oven close by to the extent possible, with the further processability of the raw coal tar in mind.

With stamping, the filling gases must be transferred in the raw gas to the extent possible.

Filling gases which cannot be transferred must be taken to an incineration facility. Dust-containing emissions in the gaseous effluent of the incineration may not exceed 25 mg/m^3.

With the levelling activities with the dumping of coal, the emissions of filling gases must be reduced by the sealing of the levelling opening.

Art. 5.20.3.3 Filling opening covers

Emissions with filling opening covers must be avoided to the extent possible, for example by using filling opening covers with large sealing surfaces, coating the filling opening covers will loam each time after filling the ovens and the regular cleaning of the filling opening frames and filling opening covers before the filling openings are closed. Coal remains must be regularly removed from the oven roof.

Art. 5.20.3.4 Riser pipe covers

For the avoidance of gas and coal tar emissions, riser pipe covers must be fitted with devices for keeping wet with water or equivalent devices.

Art. 5.20.3.5 Coke oven operating machines

Coke oven operating machines must be fitted with devices for the cleaning of the sealing surfaces at the oven door frames.

Art. 5.20.3.6 Coke oven doors

Coke oven doors with a large sealing effect must be used, for example diaphragm doors or doors with an equivalent sealing effect. The sealing surfaces of the oven doors must be regularly cleaned.
Unless specified otherwise in the environmental licence, the coke oven batteries are to be arranged in such a way that on the machine side and on the coke side door extraction units with dedusting devices can be installed.

Art. 5.20.3.7 Pushing out of coke

With the pushing out of coke the spent gases must be collected and led to a dedusting installation.
Unless specified otherwise in the environmental licence, the dust concentration in the emissions will not exceed the emission limit value of 50 mg/Nm^3, and the dust-containing emissions may not exceed 5 gram per tonne of produced coke.

Art. 5.20.3.8 Coke cooling

§ 1. If dry cooling is applied, unless specified otherwise in the environmental licence, the dust emissions in the gaseous effluent may not exceed 20 mg/m^3.

§ 2. If wet cooling is applied, the quenching tower used must be fitted with built-in dust extractors.
As a derogation from the general emission limit values laid down in article 4.4.3.1, the emission limit values are expressed in gram per tonne of coke. Unless specified otherwise in the environmental licence, an emission limit value of 60 gram suspended particulates per tonne coke, measured according to the VDI directive VDI 2303 or another equivalent measuring method approved by an environmental expert accredited in the discipline air, may not be exceeded.

Art. 5.20.3.9 Operating manual

An operating manual must contain measures for the reduction of emissions with the operation of the coke oven, in particular regarding:

1. the sealing of the openings
2. the guaranteeing that only fullycoked material will be pushed out
3. the avoidance of unburned gases escaping into the atmosphere.

Art. 5.20.3.10 Existing installations

For existing installations the provisions of this section apply as of 1 January 1998.

Section 5.20.4 The production of glass fibre or rock fibre and glass wool, the manufacture of glass (flat, concave and special glass) and the manufacture of crude ceramics

Subsection 5.20.4.1 The production of glass (flat, concave and special glass) and of glass fibre or rock fibre

Art. 5.20.4.1.1

§ 1. Reference value
The emission limit values for flame-heated glass melting furnaces concern a volume level of 8 %, and with flame-heated crucible kilns and open tiling a volume level of oxygen in the spent gas of 13 %.

§ 2. Nitrogen oxides
The emissions of nitrogen monoxide and nitrogen dioxide, expressed in nitrogen dioxide, in the gaseous effluent may not exceed the following values:

	oil fired [g/Nm^3]	gas fired [g/Nm^3]
crucible kilns	1.2	1.2
tiling with recuperative heat recovery	1.2	1.4
open tiling	1.6	1.6
U-fire tiling with regenerative heat recovery	1.8	2.2
crossfiring tiling with regenerative heat recovery	3.0	3.5

Insofar from production quality considerations purification with nitrate is necessary, the emissions may not exceed double the values specified in the previous subsection.
All possibilities for the reduction of emissions of nitrogen oxides by means technical heating measures and other available measures are to be applied.

§ 3. sulphur oxides.
The emissions of sulphur dioxide and sulphur trioxide in the spent gas, expressed in sulphur dioxide, may not exceed the following values at a mass flow of 10 kg/h or more with firing:

a) glass melting furnaces: 1.8 g/Nm^3
b) crucible kilns and open tiling: 1.1 g/Nm^3

Subsection 5.20.4.2 Production of crude ceramics

Art. 5.20.4.2.1

§ 1. Reference value
The emission limit values concern a volume level of oxygen in the gaseous effluent of 18 %.

§ 2. Sulphur oxides
With a sulphur content of the raw materials of less than 0.12 %, the emissions of sulphur dioxide and sulphur trioxide, expressed in sulphur dioxide in the gaseous effluent at a mass flow of 10 kg/h or more, may not exceed 0.5 g/Nm^3.

With a sulphur content of the raw materials of 0.12 % or more, the emissions of sulphur dioxide and sulphur trioxide, expressed in sulphur dioxide in the gaseous effluent at a mass flow of 10 kg/1 hour2 or more, may not exceed 1.5 g/Nm^3.

All possibilities for the reduction of emissions by cleaning installations for gaseous effluent must be applied.

§ 3. For existing establishments, as referred to in section 30.9 of the classification list, the provisions of chapter 5.30 also apply.

Section 5.20.5   Installations for the production of hydroelectric energy as well as installations for the abstraction of wind power for energy production

Art. 5.20.5.1

§ 1. The provisions of this section are applicable to subsections 20.1.5 and 20.1.6 of the classification list.

§ 2. As a derogation from the provisions of chapter 4.5, in this case no noise standards are applicable. In the environmental licence noise emission limits can be imposed depending on local conditions.

3. DENMARK

No information supplied

4. FINLAND

The Finnish environmental protection legislation has been revised recently and a new Environmental Protection Act came into force on the 1st of March, 2000. The new act totally implements the EU Directive on Integrated Pollution Prevention and Control (IPPC) and has an integrated approach to control emissions caused by the industry. According to the Environmental Protection Act an environmental permit is required for installations of the chemical industry.

In the permitting procedure the environment is considered as a whole and all the environmental effects of the activity are estimated at the same time. All necessary permit conditions are set in a single permit. The application for a permit is dealt with by one competent authority.

In Finland permit conditions are set mainly based on case-by-case consideration. At the moment there are no special regulations concerning the emissions to air or waste water from the chemical industry. Instead there are some general Council of State Decisions on discharging certain compounds into public sewer systems or into water bodies. In addition to that there are regulations banning or restricting the use of certain hazardous chemicals. All of them are valid in the chemical industry as well as in all other branches of industry.

International recommendations, e.g. HELCOM-recommendations (HELSINKI COMMISSION, Baltic Marine Environment Protection Commission), are also taken into consideration in setting the permit conditions.

5. FRANCE

The legislation for the chemical sector is composed of:

- the general framework for the control of industrial pollution and risk prevention, as provided by the "classified installations law" of the 19th July 1976, and the Order of the 2nd February 1998. This Order specifies that emission limit values should be based on BAT and local conditions of the environment. The Order gives general emission limit values for air and water, for all classified installations, and also specific limit values for many industrial activities, many of which included in the chemical sector.

- special legislation, each targeting a particular sector of the chemical industry, and detailing the general provisions of the general framework for that particular sector. The main sectors covered by such special legislation are:

    production of superphosphates
    production of organic sulphuric compounds
    production of detergent and of soap
    steam extraction of perfumes, essential oils
    production of dyes
    production of pharmaceuticals
    production of plastics, rubber
    use or re-use of plastics, rubber
    storage of plastics, rubber
    storage of tyres
    production of accumulators.

6. GERMANY

Important regulations relevant for industrial installations in Germany are laid down in the Federal Immission Control Act [Bundesimmissionsschutzgesetz - BImSchG], the Federal Water Act [Wasserhaushaltsgesetz - WHG] and the Federal Recycling and Waste Management Act [Kreislaufwirtschafts- und Abfallgesetz - KrW-/AbfG]. Germany uses a media segregated permit system for the different environmental media, but the final decision on an application is made by the assessment of environmental impacts over all media by the competent authorities. Also noise requirements are considered in the licensing procedure. The "precautionary principle" has a legal status which permits the setting of standards. Legal standards are not subject to any negotiation in the licensing process in Germany.

In compliance with the federal structure of Germany, the implementation of environmental laws and decrees is under the responsibility of the federal states (Bundesländer), which may implement the administrative procedure differently. For new plants, that are regarded as relevant with respect to emissions and releases into the environment, also an environmental impact assessment is required during the licensing procedure ['Gesetz über die Umweltverträglichkeitsprüfung [UVPG]', (Environmental Impact Assessment Act)].

Regulations on Air Quality
The basic law for air pollution control is the Federal Immission Control Act [Bundes-Immissionsschutzgesetz BImSchG]. It is specified by 21 ordinances and the Technical Instructions on Air Quality [TA Luft].

The Technical Instructions on Air Quality (TA Luft) have been set up as general administrative regulations in connection with §48 BImSchG. The TA Luft further specifies the requirements to be met by installations subject to licensing. Therefore, it prescribes emission limit values for virtually all air pollutants as well as structural and operational requirements designed to limit diffuse emissions.

The emission limit values contained in the TA Luft represent state-of-art for technical measures for reducing emissions (dating from 1986). These values were developed referring to scientific findings and research, taking into account toxicological, bioaccumulative and epidemiological aspects.

Emitted substance (TA Luft section)	Class	Substances		Mass flow threshold [g/h]	Concentration limit [mg/m³]
Emission control requirements laid down in the TA Luft					
Total dust				≤500	150
				≥500	50
Inorganic dust particles (3.1.4)	I	(Hg, Cd, Tl)	Sum of substances	≥1	0.2
	II	(As, Co, Ni, Te, Se)	Sum of substances	≥5	1
	III	(e.g. Sb, Pb, Cr, CN, F, Cu, Mn, Pt, Pd, Rn, V, Sn, substances wich are strongly suspected to cause cancer)	Sum of substances	≥25	5
	I+II		Sum of substances		1
	I+III, II+III		Sum of substances		5
Vaporous or gaseous inorganic substances (3.1.6)	I	(e.g. AsH_3)	Per substance	≥10	1
	II	(e.g. HF, Cl_2, H_2S)	Per substance	≥50	5
	III	(e.g. Cl-compounds as HCl)	Per substance	≥300	30
	IV	(e.g. $SO_2 + SO_3$ as SO_2, $NO + NO_2$ as NO_2)	Per substance	≥5000	500
Organic substances (3.1.7)	I	(e.g. Chlormethane)	Classification according to Annex E of TA Luft	≥100	20
	II	(e.g. Chlorbenzene)		≥2000	100
	III	(e.g. Alkylalcohols)		≥3000	150
Vaporous or gaseous emissione during treatment and refilling of organic substances (3.1.8)	Requirements for the minimization of diffuse organic emyission by the installation of technical equipment, e.g. pumping units, compressors, flanged joints, stop valves and in sampling stations				
Carcinogens (2.3)	I	(e.g. Cd[1], As[1], asbestos, benzo(a)pyren)	Sum of substances	≥0.5	0.1
	II	(e.g. Ni, chromium VI)	Sum of substances	≥5	1
	III	(e.g. Acrylonitrite, benzene)	Sum of substances	≥25	5

[1] Based on the decision adopted by the Conference of the Federal Government/Federal States Ministers for the Environment on 21/22. November 1991, an emission concentration value of 0.1 mg/m³ has been stipulated for Cd and its compounds, given as Cd, as well as for As and its compounds, given as As.

The required emission limits are given in mass of emitted substances related to the volume of emitted gas under standard conditions (0°C, 101.3 kPa) after subtraction of the water vapour content.

If organic substances in several classes are present, the mass concentration in the emitted gas should not exceed a total of 0.15 mg/Nm^3 with a total mass flow of 3 kg/h or more.

In the case of high emission mass flows, emissions have to be monitored continuously.

No daily mean value of the respective emitted substances should exceed the required emission limits, 97 % of all half-hourly means should not exceed six fifths of the required emission limits, and all half-hourly means should not exceed the required emission limits by more than twice.

Specific emission control requirements laid down in the TA Luft for organic chemical industry	
Sector	**Requirements**
Production of 1,2-dichloro-ethane (EDC) and vinylchloride (VC) (3.3.4.1.g.1)	Limit emission concentration: 5 mg/Nm^3 EDC or VC
Production of acrylnitrile (AN) (3.3.4.1.g.2)	Limit emission concentration: 0,2 mg/Nm^3 AN Waste gases from distillation or refilling have to be reduced
Production of pesticide agents (3.3.4.1.g.3)	Dust In the case of production of pesticides, which are pesistent or accumulating or restricted according to the directive on Bans on the Placing on the Market and the Use of Plant Protecting Agents Containing Particular Active Substances limit emission concentration: 5 mg/Nm^3 (mass flow threshold: ≥25 g/h)
Plant for milling, mixing, refilling and packaging of pesticides (3.3.4.2.1)	Limit emission concentration: 5 mg/Nm^3 dust

Regulations on Water Quality

The legal framework for water management is the Federal Water Act [Wasserhaushaltsgesetz - WHG]. The WHG applies to waste water generated by various industrial processes. The usage of surface, coastal, and ground waters requires the approval of the competent authority. **Discharges into water** are regulated in the Waste Water Ordinance including its Annexes [Abwasserverordnung, AbwV]. It specifies the minimum requirements to be stipulated when granting a permit to discharge waste water from the source categories listed in the Appendices into receiving water.

Issued by the Federal Government in consent with the Federal States (Länder), these minimum requirements bind the authority competent for licensing and controlling the discharges. Depending on the local conditions, more stringent requirements can be established. The minimum requirements are based on the 'emission principle' and the precautionary principle. General requirements according to the Waste Water Ordinance are covered by the Article 3 listed below:

General requirements

  i. unless otherwise stated in the Appendices, a permit to discharge waste water into waterbodies shall only be granted if the pollutant load at the site of occurrence, based on an examination of the conditions in each individual case, is kept as low as the use of water-saving procedures such as washing and cleaning operations, indirect cooling and the use of low-pollutant feedstocks and auxiliary materials permit
 ii. the requirements of this Ordinance must not be met by means of procedures whereby environmental pollution is transferred to other environmental media such as air or soil, contrary to state-of-art
iii. requirements specified in the form of concentration levels must not be achieved via dilution, contrary to state-of-art
 iv. if requirements prior to blending are specified, then blending shall be permissible for the purpose of joint treatment, provided at least the same overall reduction of contaminant load per parameter is achieved as would be the case via separate compliance with the relevant requirement
  v. if requirements are specified for the site of occurrence of waste water, blending is only permissible provided these requirements are adhered to
 vi. if waste water flows which are subject to differing requirements are discharged jointly, then the relevant decisive requirement for each parameter shall be determined by means of alligation
vii. if requirements governing the site of occurrence of the waste water or prior to blending are imposed in the applicable Appendices, then paragraphs iv and v shall remain unaffected.

The requirements refer to the point at which the waste water is discharged into the waterbody and, when specified in the appendices to this ordinance, also to the site of occurrence of the waste water or the site prior to blending thereof. The point of discharge is synonymous with the outlet from the waste water plant where the waste water was last treated. The site prior to blending is also the point of discharge into a public waste water plant.

If a level specified by this ordinance is not complied with based on the results of analysis within the context of government monitoring, it shall nevertheless be deemed to have been met, provided the results of this and the four preceding government analyses do not exceed the level in four cases and no result exceeds the level by more than 100 %. Analyses conducted more than three years ago shall be disregarded.

The productions of the specific sectors are covered by Annexesof this regulation. The relevant annexes for the chemical sector are:

- Annex 22 (Chemical industry)
- Annex 36 (Production of hydrocarbons)

Appendix 22 on Chemical industry

"A. Scope of application
(1) This Appendix shall apply to waste water originating primarily from the production of substances using chemical, biochemical or physical techniques, including the related pretreatment, intermediate treatment and after-treatment.
(2) This Appendix shall not apply to waste water discharges of less than 10 m^3 per day.
(3) For waste water derived from formulation (i.e. the manufacture of substances and preparations by blending, dissolving or bottling) which is discharged without being blended with other waste water falling under the scope of application of this Appendix, only part B of this Appendix shall apply.

B. General requirements
A permit for the discharge of waste water into waterbodies shall only be granted, subject to the requirement that the contaminant load at the site of occurrence of the waste water is kept as low as the following measures permit, after investigating the situation in each individual case:

- Use of water-saving techniques, such as countercurrent washing
- Multiple use and recirculation, e.g. with washing and purifying processes
- Indirect cooling, e.g. to cool vapour phases instead of using jet condensers or jet coolers
- The use of waste water-free techniques to generate vacuums and for waste air purification
- The retention or recovery of substances via the preparation of mother liquor and by means of optimised techniques
- The use of low-pollutant raw and auxiliary materials.

Proof of compliance with the general requirements shall be furnished in the form of a waste water register.

C. Requirements for waste water at the point of discharge
(1) The following requirements apply to the waste water at the point of discharge into the waterbody:

1. Chemical oxygen demand (COD)
   a) For waste water flows whose COD concentration at the site of occurrence of waste water is more than 50000 mg/l, a COD concentration of 2500 mg/l shall apply
   b) more than 750 mg/l, a COD concentration equivalent to a 90% reduction in COD shall apply
   c) 750 mg/l or less, a COD concentration of 75 mg/l shall apply
   d) less than 75 mg/l, the actual COD concentration at the site of occurrence shall apply.

The requirements shall also be deemed to have been met provided a COD concentration of 75 mg/l in the qualified random sample or 2-hour composite sample is adhered to, with due regard for part B.

2. Total nitrogen as the sum of ammonia, nitrite and nitrate nitrogen (N_{tot}): 50 mg/l in the qualified random sample or 2-hour composite sample. A higher concentration of up to 75 mg/l may be specified in the water discharge licence, provided a 75 % reduction in the nitrogen load is adhered to. The set value shall also be deemed to have been met, provided the level defined as "total bounded nitrogen (TN_b)" is adhered to.

3. Total phosphorous: 2 mg/l in the qualified random sample or 2-hour composite sample. This requirement shall also be deemed to have been met provided the level defined as "phosphorous compounds as total phosphorous" is adhered to.

4. Toxicity

Fish toxicity	T_F	=	2
Daphnia toxicity	T_D	=	8
Algae toxicity	T_A	=	16
Luminescent bacteria test	T_L	=	32
Mutagenic potential (umu test)	T_M	=	1.5

The requirements refer to the qualified random sample or the 2-hour composite sample.

(2) If process-integrated measures are applied to reduce the COD load by arrangement with the water authority, then the decisive load prior to implementation of the measure shall be used as a basis.

(3) For chemical oxygen demand (COD), the total load in 0.5 or 2 hours shall be limited in the water discharge licence. The total load is the sum of the individual loads from the individual waste water flows. The total load which must not be exceeded refers to the concentration in the qualified random sample or 2-hour random sample and the volumetric flow of waste water in 0.5 or 2 hours corresponding to sampling.

D. Requirements on waste water prior to blending
(1) The following requirements apply to waste water prior to blending with other waste water:

Adsorbable organic halogens (AOX)	
a) Waste water from the manufacture of epichlorhydrin, propylene oxide and butylene oxide	3 mg/l
b) Waste water from the two-stage manufacture of acetaldehyde	80 g/t
c) Waste water from the single-stage manufacture of acetaldehyde	30 g/t
d) Waste water from the manufacture of AOX-relevant organic colorants and aromatic intermediate products, where these are predominantly used to manufacture organic colorants	8 mg/l
e) Waste water from the manufacture of AOX-relevant active pharmaceutical ingredients	8 mg/l
f) Waste water from the manufacture of C1 chlorinated hydrocarbons by means of methane chlorination and methanol esterification, and of carbon tetrachloride and perchloroethane by means of perchlorination	10 g/t
g) Waste water from the manufacture of 1,2 dichloroethane (EDC), including further processing to vinyl chloride (VC) The load level refers to the production capacity for purified EDC. The capacity should be specified with due regard for the EDC portion which is not cracked in the VC unit linked to the EDC production unit and which is returned to the production cycle in the EDC purification plant.	2 g/t
h) Waste water from the manufacture of polyvinyl chloride (PVC)	5 g/t
i) Waste water flows with an AOX concentration of more than 0.1 mg/l and less than 1 mg/l without targeted measures	0.3 mg/l
j) Waste water flows from the manufacturing, further processing and application of substances which are not separately regulated elsewhere witha concentration of more than 1 mg/l is exceeded or less than 1 mg/l via targeted measures	1 mg/l or 20 g/t
The load level refers to the capacity of the organic target products. It does not apply to the application of substances.	

Other substances		
	Qualified random sample or 2-hour composite sample [mg/l]	
Mercury	0.05	0.001
Cadmium	0.2	0.005
Copper	0.5	0.1
Nickel	0.5	0.05
Lead	0.5	0.05
Total chromium	0.5	0.05
Zinc	2	0.2
Tin	2	0.2
The requirements in column I apply to waste water flows from the manufacturing, further processing or application of these substances. The requirements in column II refer to waste water flows not originating from the manufacturing, further processing or application of these substances but which are nevertheless contaminated with such substances below the concentration levels in column I.		

(2) Upon compliance with the AOX requirements and the general requirements pursuant to part B, the requirements of Appendix 48, part 10 shall also be deemed to have been met.

(3) The AOX requirements shall not apply to iodo-organic substances in waste water from the manufacturing and bottling of X-ray contrast media.

(4) For adsorbable organic halogens (AOX) and the substances limited in paragraph (1), number 2, the total load per parameter in 0.5 or 2 hours shall be limited in the water discharge licence. The respective total load is derived from the sum of the individual loads of the separate waste water flows. The total load which must not be exceeded refers to the concentration in the qualified random sample or 2-hour composite sample and the volumetric flow of waste water in 0.5 or 2 hours corresponding to sampling.

(5) A waste water flow may only be blended with other waste water, subject to the furnishing of proof that the load of total organically bonded carbon (TOC) in this waste water flow ascertained for the site of occurrence is reduced by 80 % overall. This requirement shall not apply where the residual TOC load discharged from the respective waste water flow into waterbodies does not exceed 20 kilograms per day or 300 kilograms per year or 1 kilogram per tonne of production capacity of the organic target product. When proving the reduction in load, in the case of physico-chemical waste water treatment plants, the TOC elimination level of such plants shall be used as a basis, whereas in the case of biological waste water treatment plants, the result of a study pertaining to number 407 of the Annex to Article 4 shall be used as a basis.

E. Requirements on the waste water at the site of occurrence

(1) For chromium VI, a concentration of 0.1 mg/l in the random sample shall be adhered to.

(2) For volatile organically bonded halogens, a concentration of 10 mg/l in the random sample shall be adhered to. This requirement shall be deemed to have been met, provided it is achieved prior to the inlet into a sewage system without prior risk of leakage losses and without the waste water having been diluted.

F. Requirements for existing discharges

(1) For existing discharges of waste water from installations which were lawfully in operation prior to 1 January 1999 or whose construction had lawfully commenced by this date, the provisions in parts A, B, C and D shall only apply insofar as no requirements to the contrary are specified in paragraphs (2) to (5).

(2) Notwithstanding part B, proof of compliance with the general requirements in a waste water register must only be provided for 90 % of the parameter-related total loads in each case. The use of waste water-free techniques to generate a vacuum and for waste air purification must only be tested for the parameters specified in parts D and E. Additional testing with respect to other parameters is unnecessary.

(3) The requirements of part C pertaining to COD shall not apply to waste water from the manufacture of polyacrylonitrile.

(4) Notwithstanding part D, the following AOX requirements shall apply to the following waste water flows prior to blending with other waste water:

1. Waste water from the production of EDC, including further processing to VC: 5 g/t (production capacity of purified EDC)
2. Waste water from the manufacture of PVC: 1 mg/l or 20 g/t

(5) The requirements concerning mutagenic potential (umu test) pursuant to part C, paragraph (1) and TOC pursuant to part D, paragraph (5) shall not apply."

<u>Appendix 36 on Production of hydrocarbons</u>

"A. Scope of application

(1) This Appendix shall apply to waste water whose contaminant load originates primarily from the following areas of hydrocarbon production:

- The production of certain hydrocarbons, primarily olefin hydrocarbons, with 2 to 4 carbon atoms, as well as benzene, toluene and xylene from mineral oil products by cracking with the aid of steam (steam cracking)
- The production of pure hydrocarbons or certain blends of hydrocarbons from mineral oil products using physical separation methods
- The conversion of hydrocarbons into other hydrocarbons using the chemical techniques of hydration, dehydration, alkylation, dealkylation, hydrodealkylation, isomerisation or disproportionation.

This shall also include any precipitation water coming into contact with hydrocarbons in the process area of the production plant.

(2) This Appendix shall not apply to waste water from the production of pure paraffins from slack wax, from petroleum refining, from indirect cooling systems or from process water treatment facilities.

B. General requirements

No requirements above and beyond Article 3 are imposed.

C. Requirements for waste water at the point of discharge

(1) The following requirements apply to the waste water at the point of discharge into the waterbody:

	Qualified random sample or 2-hour composite sample [mg/l]
Chemical oxygen demand (COD)	120
5-day biochemical oxygen demand (BOD$_5$)	25
Total nitrogen as the sum of ammonia, nitrite and nitrate nitrogen (N$_{tot}$)	25
Total phosphorous	1.5
Total hydrocarbons	2

(2) For COD, a concentration of up to 190 mg/l in the qualified random sample or 2-hour composite sample may be conceded, provided the COD load is reduced by at least 80 % in a central waste water treatment plant. The reduction in COD load refers to the ratio between the COD load in the effluent of the gravity-type oil-water separator and that of the effluent from the biological waste water treatment plant over a representative period of time not exceeding 24 hours.

(3) For total nitrogen, a higher concentration is permissible, provided the nitrogen load is reduced by at least 75% in a central waste water treatment plant. The reduction in the nitrogen load refers to the ratio between the nitrogen load of the effluent from the gravity-type oil-water separator and that of the effluent from the biological waste water treatment plant over a representative period of time which should not exceed 24 hours. Total bonded nitrogen (TN$_b$) should be used as a basis when calculating the loads.

D. Requirements on waste water prior to blending
The following requirements shall apply to the waste water prior to blending with other waste water:

	Qualified random sample or 2-hour composite sample [mg/l]	Random sample [mg/l]
Adsorbable organic halogens (AOX)	-	0.1
Phenol index after distillation and dye extraction	0.15	-
Benzene and derivatives	0.05	-
Sulphide sulphur and mercaptan sulphur	0.6	-

If hydrocarbon production also includes the manufacture of ethylbenzene and cumene, an AOX level of 0.15 mg/l shall apply.

E. Requirements on waste water for the site of occurrence
Waste water from the production of ethylbenzene and cumene must not exceed a level of 1 mg/l for adsorbable organic halogens (AOX) in the random sample."

7. GREECE

No information supplied.

8. IRELAND

Releases to air:
The reference conditions for concentrations of substances in emissions to air from contained sources are:

For non-combustion gases: Temperature: 273 K
                               Pressure: 101.3 kPa
                               no correction for water vapour

For combustion gases: Temperature: 273 K
                               Pressure: 101.3 kPa
                               dry gas
                               Oxygen content: 3 % (dry) for liquid and gaseous fuel
                                               6 % (dry) for solid fuel

Achievement of emission limit value (ELV) concentrations by the introduction of dilution air is not permitted.

For continuously monitored emissions, the following will be required for compliance with measurements based on 30 minute mean values (unless otherwise stated):

  i.   97 % of all 30 minute mean measurements shall be below 1.2 times the emission limit
  ii. no 30 minute measurement shall exceed 2.0 times the emission limit
  iii. all daily mean values shall be less than the emission limit.

Where periodic monitoring is used to check compliance, all samples should meet the consent conditions.

Emission Limit Values for Fertiliser Production		
Process	**Source**	**ELV (mg/Nm^3)**

Ammonium nitrate production	Prill towers
	    - particulate
	    - ammonia
		
		15
		10

Ammonium nitrate production	Neutralisers/reactors/coolers/driers
	    - particulate
	    - ammonia
		
		30
		50

Ammonium nitrate procuction	Evaporators
	    - particulate
	    -ammonia
		
		15
		50

Ammonium phosphate production	- particulate - ammonia	15 10
Other fertiliser production	- particulate - sulphur oxides (as SO_2) - nitrogen oxides (as NO_2) - ammonia - fluorides (as HF)	50 200 200 50 10

Emission Limit Values for Sulphuric Acid Production	
Process	**Minimum conversion rate (SO_2 to SO_3)**
New process	Steady state: 99.7 % Start up: 98 % (hourly average for first 5 hours)

Emission Limit Values for Ammonia Production		
Source	**Emission**	**ELV (mg/Nm^3)**
Steam reforming plants	Nitrogen oxides (as NO_2 at 3 % O_2)	450
	Sulphur dioxide (natural gas fuelled)	2
	Carbon monoxide	10
	Diffuse emissions	1 t/yr
	Nitrogen oxides (non-continuous emissions as NO_2)	20 kg/h
	Purge gas scrubber	40 g NH_3 per tonne NH_3 produced
Partial oxidation plants – auxiliary boiler flue gas	Sulphur dioxide	1700
	Nitrogen oxides (as NO_2)	700
	Carbon monoxide (hourly maximum) (daily average)	175 10
	Particulates (hourly maximum) (active ingredient) (daily average)	50 10
Partial oxidation plants – steam superheater flue gas	Nitrogen oxides (as NO_2)	450
	Sulphur dioxide (natural gas fuelled)	2
	Carbon monoxide	30
	Hydrogen sulphide	0.3
	Methanol	100

Emission Limit Values for Specific Materials		
Parameter	**mg/Nm^3**	**Mass flow threshold for ELVs**
Cadmium	0.1	>1 g/h
Chlorides (as HCl)	10	>0.3 kg/h
Iodides (as HI)	5	>50 g/h
Carbon disulphide	5	>0.1 kg/h
Hydrogen cyanide	2	>50 g/h
Mercaptans	2	>0.1 kg/h
Amines (total)	10	>0.1 kg/h
Trimethylamine	2	>0.1 kg/h
Phenols / cresols / xylols	10	>0.1 kg/h
1,2-Dichloroethane	5	>0.1 kg/h

Emission Limit Values for Specific Materials		
Parameter	**mg/Nm^3**	**Mass flow threshold for ELVs**
Dust – pesticide contaminated [a]	0.15	>1 g/h
Dust – pharmaceutical [a]	0.15	>1 g/h
Bromine	10	>50 g/h
Chlorine	10	>50 g/h
Iodine	10	>50 g/h
Mercury	0.1	>1 g/h
Total heavy metals	1.5	>5 g/h
Nitrogen oxides (as NO$_2$)	300	>3 kg/h
Sulphur oxides (as SO$_2$)	300	>3 kg/h
Particulates - general	20	>0.5 kg/h
1,1-Dichloroethene	5	>0.1 kg/h
Acrylonitrile	20	>0.1 kg/h
Toluene diisocyanate	1	>0.1 kg/h
Ethyl acrylate	1	[b]
Isobutyl acrylate	1	[b]
Methyl acrylate	5	[b]
n-Butyl acrylate	5	[b]
t-Butyl acrylate and higher acrylate esters	20	[b]
[a] Dust as active ingredient [b] Only applicable to vents from bulk storage (>20 tonnes)		

Emission Limit Values for General Emissions to Air (excluding Incinerator Emissions) for Materials not already covered by the Tables above			
Constituent group [a] or parameter	**Class**	**Mass flow threshold for ELV [b]**	**ELV (mg/Nm^3)**
Carcinogenic substances	T.A. Luft I T.A. Luft II T.A. Luft III Substances (other than those above) with R45 designation	>0.5 g/h >5.0 g/h >25.0 g/h >0.5 kg/h	0.1 1.0 5.0 5.0
Inorganic dust particles	T.A. Luft I T.A. Luft II T.A. Luft III	>1 g/h >5 g/h >25 g/h	0.2 1.0 5.0
Vaporous or gaseous inorganic substances	T.A. Luft I T.A. Luft II T.A. Luft III T.A. Luft IV	>10 g/h >50 g/h >0.3 kg/h >5.0 kg/h	1 5 30 500
Organic substances with photochemical ozone potential - POCP	U.K. AEA 1 U.K. AEA 2	>0.5 kg/h >2.0 kg/h	20 50
Organic substances [c]	T.A. Luft I T.A. Luft II T.A. Luft III	>0.1 kg/h >2.0 kg/h >3.0 kg/h	20 100 150
General dusts		<0.5 kg/h >0.5 kg/h	150 20
Pharmaceutical and pesticide dust (as active ingredient)		>1 g/h	0.15
Fugitive emission			[d]

Footnotes to the table:

[a] Where a substance falls into more than one category, the lower ELV applies.

[b] The mass flow is calculated in kg/h for the raw gas and is determined at the point before any gas cleaning or abatement plant, but after any devices inherent in the process (e.g. after reactor overhead condensers or after product cyclones). Mass flow is the maximum emission which can occur over any one hour period of plant operation, from the entire site. Where the mass flow exceeds the mass threshold, then abatement will be required down to the appropriate ELV, unless the concentration of the raw gas is already below the ELV, in which case no further abatement is required.

^c Where organic substances of several classes are present, in addition to the above limit, the sum of classes I and II shall not exceed the class II limit and the sum of classes I, II and III shall not exceed the class III limit.
^d Fugitive solvent emissions should comply with the requirement of the Solvent Directive (Council Directive 1999/13/EC [cww/tm/88]) or licence as appropriate

Releases to water:
The ELVs for discharges to water are based on 24 hours flow proportional composite samples, unless otherwise specified.

Effluent load should be minimised by recovery of materials wherever practible. The use of lower quality water may be possible for some parts of the process rather than fresh water.

Excluding uncontaminated rainwater, all releases to waters are subject to a licence from the Environmental Protection Agency. However, any discharge to a sewer will require the consent of the local authority or sewerage undertaker. BATNEEC to minimise the release of substances will generally include minimisation at source and either specific treatment of contaminated waste streams to remove particular substances or co-treatment of combined effluent streams or both.

Emission Limit Values for Discharges to Water ^a		
Constituent group or parameter	**ELV**	**Footnote**
pH	6-9	5
Number of Toxicity Units	10	2, 5
Total Nitrogen (as N)	>80 % removal or 15 mg/l	5
Total phosphorous (as P)	>80 % removal or 2 mg/l	5
Total ammonia (mg/l as N)	10	5
Oils, fats and grease (mg/l)	10	5
Organohalogens (mg/l)	0.1 (monthly means)	4, 5
Phenols (mg/l)	1.0	5
Cyanide (mg/l as CN)	0.2	5
Mercury (mg/l)	0.05	5, 7
Tin (mg/l)	2.0	5, 7
Lead (mg/l)	0.5	5, 7
Chromium(VI) (mg/l as Cr)	0.1	5, 7
Total chromium (mg/l as Cr)	0.5	5, 7
Cadmium (mg/l)	0.05	5, 7
Zinc (mg/l)	0.5	5, 7
Copper (mg/l)	0.5	5, 7
Mineral oil (mg/l) interceptors	20	5
Mineral oil (mg/l) biological treatment	1.0	5
Directive 76/464/EC, List 1	according to list 1	
BTX (mg/l combined)	0.1 (monthly means)	
Genetically modified organisms	as per Directive 90/219/EEC and S.I. No. 345 of 1994	
BOD	≥91 % total removal	1
COD	≥75 % total removal	1, 6
Fish tainting	No tainting	3

Footnotes to the table:
^a All values refer to daily averages, exept where otherwise stated to the contrary, and except for pH which refers to continuous values.
¹ The daily raw waste load for BOD/COD is defined as the average daily mass arising for treatment over any three month period. Calculation of the removal rates for BOD/COD should be based on the differences between the waste loads arising for disposal and those discharges to the receiving waters. The amounts removed by treatment (physical, chemical, biological) may be included in the calculation. Calculation of the raw waste loads of BOD/COD shall exclude any waste load associated with microbial cell biomass removal and solvent recovery. However, residual amounts remaining after these practices may be included in the raw waste load

calculation. For certain specific effluents where the BOD/COD removal rates are unattainable, a concentration limit may be more appropriate. This will be a matter for inclusion in a licence.

[2] Toxicity unit = 100/x hour E(L)C50 in vol-%, where x is defined by the test procedure. The toxicity of the process effluent to at least two appropriate aquatic species shall be determined.

[3] No substance shall be discharged in a manner, or at a concentration which, following initial dilution, causes tainting of fish or shellfish, interferes with normal patterns of fish migration or accumulates in sediments or biological tissues to the detriment of fish, wildlife or their predators.

[4] Within 6 months of the commencement of production (or as may be relevent on a campaign basis), the effluent should be screened for a priority pollutant list.

[5] Consent conditions for these parameters for discharge to municipal treatment plants can be established with the licencing authority and different values may apply.

[6] This limit applies only to
  - manufacture of chemicals in an integrated chemical installation
  - manufacture of olefins and their derivatives or of monomers and polymers, including styrene and vinyl chloride
  - manufacture, by way of chemical reaction processes, of organic or organo-metallic chemical products
  - manufacture of pesticides, pharmaceutical or veterinary products and their intermediates.

[7] Where the metallic content of the effluent arises as an unavoidable contaminant of raw materials, then these limits may not apply

9. ITALY

Emissions to Air

"Emission limit values for the containment of pollutant emissions from existing plants"
[Supplemento ordinario N. 51 alla Gazzetta Ufficiale Italiana n. 176 del 30 luglio 1990 – Serie generale]

The emission limit values for existing plants (i.e. plants built or authorised before the approval of the law above) are set by three Annexes:

Annex 1 reports general emission limit values
Annexes 2 and 3 list specific limits and prescriptions for the activities reported therein
Annex 4 reports sampling, analysis and emissions assessment methods
Annex 5 reports abatement techniques
Annex 6 reports diffuse emissions
Annex 7 reports fugitive emissions

Please note:
Only an extract of Annex 2 is reported in this document.
Limit emission values have not yet been set for the new plants in Italy.

ANNEX 1 (GENERAL EMISSION LIMIT VALUES):

1.1 Substances considered as carcinogenic and/or teratogenic and/or mutagenic (Table A1)
1.2 Substances with very high toxicity and bioaccumulability (Table A2)
2. Inorganic substances, preferably in the form of dust (Table B)
3. Inorganic substances, preferably in the form of gas or vapour (Table C)
4. Organic substances in the form of gas, vapour or dust (Table D)
5. Total dust

ANNEX 2 (SPECIFIC EMISSION LIMITS FOR THE PLANTS LISTED BELOW):

1. Combustion plants with thermal power <50 MW
2. Essication plants
3. Internal combustion engines
4. Gas turbines fixed
5. Waste incinerators
6. Cement plants
7. Furnaces for the calcination of bauxite, dolomite, gypsum, limestone, diatomite, magnesite, quartzite
8. Furnaces for the production of glass
9. Furnaces for the baking of clay ceramic products
10. Plants for the fusion of mineral products, particularly of basalt, diabase or slag
11. Plants for the production of ceramic tiles
12. Plants for the agglomeration of pearlite, schist or expanded clay
13. Plants for the production or the fusion of compounds of bitumen of tars, and mineral products included the plants for the preparation of roads works materials based on bitumen and the plants for the production of rubble of tar
14. Dry coal distillation plants (cokeries)
15. Plants for the agglomeration of iron mineral
16. Plants for the production of pig iron
17. Plants for the steel production by converter. Electric arc furnaces and under vacuum fusion furnaces
18. Iron and steel foundry
19. Heat treatments furnaces for lamination plants and other treatments
20. Plants for metal surface finishing with melted zinc
21. Plants for metal surface treatments by nitric acid
22. Plants for the production of iron alloys by electrothermal or pyrometallurgic processes
23. Plants for the primary production of non-ferrous metal processes
24. Plants for the production of aluminium
25. Plants for the fusion of aluminium
26. Plants for the secondary fusion of others non-ferrous metal and their alloys
27. Plants for the production of lead accumulators
28. Plants for the production of sulphur oxide, sulphuric acid and oleum
29. Plants for the production of chlorine
30. Claus plants for the production of sulphur
31. Plants for the production, granulation and essication of phosphorous, nitrogen or potassium containing fertilizers
32. Plants for the production of acrylonitrile
33. Plants for the production of pesticides active ingredients
34. Plants for the production of polivinyl choride (PVC)
35. Plants for the production of poliacrylonitrile polymers
36. Plants for the production and manufacturing of viscose
37. Plants for the production of nitrosylsulphuric acid
38. Plants for the production of poliesters
39. Plants of production of cellulose acetate fibres
40. Plants for the production of poliammidic fibres
41. Plants for the formulation specialties pesticides
42. Plants for the nitration of cellulose
43. Plants for the production of titanium dioxide
44. Plants for the production of acrylic fibres
45. Plants for the production of polycarbonate
46. Plants for the production of black carbon
47. Plants for the production of carbon or electrographite with burning, example electrodes production
48. Plants for the series painting of the automotives bodies and their components with exception of bus bodies

ANNEX 3 (LARGE UTILITIES AND SPECIFIC FIELDS):

A: Large Combustion Plants
Field of application
Emission values   time requirements for compliance
Abatement technique   malfunction of abatement plants

B: Mineral Oil Refineries
Field of application
Emission values
Measurements
Other prescriptions
Time requirements for compliance of Refineries

C: Plants for the cultivation of hydrocarbons and geothermal fluids
Application field
Cultivation of hydrocarbons
Plants using geothermal fluids

ANNEX 4 (SAMPLING, ANALYSIS AND EMISSIONS ASSESSMENT METHODS)

ANNEX 5 (ABATEMENT TECHNIQUES)

Summary table
Application criteria

ANNEX 6 (DIFFUSE EMISSIONS)

ANNEX 7 (FUGITIVE EMISSIONS)

ANNEX 1: Mass flow threshold and concentration limits
(standard conditions: 0 °C, 101.3 kPa; hourly values)

1.1 Substances considered as carcinogenic and/or teratogenic and/or mutagenic (Table A1)

Table A1

Class I

If the mass flow equals or exceeds 0.5 g/h: 0.1 mg/Nm^3
- Asbestos (chrysotile, crocidolite, amosite, antofillite, actinolite and tremolite)
- Benzo(a)pyrene

- Beryllium and its compounds, expressed as Be
- Dibenzo(a,h)anthracene
- 2-Naphthylamine and its salts

- Benzo(a)anthracene
- Benzo(b)fluoranthene
- Benzo(j)fluoranthene
- Benzo(k)fluoranthene
- Dibenzo (a,h) acridine

- Dibenzo(a)pyrene
- Dimethylnitrosamine
- 5-Nitroacenaphthene
- 2-Nitronaphthalene
- 1-Methyl-3-Nitro-1-Nitrosoguanidin

Class II

If the mass flow equals or exceeds 5 g/h: 1 mg/Nm^3
- Arsenic and its compounds, expressed as As
- Chromium(VI) and its compounds, expressed as Cr
- Cobalt and its compounds, expressed as Co
- 3,3'-Dichlorobenzidine and its salts
- Dimethyl sulphate
- Ethylenimine
- Nickel and its compounds, expressed as Ni
- 4-Aminobiphenyl and its salts

- Benzidine and its salts
- 4,4'-Methylene-bis(2-Chloroanilin) and its salts
- Diethyl sulphate
- 3,3'-Dimethylbenzidine and its salts
- Hexamethylphosphorotriamide
- 2-Methylaziridine
- Methyl azoxymethyl acetate
- Sulfallate
- Dimethyl carbamoylchloride
- 3,3'-Dimethoxybenzidine and its salts

Class III

If the mass flow equals or exceeds 25 g/h: 5 mg/Nm^3
- Acrylonitrile
- Benzene
- 1,3-Butadiene
- 1-Chloro-2,3-epoxipropane (epichlorohydrine)
- 1,2-Dibromoethane
- 1,2-Epoxipropane
- 1,2-Dichloroethane
- VCM
- 1,3-Dichloro-2-propanol

- Chloromethyl methyl ether
- N,N-Dimethylhydrazine
- Hydrazine
- Ethylene oxide
- Ethylene thiourea
- 2-Nitropropane
- Bis-Chloromethylether
- 3-Propanolide
- 1,3-Propane sultone
- Styrene oxide

1.2 Substances with very high toxicity and bioaccumulability (Table A2)

Table A2

Class I

If the mass flow equals or exceeds 0.02 g/h: 0.01 mg/Nm^3
- PCDD

- PCDF

Class II

If the mass flow equals or exceeds 0.5 g/h: 0.5 mg/Nm^3
- PCB
- PCT

- Polychloronaphthenes

2. Inorganic substances, preferably in the form of dust (Table B)

Table B

Class I

If the mass flow equals or exceeds 1 g/h: 0.2 mg/Nm^3
- Cadmium and its compounds,   - Thallium and its compounds, expressed
  expressed as Cd   as Tl
- Mercury and its compounds, expressed
  as Hg

Class II

If the mass flow equals or exceeds 5 g/h: 1 mg/Nm^3
- Selenium and its compounds, expressed   - Tellurium and its compounds,
  as Se   expressed as Te

Class III

If the mass flow equals or exceeds 25 g/h: 5 mg/Nm^3
- Antimony and its compounds,   - Platinum and its compounds, expressed
  expressed as Sb   as Pt
- Cyanides, expressed as CN   - Quartz, pulverised, if in the form of
- Chromium(III) and its compounds,   crystallised silicon expressed as SiO2
  expressed as Cr   - Copper and its compounds, expressed
- Manganese and its compounds,   as Cu
  expressed as Mn   - Rhodium and its compounds, expressed
- Palladium and its compounds,   as Rh
  expressed as Pd   - Tin and its compounds, expressed as Sn
- Lead and its compounds, expressed as   - Vanadium and its compounds,
  Pb   expressed as V

3. Inorganic substances, preferably in the form of gas or vapour (Table C)

Both mass flows and concentrations refer to single substances or substances families.

Table C

Class I

If the mass flow is equals or exceeds 10 g/h: 1 mg/Nm^3
- Chlorocyanide   - Phosgene
- Phosphine

Class II

If the mass flow equals or exceeds 50 g/h: 5 mg/Nm^3
- Hydrocyanidric acid   - Fluorine and its compounds, expressed
- Bromine and its compounds, expressed   as hydrofluoric acid
  as hydrobromic acid   - Hydrogen sulphide
- Chlorine

Class III

If the mass flow equals or exceeds 0.3 kg/h: 30 mg/Nm^3
- gaseous or vaporous inorganic chlorine compounds, excluded chlorocyanide and phosgene, expressed as hydrochloric acid

Class IV

If the mass flow equals or exceeds 2 kg/h: 250 mg/Nm^3
- Ammonia

Class V

If the mass flow equals or exceeds 5 kg/h: 500 mg/Nm^3
- NO$_x$ (NO and NO$_2$), expressed as NO$_2$ -   SO$_x$ (SO$_2$ and SO$_3$), expressed as SO$_2$

4. Organic substances in the form of gas, vapour or dust (Table D)

Table D

Class I

If the mass flow equals or exceeds 25 g/h: 5 mg/Nm^3
- Anisidine   -   Diglycidyl ether
- Butylmercaptan   -   Ethyl acrylate
- Chlorpicrine   -   Ethylene imine
- Diazomethane   -   Ethylmercaptan
- Dichloroacetylene   -   Isocyanates
- Dinitrobenzene   -   Methyl acrylate
- Dinitrocresol   -   Nitroglycerine
- Hexachlorobutadiene   -   Perchloromethylmercaptan
- Hexachlorocyclopentadiene   -   1,4-Dioxane
- Hexafluoroacetone

Class II

If the mass flow equals or exceeds 0.1 kg/h: 20 mg/Nm^3
- Acetaldehyde   -   Chloroacetaldehyde
- Chloroacetic acid   -   1-Chloro-1-nitropentane
- Formic acid   -   Cresol
- Thioglycolic acid   -   Crotonaldehyde
- Trichloroacetic acid   -   1,2-Dibutylaminoethanol
- Phthalic anhydride   -   Dibutylphosphate
- Maleic anhydride   -   o-Dichlorobenzene
- Aniline   -   1,1-Dichloroethene
- Benzylchloride   -   Dichloroethylether
- Biphenyl   -   Dichlorophenol
- Butyl acrylate   -   Dichloromethane
- Butylamine   -   Diethylamine
- Camphor synthetic   -   Diphenylamine
- Tetrabromomethane   -   Diisopropylamine
- Tetrachloromethane   -   Dimethylamine
- Cyclohexylamine   -   Ethylamine

- Ethanolamine
- 2-Ethoxyethanol
- 2-Ethoxyethyl acetate
- Phenol
- Phthalates
- 2-Furaldehyde
- Furfurol
- Triiodomethane
- Isophorone
- Isopropylamine
- Methylacrilonitrile
- Methylamine
- Methylaniline
- Bromomethane
- Methyl n-butylbromide
- Chloromethane
- Methyl 2-cyanoacrilate
- Methylstyrene
- 2-Methoxyethanol
- 2-Methoxyethanol acetate
- Nitroethane

- Nitromethane
- 1-Nitropropane
- Nitrotoluene
- Pyretre
- Pyridine
- Lead alkyls
- 2-Propenal
- 1,1,2,2-Tetrachloroethane
- Tetrachloroethene
- Tetranitromethane
- m- and p-Toluidine
- Tributyl phosphate
- Trichlorophenol
- Trichloroethene
- Trichloromethane
- Triethylamine
- Trimethylphosphine
- Vinylbromide
- Xylenes (excluded 2,4-xylene)
- Formaldehyde

Class III

If the mass flow equals or exceeds 2 kg/h: 150 mg/Nm^3
- Acrylic acid
- Acetonitrile
- Propionic acid
- Acetic acid
- n-Butanol
- i-Butanol
- sec-Butanol
- tert-Butanol
- Methanol
- Butyraldehyde
- p-tert-Butyltoluene
- 2-Butoxyethanol
- Caprolactam
- Carbon disulphide
- Cyclohexanone
- Cyclopentadiene
- Chlorobenzene
- 2-Chloro-1,3-butadiene
- o-Chlorostyrene
- o-Chlorotoluene
- p-Chlorotoluene
- Cumene
- Diacetonalcohol (4-hydroxy-4-methyl-2-pentanone)
- 1,4-Dichlorobenzene
- 1,1-Dichloroethane
- Dichloropropane
- Diethanolamine
- Diethylformamide
- Diisobutylketone

- N,N-Dimethylacetamide
- N,N-Dimetylformamide
- Dipropylketone
- Hexamethylendiamine
- n-Hexane
- Ethylamylketone
- Ethylbenzene
- Ethylbutylketone
- Ethyleneglycol
- Isobutylglycidyl ether
- Isopropoxyethanol
- Methyl methacrylate
- Methylamylketone
- o-Methylcyclohexanone
- Methyl chloroform
- Methylformiate
- Methylisobutylketone
- Methylisobutylcarbinol
- Naphthalene
- Propyleneglycol
- Propyleneglycol monomethyl ether
- Propionaldehyde
- Styrene
- Tetrahydrofurane
- Trimethylbenzene
- n-Veratraldehyde
- Vinyl acetate
- Vinyltoluene
- 2,4-Xylene

Class IV

If the mass flow equals or exceeds 3 kg/h: 300 mg/Nm^3
- Propanol
- Isopropanol
- n-Amyl acetate
- Methyl benzoate
- n-Butyl acetate
- Isobutyl acetate
- Diethylketone
- Difluorodibromomethane
- sec-Hexyl acetate
- Ethyl formiate
- Methyl acetate
- Methylethylketone
- Methylisopropylketone
- N-Methylpyrrolidone
- Pinene
- n-Propyl acetate
- Isopropylen acetate
- Toluene
- Xylene

Class V

If the mass flow equals or exceeds 4 kg/h: 600 mg/Nm^3
- Acetone
- Ethanol
- Butane
- Cyclohexane
- Cyclohexene
- Chloropentane
- Chlorobromomethane
- Chlorodifluoromethane
- Chloropentafluoroethane
- Dibromodifluoroethane
- Dibutylether
- Dichlorofluoromethane
- Dichlorotetrafluoroethane
- Diethylether
- Diisopropylether
- Dimethylether
- Heptane
- Hexane (technical)
- Isopropyl ether
- Ethyl acetate
- Methylacetylene
- Methylcyclohexane
- Pentane
- 1,1,1,2-Tetrachloro-2,2-difluoroethane
- 1,1,2,2-Tetrachloro-1,2-difluoroethane
- Trichlorofluoromethane
- 1,1,2-Tricloro-1,2,2-trifluoroethane
- Trifluoromethane
- Trifluorobromomethane

5. Total dust

The emission values are:

Class I

If the mass flow equals or exceeds 0.5 kg/h: 50 mg/Nm^3

Class II

If the mass flow equals or exceeds 0.1 kg/h and remains below 0.5 kg/h: 150 mg/Nm^3

Asbestos (particles in suspension and fibres): Emission limit value must not exceed 0.1 mg/Nm3 [DLGS 17/03/1995, n. 114 Gazz. Uff. – Serie generale n. 92 del 20 Aprile 1995]

Extract of Annex 2

32. Installations for the production of acrylonitrile

The waste gas produced by the reactor and the absorber must be burnt. The gaseous emission produced during the purification products of distillation by reaction and the one coming from the transfer must be conveyed to suitable abatement systems.

34. Installations for the production of PVC

VCM (vinyl chloride monomer) residues in the polymer must be reduced to minimal values, especially in the boundaries between open and closed system; the final value is to further reduce vinyl chloride concentration in the gaseous stream coming from the dryer.

PVC mass flow	10 mg VCM/kg PVC
Homopolymers in suspension	100 mg VCM/kg PVC
Copolymers in suspension	400 mg VCM/kg PVC
PVC in micro-suspension and emulsion of PVC	1500 mg VCM/kg PVC

The gaseous stream coming from the dryer must be used as raw material in a combustion plant, to further reduce vinyl chloride concentration.

Emissions to Water

Provisions for the water protection against pollution and adoption of the Council Directive 91/271/EEC concerning urban waste water treatment and of the Council Directive 91/676/EEC concerning the protection of waters against pollution caused by nitrates from agricultural sources [Decreto legislativo 11 May 1999, no. 152, updated by D. Lgs 18 august 2000, n. 258)].

Emission limit values for wastewater discharges in surface water bodies and in municipal sewage systems.

Parameter	Unit	Discharge into surface water bodies	Discharge into municipal collecting systems	Discharge into Venice Lagoon and surface water bodies of its draining area (extract)
pH		5,5-9,5	5,5-9,5	6.0 – 9.0
Temperature	°C	(1)	(1)	
Colour		not perceptible after dilution of 1:20	not perceptible after dilution 1:40	not perceptible after dilution of 1:10
Odour		must not cause nuisance	must not cause nuisance	must not cause nuisance
Coarse material		absent	absent	absent
TSS	mg/l	80	200	35
BOD$_5$ (as O$_2$)	mg/l	40	250	25
COD (as O$_2$)	mg/l	160	500	120
Aluminium	mg/l	1	2.0	
Arsenic	mg/l	0.5	0.5	
Barium	mg/l	20	-	
Boron	mg/l	2	4	
Cadmium	mg/l	0.02	0.02	
Total Chromium	mg/l	2	4	
Chromium(VI)	mg/l	0.2	0.20	
Iron	mg/l	2	4	
Manganese	mg/l	2	4	
Mercury	mg/l	0.005	0.005	
Nickel	mg/l	2	4	
Lead	mg/l	0.2	0.3	
Copper	mg/l	0.1	0.4	
Selenium	mg/l	0.03	0.03	
Tin	mg/l	10		

Parameter	Unit	Discharge into surface water bodies	Discharge into municipal collecting systems	Discharge into Venice Lagoon and surface water bodies of its draining area (extract)
Zinc	mg/l	0.5	1.0	
Total Cyanide (as CN)	mg/l	0.5	1.0	
Free active chlorine	mg/l	0.2	0.3	
Sulphide (as S)	mg/l	1	2	
Sulphite (as SO$_2$)	mg/l	1	2	
Sulphate (as SO$_3$) (2)	mg/l	1000	1000	
Chloride (2)	mg/l	1200	1200	
Fluoride	mg/l	6	12	
Total phosphorus (as P) (3)	mg/l	10	10	
Ammonium (as NH$_4$) (3)	mg/l	15	30	
Nitrite (as N) (3)	mg/l	0.6	0.6	
Nitrate (as N) (3)	mg/l	20	30	
Fat and animal/vegetable oil	mg/l	20	40	
Total hydrocarbons	mg/l	5	10	
Phenols	mg/l	0.5	1	
Aldehydes	mg/l	1	2	
Aromatic organic solvents	mg/l	0.2	0.4	
Nitrogen containing organic solvents	mg/l	0.1	0.2	
Total surfactants	mg/l	2	4	
Pesticides (containing phosphorus)	mg/l	0.10	0.10	
Total pesticides (exclusive phosphorous containing ones), and also:	mg/l	0.05	0.05	
- Aldrin	mg/l	0.01	0.01	
- Dieldrin	mg/l	0.01	0.01	
- Endrin	mg/l	0.002	0.002	
- Isodrin	mg/l	0.002	0.002	
Chlorinated organic solvents	mg/l	1	2	
Escherichia coli (4)	cfu/100 ml	Footnote		
Acute toxicity test (5)		Sample considered not to be acceptable if after 24 hours the fraction of immobilised test organisms 50 %	Sample considered not to be acceptable if after 24 hours the fraction of immobilised test organisms 80 %	

Footnotes to the table:
(1) Dependent on the receiving water bodies, the following prescriptions apply:
- Running waters: The maximum temperature difference before and after the discharge point is 3°C
- Lakes: The wastewater temperature must be 30 °C and further than 50 meters from the discharge point the temperature increase in the water body must be 3 °C

- Artificial channels: The maximum mean value temperature in any section must not exceed 35 °C
- Sea and estuary/delta zones of non significant rivers: The wastewater temperature must not exceed 35°C and further than 1000 meters from the discharge point the temperature increase in the water body must be 3 °C.

(2) These limits do not apply to wastewaters discharged into the sea (assimilation is provided for sea coastal waters).

(3) Industrial wastewaters discharged into sensitive areas must respect the total phosphorous and total nitrogen limits of 1 mg/l and 10 mg/l, respectively.

(4) The general limit 5000 cfu/100 ml is recommended. The competent authority will establish the most appropriate limit according to environmental, hygienic and sanitary situation of the water body and to existing uses.

(5) The toxicity test is obligatory. In addition to Daphnia magna test, acute toxicity tests can be done on Ceriodaphnia dubia, Selenastrum capricornutum, bioluminescent bacteria or other organisms such as Artemia salina for salt containing wastewater effluents or other organisms that will be indicated. The worst test result must be considered. A positive test is not straight penalised, but the following actions are required: a deep analytical investigation, the search of the toxicity sources and their removal.

10. LUXEMBURG

No information supplied.

11. THE NETHERLANDS

The Netherlands has two main framework environmental acts: the '**Environmental Management Act**' and the '**Surface Water Pollution Act**'. These acts together provide the framework for issuing environmental permits and for setting the conditions of the permits. The acts comply with the requirements of the IPPC Directive and integrated permitting is guaranteed by a co-ordinated licensing procedure from the competent authorities. Both framework acts govern a number of Decrees and Regulations that provide requirements with regard to potentially polluting activities.

The **Netherlands emission Regulations** (NeR) are concerned with process emissions to air and function as guidelines for the issuing of licences and/or for the adjustment of licensing conditions. The NeR has been used for guidance in the granting of licences from 1 May 1992.
In the NeR, concentration standards for different substances are given, which constitute upper limits for distinct point sources, depending on mass flow. Furthermore, in 'special regulations' rules departing from the 'general emission standards' for certain industries or specific installations are given.

The emissions standards in the NeR are not legally binding and the NeR does not replace existing binding agreements. However, if the licensing authority wishes to depart from the NeR, the reasons for doing so must be stated explicitly in the preamble to the licence.

Voluntary agreements
Voluntary agreements or covenants (in Dutch: Convenanten) are declarations of intent on the implementation of environmental policy for certain industrial sectors. The declarations of intent are agreements between the authorities and the industry. Participation in a covenant gives the authorities and companies the advantage of a more transparent, coherent and predictable path of environmental improvement and investments. The covenants are applied in two fields:

- general environmental performance on 'traditional' pollutants
- energy efficiency.

General Environmental Performance on 'Traditional' Pollutants

In the declaration of intent of this voluntary agreement, the authorities have drawn up an **Integral Environmental Target Plan** (IETP), based on the **National Environmental Policy Plan** (NEPP), the **Memorandum on Water Management**, the **North Sea Action Plan**, the **Rhine Action Programme**, the **Memorandum on Energy Conservation** and other official plans at the time of signature.

The Integral Target Plan is concerned with environmental pollution of the traditional pollutants (SO_x, NO_x, VOC, heavy metals, PAH, etc.) caused by the relevant industrial sector. The IETP has been drawn up in 1994/1995, and will be adjusted in 2000 and 2010. Apart from the reduction of emissions into the air, water and soil, the IETP also incorporates policy with regard to energy conservation, water conservation, soil clean up, hazard risk, odour nuisance, noise and internal management systems. However, especially for energy conservation and CO_2 reduction, two other covenants have been agreed upon.

For the chemical industry a declaration of intent was signed on April 2, 1993. A significant factor is the understanding that in view of the wide range of disparate companies in the chemical industry, the contribution of each individual company to the implementation of the IETP in the industry may vary. The responsibility of individual companies to contribute to the implementation of the IETP in the industry requires that these companies take an active stance. The contribution of a company will be defined in Company Environmental Plans ('BMPs'), which are drawn up by each company. These BMPs are renewed every four years and must be agreed upon by the licensing authority.

Energy Efficiency: Long-Term Agreements on Energy Efficiency

In the Netherlands, '**Long-Term Agreements on Energy Efficiency** (MJAs)' have been made between the Ministry of Economic Affairs and representative organisations of many industrial sectors. The most important aspect of the MJAs is the target value for improvement of energy efficiency in the relevant industrial sector within a certain time frame. For the elaboration of the MJAs, bilateral agreements are made between the individual companies and the facilitating agency, which is NOVEM. For the chemical industry, an MJA was signed on 24 November 1993 and the agreed improvement of energy efficiency was 20% over the period 1989-2000. The target has been achieved by the sector and a second round of MJAs is now in preparation, although most of the chemical industry companies will probably join the 'Benchmarking' covenant.

Energy Efficiency: Benchmarking covenant

The Benchmarking covenant is an agreement between the Dutch authorities and the Dutch energy intensive industry. In contrast to the above mentioned MJAs, no fixed quantified target for energy efficiency improvement is set. Instead, the industry agrees to belong to the world top in energy efficiency and the authorities will then refrain from impairing additional energy tax measures. The reason for this different approach is that in the light of international competition, industry has asked the government to look at the relative effort on energy efficiency of Dutch industry in relation to their foreign competitors. The agreement is open to all companies with an energy use of 0,5 PJ per year or more. The principle agreement was signed on July 6, 1999, between the industrial organisations and the authorities. Now that the principle agreement has been signed, the agreement is open to individual companies to sign up to the covenant.

Emission Levels Associated With BAT for Process Emissions

Categories**	Emission level associated with BAT (mg/Nm^3)	Threshold (kg/hr)	Remark
Extremely hazardous substances			
Dioxins & furans	0-0.1 ng/Nm^3 I-TEQ	no threshold	Minimisation obligated
PCB's	0-0.1 ng/Nm^3 pcb-TEQ	no threshold	Minimisation obligated
Particulates			
Particulate matter	5–25	no threshold	Depending on technique applied and process conditions
Carcinogenic substances*			
$\sum$ C1	0-0.1	0.0005	Minimisation required
$\sum$ C1 + C2	0-1.0	0.005	Minimisation required
$\sum$ C1 + C2 + C3	0-5.0	0.025	Minimisation required
Organic subst. (gas and vapour)*			
$\sum$ gO1	20	0.1	
$\sum$ gO1 + gO2	100	2.0	
$\sum$ gO1 + gO2 + gO3	100-150	3.0	
Organic subst. (solid)*			
$\sum$ sO1	5–10	no threshold	See particulate matter
$\sum$ sO2 and sO3	5–25	no threshold	See particulate matter
Inorganic subst. (gas and vapour)			
gI1	1.0	0.01	
gI2	5.0	0.05	
gI3	30	0.3	
gI4	200	5	
Inorganic substances (solid)*			
$\sum$ sI1	0.2	0.001	
$\sum$ sI1 + sI2	1.0	0.005	
$\sum$ sI1 + sI2 + sI3	5.0	0.025	

  *   For the category of substances marked with an asterisk, the summation rule applies. This means that the given emission level applies to the sum of the substances in the relevant category plus those of the lower category.

 **   The different substances are classified below.

Classification of carcinogenic substances

Category	Substance
C1	benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, dibenzo(a,h)anthracene, 2-naphtylamine, 2-nitropropane, beryllium (and compounds) as Be, chromium (VI) (and compounds) as Cr.
C2	3,3-dichlorobenzidine, diethylsulphate, dimethylsulphate, ethylene oxide, nickel (and compounds) as Ni.
C3	acrylonitrile, benzene, buta-1,3-diene, 1,2-dibromomethane, 1,2-dichloroethane, epichlorohydrine, hydrazine, propylene oxide, vinyl chloride.

Organic substances

The organic substances have been classified according to their ecotoxicity. Distiction is made between gases/vapours and solids (gO and sO). The standard applies to the emission of the sum of the substances (so called 'summation rule'). Note that the classification as given above is not complete (the total list includes several hundred components), but some relevant substances have been included here.

Classification of organic substances

Category	Substance
O1	many components (e.g. acetaldehyde, acroleine, acrylic acid, amino benzene/ethane/methane, anilin, anthracene, bisphenol A, caprolactam, 1,2-dichlorobenzene, dichlorophenols, formaldehyde, methylamine, nitro-monocyclic-aromatics, organotins, phenol, pyridine, tetrachloromethane, trichlormethane).
O2	many components (e.g. 1,3/4-dichlorobenzene, cumene, ethyl-benzene, monochlorobenzene, styrene, tetrachloroethene, toluene, 1,1,1-trichloroethane, trichlorethene, xylenes)
O3	many components (e.g. dichloromethane, many alcohols, alkanes and ketones)

Inorganic substances

Distinction is made between gaseous and solid inorganics (gI and sI respectively). The reason for doing so is that the techniques that can be applied to reduce the emissions for gaseous and solid components are different. The substances have been classified according to their ecotoxicity. The standard for solid inorganics applies to the emission of the sum of the substances (so called 'summation rule').

Classification of inorganic substances

Category	Substance
gI1	arsine, chlorocyane, chlorodioxide, diborane (B_2H_6), phosphine, phosgene.
gI2	bromine (and compounds) as HBr, boron trichloride/trifluoride, chlorine, cynaic acid, fluorine (and compounds) as HF, phosphoric acid, germaniumhydride, silicon tetrafluoride/tetrahydride, nitrogen trifluoride, hydrogen sulpide, sulphuric acid.
gI3	chlorine compounds as HCl, dichloro-siliconhydride, nitric acid, silicon tetrachloride, trichloro siliconhydride, sulphur hexafluoride (SF_6)
gI4	ammonia, nitrogen oxides (as NO_2), sulphur oxides (as SO_2)
sI1	asbestos fibres*, arsenic (and compounds) as As*, cadmium (and compounds) as Cd*, iron pentacarbonyl, mercury (and compounds) as Hg, platinum compounds as Pt, rhodium compounds as Rh, silica (cristoballite, tridymite)*, silver (and compounds) as Ag, thallium (and compounds) as Tl, vanadium compounds (especially oxides, halides, sulphates and vanadates) as V.
sI2	chromylchloride, cobalt (smoke and compounds) as Co, copper smoke as Cu, lead (and inorganic lead compounds) as Pb, silica (ex cristoballite and tridymite) as respirable dust, rhodium (and non-water-solvable compounds) as Rh, selenium (and compounds) as Se, tellurium (and compounds) as Te.
sI3	antimony (and compounds) as Sb, barium (and compounds) as Ba, calciumoxide, chromium (and compounds, ex. Cr(VI)) as Cr, copper (and compounds ex smoke) as Cu, cyanides as CN, fluorides as F, manganese (smoke and compounds) as Mn, palladium (and compounds) as Pd, platinum (and non-water-solvable compounds) as Pt, potassium/sodium hydroxide, tin (and inorganic tincompounds) as Sn, vanadium (and alloys and carbide) as V, zinc chloride (smoke).
* Compounds marked with asterisk are considered carcinogenics with a threshold value. Special attention should be paid to these components	

12. PORTUGAL

No information supplied.

13. SPAIN

No information supplied.

14. SWEDEN

1. The Swedish legal situation is laid down in the Environmental Code. Each facility is tried on its own and the requirements with regard to water and gas treatment are set individually with a view to the recipient situation etc. In the Code this is formulated as a series of principles:

- the burden of proof principle - the operators must demonstrate that their operations are undertaken in an environmentally acceptable manner; the burden of proof is always on the operator
- the knowledge requirement - persons who pursue an activity must possess the knowledge that is necessary in view of the nature and scope of the activity. The purpose of the provision is to ensure that operators acquire the relevant expertise before starting operations, thus preventing damage and detriment
- the precautionary principle - the mere risk of damage or detriment involves an obligation to take the necessary measures to combat or prevent adverse health and environmental effects
- best possible technology - applies to the technology used for the operation itself and for the construction, operation and decommissioning of the plant. An essential condition is that it must be feasible in industrial and economic terms in the line of business concerned
- the polluter pays principle - the operation must pay for the preventative or remedial measures that must be taken
- the resource management and ecocycle principles - an operation must be undertaken in such a way as to ensure efficient use of raw materials and energy and minimisation of consumption and waste
- the reasonableness principle - all the rules of are to be applied in the light of benefits and costs. It is the operator who, in accordance with the burden of proof principle, must demonstrate that the cost of a protective measure is not justified from an environmental point of view or that it represents an unreasonable burden.

Hence in the permitting process, the operator will have to demonstrate what treatment techniques are valid, and suggest one or several of them to treat wastewater and wastegas etc. as required. Chosen technologies and conditions set will depend on BAT to the extent that it is available for the chemical industry, the technology is proven in similar production elsewhere, etc. A range of solutions and conditions are possible, depending on location, process technology, etc.

2. It more or less follows from this that there is no general reference literature with respect to permit writing. The technical officer in an environmental authority needs a good command of the technologies used and available or access to such knowledge, as well as the impact on the environment and what can be achieved to counter such impact. These officers give statements to the court on what is acceptable influence on the environment and how this influence should be controlled.

The actual permit is written by an Environment Court in the case of major process industries. The ruling is based on the information and advice given from national, regional and local authorities as well as the operator himself.

15. UNITED KINGDOM

No information supplied.

GLOSSARY OF TERMS AND ABBREVIATIONS

Chemical symbols

Al	Aluminium
Al_2O_3	Aluminium oxide
As	Arsenic
Cd	Cadmium
Br^-	Bromide ion
Br_2	Bromine
$Ca(OH)_2$	Calcium hydroxide, lime
Cl^-	Chloride ion
Cl_2	Chlorine
OCl^-	Hypochlorite ion
ClO_3^-	Chlorate ion
CN^-	Cyanide ion
CO	Carbon monoxide
CO_2	Carbon dioxide
COS	Carbon oxysulphide
Cr	Chromium
Cr^{3+}	Chromium(III) ion
CrO_4^{2-}	Chromate ion
CS_2	Carbon disulphide
Cu	Copper
F^-	Fluoride ion
Fe	Iron
HBr	Hydrogen bromide
HCl	Hydrogen chloride
	Hydrochloric acid
HCN	Hydrogen cyanide
HF	Hydrogen fluoride
Hg	Mercury
H_2O_2	Hydrogen peroxide
H_2S	Hydrogen sulphide
H_2SO_4	Sulphuric acid
HNO_3	Nitric acid
N_2	Nitrogen gas
NaOH	Sodium hydroxide
Na_2CO_3	Sodium carbonate, soda
$NaHCO_3$	Sodium hydrogencarbonate, -bicarbonate
NaOCl	Sodium hypochlorite
$NaClO_3$	Sodium chlorate
$NaHSO_3$	Sodium hydrogensulphite, -bisulphite
NH_2CN	Cyanamide
$(NH_2)_2CO$	Urea
NH_3	Ammonia
NH_4^+	Ammonium ion
Ni	Nickel
N_2O	Nitrous oxide
NO	Nitrogen oxide
NO_2	Nitrogen dioxide
NO_2^-	Nitrite ion
NO_3^-	Nitrate ion
NO_x	Nitrogen oxides (mixture of NO and NO2)
O_2	Oxygen
O_3	Ozone
P	Phosphorous

Pb	Lead
PO_4^{3-}	Phosphate ion
PO_4-P	Phosphate (calculated as P)
Sn	Tin
S^{2-}	Sulphide ion
SO_2	Sulphur dioxide
SO_3	Sulphur trioxide
SO_3^{2-}	Sulphite ion
SO_4^{2-}	Sulphate ion
SO_x	Sulphur oxides (mixture of SO_2 and SO_3)
Zn	Zinc

Prefixes

p	pico	10^{-12}
n	nano	10^{-9}
μ	micro	10^{-6}
m	milli	10^{-3}
c	centi	10^{-2}
d	deci	10^{-1}
h	hecto	10^{2}
k	kilo	10^{3}
M	mega	10^{6}
G	giga	10^{9}
T	tera	10^{12}
P	peta	10^{15}

Units and conversion factors

billion	1000 million
°C	degree Celsius, centigrade
cm	centimetre
d	day
g	gram
h	hour
I-TEQ	international toxicity equivalents of dioxins
J	Joule (1 J = 0.239 cal)
kg	kilogram
kPa	kilopascal (1 kPa = 10 mbar)
kWh	kilowatt-hour (1 kWh = 3.6 MJ)
l	litre (1 l = 0.001 m^3)
m	metre
mg	milligram
m^2	square metre
m^3	cubic metre
MJ	megajoule (1 MJ = 239 kcal = 0.2778 kWh)
MPa	megapascal (1 MPa = 10 bar)
Nm^3	Normal m^3 (cubic metre for gases, measured at 101.3 kPa and 273.15 K)
Pa	pascal (pressure; 1 Pa = 1 N/m^2)
ppm	parts per million (by weight)
ppmv	parts per million (by volume) (ppm x molecular weight/22.41 = mg/Nm^3; 1 ppm NO_2 = 2.05 mg/Nm^3 NO_2)
s	second
S	siemens
tonne	metric tonne (1 tonne = 1000 kg)
v-%	percentage by volume
wt-%	percentage by weight
yr	year
Ω	ohm

Abbreviations / Acronyms

ACP	Anaerobic Contact Process
ACR	Anaerobic Contact Reactor
AMS	Automated Measuring System (installed and operating continuously in the field)
AOX	Adsorbable Organic Halides
API	American Petroleum Institute
ATS	Austrian Schilling (currency)
BAT	Best Available Techniques, as defined in Art. 2(11) of the Directive
BEF	Belgian Franc (currency)
BOD_x	Biochemical Oxygen Demand during x days (normally 5 or 7) indicating the amount of biodegradable organic matter in waste water
BREF	Best Available Techniques Reference Document
BTEX	Benzene, Toluene, Ethylbenzene, Xylene
CEFIC	European Chemical Industry Council
COD	Chemical Oxygen Demand indicating the amount of chemically oxidisable organic matter in waste water
CONCAWE	European Refinery Association for Environment, Health and Safety
CPI	Corrugated Plate Interceptor
CSTR	Continuously Stirred Tank Reactor
CWW	BREF on Common Waste Water and Waste Gas Treatment / Management Systems in the Chemical Sector
DAF	Dissolved Air Flotation
DDT	1,1,1-Trichloro-2,2-bis-(p-chlorophenyl)ethane; a pesticide
DEM	German Mark (currency)
DTA	Direct Toxicity Assessment
EC_{50}	effluent concentration in dilution water that causes a measurable negative effect on 50 % of the test population
EIPPCB	European Integrated Pollution Prevention and Control Bureau
ELV	Emission Limit Value
EMAS	Eco-Management and Audit Scheme (Council Regulation 761/2001)
EMFA	Energy and Material Flow Analysis
EMS	Environmental Management System
EOX	Extractable Organic Halides
EQO	Environmental Quality Objectives
EQS	Environmental Quality Standards
ESP	Electrostatic Precipitator
EUR	Euro (currency)
FGD	Flue Gas Desulphurisation
FIM	Finnish Mark (currency)
FRP	Fibreglass-reinforced Plastic
GAC	Granular Activated Carbon
GBP	British Pound (currency)
GMP	Good Manufacturing Practice
HAP	Hazardous Air Pollutants
HEAF	High Efficiency Air Filter
HEAP	High Efficiency Particle Air (filter)
HEL	Higher Explosion Limit
HSE	Health, Safety and Environment
IAF	Induced Air Flotation
ICC	International Chamber of Commerce
IMPEL	European Union Network for the Implementation and Enforcement of Environmental Law
IPPC	Integrated Pollution Prevention and Control
IR	Infrared
ISO	International Organisation for Standardisation

LC$_{50}$	effluent concentration in dilution water that causes mortality to 50 % of the test population
LCA	Life Cycle Assessment
LDAR	Leak Detection And Repair
LEL	Lower Explosion Limit
LID	Lowest Ineffective Dilution; numeric value given as reciprocal dilution value (dimensionless) of the waste water at which no effects are observed
LVIC	BREF on Large Volume Inorganic Chemical Industry
LVOC	BREF on Large Volume Organic Chemical Industry
MEK	Methyl Ethyl Ketone
MF	Microfiltration (membrane process, waste water section)
MIBK	Methyl Isobutyl Ketone
NF	Nanofiltration (membrane process, waste water section)
NFL	Dutch Gulden (currency)
NH$_4$-N	Ammonium (calculated as N)
NO$_2^-$-N	Nitrite (calculated as N)
NO$_3^-$-N	Nitrate (calculated as N),
OFC	BREF on Organic Fine Chemical Industry
ORP	Redox potential
OSPAR	Oslo and Paris Convention for the Protection of the Marine Environment of the North East Atlantic
PAC	Powdered Activated Carbon
PAH	Polycyclic Aromatic Hydrocarbons
PCDDs	Polychlorinated dibenzodioxins
PCDF	Polychlorinated dibenzofurans
p.e.	Population equivalent
PM	Particulate Matter (air contaminant)
PM$_x$	Particulate Matter, x μm aerodynamic diameter (air contaminant)
POP	Persistent Organic Pollutant
PPI	Parallel Plate Interceptor
PSA	Pressure-swing Adsorption
PTFE	Poly Tetrafluoro Ethene (TEFLON)
PVC	Polyvinyl Chloride
RO	Reverse Osmosis (membrane process, waste water section)
SAC	Strong Acid Cation Exchanger
SBA	Strong Base Anion Exchanger
SCA	Specific Collection Area (ESP: ratio of surface area of collection electrodes to gas flow)
SCR	Selective Catalytic Reduction (NO$_x$-reduction)
SCWO	Super Critical Water Oxidation
SIC	BREF on Speciality Inorganic Chemical Industry
SME	Small and Medium-size Enterprises
SNCR	Selective Non-catalytic Reduction (NO$_x$-reduction)
SPC	Statistical Process Control
SVI	Sludge Volume Index: Volume in ml occupied by 1 g of activated sludge after settlement under specified conditions for a specified time
T$_A$	Algae toxicity; determination of the non-toxicity of waste water to green algae (Scenedesmus subspicatus CHODAT), using various dilutions of waste water; value is a dimensionless number, giving the dilution factor
T$_D$	Daphniae toxicity; determination of the acute non-toxicity of waste water to daphniae (Daphnia magna STRAUS) over a 24 hour exposure period, using various dilutions of waste water; value is a dimensionless number, giving the dilution factor
T$_F$	Fish toxicity; determination of the acute non-toxicity of waste water to fish (Leuciscus idus L.) over a 48 hour exposure period, using various dilutions of waste water; value is a dimensionless number, giving the dilution factor

T_L	Luminescent bacteria toxicity; short-term determination of the inhibitive effect (sublethal toxic effects) of waste water on the light emission of Photobacterium phosphoreum, using various dilutions of waste water; value is a dimensionless number, giving the dilution factor
T_M	Mutagenity; determination of the lowest dilution level at which no genotoxicity of waste to the test organism Salmonella typhimurium TA 1535/pSK 1002 is observed; value is a dimensionless number, giving the dilution factor
TOC	Total Organic Carbon
TSS	Total Suspended Solids (in waste water)
UASB	Upflow Anaerobic Sludge Blanket reactor or process
UF	Ultrafiltration (membrane process, waste water section)
USD	US-Dollar (currency)
USEPA	United States Environmental Protection Agency
UV	Ultra-violet
VCM	Vinyl Chloride Monomer
VOC	Volatile Organic Compounds
VOX	Volatile Organic Halides
VRU	Vapour Recovery Unit
WAC	Weak Acid Cation Exchanger
WBA	Weak Base Anion Exchanger
WEA	Whole Effluent Assessment
WEER	Whole Effluent Environmental Risk
WWTP	Waste Water Treatment Plant

Terms as used in this document

Aerobic processes	biological treatment processes that occur in the presence of oxygen
Anaerobic processes	biological treatment processes that occur in the absence of oxygen
Anoxic denitrification	process by which nitrate nitrogen is converted biologically to nitrogen gas in the absence of oxygen
Biological nutrient removal	removal of nitrogen and phosphorus in biological treatment processes
Component	substance imbedded in a mixture (e.g. in waste water, waste gas or air)
Content	matter contained in a medium
Cross-media effects	possible shift of environmental pressure from one environmental compartment to the other
Denitrification	biological process by which nitrate is converted to nitrogen and other gaseous end products
Diffuse emissions	emissions that are not released via specific emission points (stacks, etc.) [cww/tm/154].
Dilution factor	used with toxicity determination in waste water; defined as ratio of total sample amount after dilution to amount of waste water contained in the sample when no effect on the test organisms is detected; high dilution factors are equivalent with high toxicity in waste water
Effluent	waste stream (waste water or waste gas) discharged from a process, an installation or a site
Emissions	direct or indirect release of substances, vibrations, heat or noise from individual or diffuse sources into the air, water or land, as defined in Art. 2(5) of the Directive
Exhaust air	air stream (waste gas) from an installation contaminated with gaseous components, normally with low concentrations

Existing installation	installation in operation or existing before the date on which this Directive into effect, according to Art. 2(4) of the Directive
Flue gas	waste gas generated by incineration process
Fugitive emissions	any emissions not in waste gases of volatile organic compounds into air, soil and water as well as solvents contained in any products. They include uncaptured emissions released to the outside environment via windows, doors, vents and similar openings [cww/tm/88].
Halogenated organic compound	an organic compound which contains at least one atom of bromine, chlorine, fluorine or iodine per molecule.
Installation	stationary technical unit where one or more activities listed in Annex I of the Directive are carried out, and any other directly associated activities which have a technical connection with the activities carried out on that site and which could have an effect on emissions and pollution (Art. 2(3) of the Directive)
Make-up water	water added to a process to start or maintain a reaction, prepare a solution, mix reactants, dilute reactants
Mother liquor:	waste water stream directly arising from a synthesis or chemical reaction, generally highly concentrated in products, starting material or by-products, especially the initial aqueous discharges
Nitrification	biological process by which ammonia is converted first to nitrite and then to nitrate
Start-up, shut down operations	operation whilst bringing an activity, an equipment item or a tank into or out of service or into or out of an idling state. Regularly oscillating activity phases are not to be considered as start-ups and shut downs [cww/tm/88].
Substance	chemical element and its compounds, as defined in Art. 2(1) of the Directive
Substantial change	change in operation which, in the opinion of the competent authority, may have significant negative effects on human beings or the environment, as defined in Art. 2(1) of the Directive
Volatile organic compound	any organic compound having at 293.15 K a vapour pressure of 0.01 kPa or more, or having a corresponding volatility under the particular conditions of use [cww/tm/88].
Waste gas	final gaseous discharge containing volatile organic compounds (VOC) or other pollutants, from a stack or abatement equipment into air [cww/tm/88].
Waste water	aqueous effluent from chemical processes, product make-up, raw material preparation, equipment cleaning, storage facilities, loading activities. Rainwater and indirect cooling water are not included because of the different definitions in the Member States for waste water. Instead rainwater and its need for treatment is dealt with separately. Cooling water is dealt with in the respective horizontal BREF on Industrial Cooling Systems